Water residence times and runoff generation in a small prealpine catchment (Rietholzbach, Northeastern Switzerland)

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Abstract

A concept of groundwater residence time distributions and flowpaths in the prealpine catchment Rietholzbach in northeastern Switzerland has been developed. The catchment covers an area of 3.18 km² and ranges from 680 to 950 m a.s.l. It is part of the Upper Freshwater Molasse overlaid by Quaternary deposits. The work was based on the use of environmental tracers and is divided into two basic parts. The first one focuses on the estimation of mean residence times and the second one treats the determination of source areas and flowpaths.

In the first part the mean water residence times were estimated by means of inverse lumped-parameter simulations of $^{18}$O output functions under quasi steady-state conditions between January, 1994 and June, 1996. Comprehensive measurements of $^{18}$O content in precipitation and at various outlet sites were carried out. The dating of the oldest groundwater component was carried out using $^{85}$Kr. New approaches for parametrization of the $^{18}$O input function were developed. They improve the quality of the simulations and consist of two techniques: (1) an extrapolation of the local input function using nearby stations Konstanz and Bern, and (2) its weighting by use of percolation water amounts of a lysimeter. The computations were performed for three groups of water: (1) stream waters at three runoff gauging sites, (2) water percolated through the soil in the lysimeter, and (3) shallow groundwaters in boreholes and captured wells representing the basic types and locations of aquifers. Investigations on the natural groundwater regime, as well as pumping tests on the boreholes, were performed. For the stream water baseflow sampled at the catchment outlet, a mean residence time of about 1 year was obtained. An even longer mean residence time of the groundwater in the Quaternary deposits close to the bottom-valley (more than 2 years) is caused by a buffering effect. The vertical fluxes through the soil layer in the lysimeter are characterized by the displacement of water previously stored within the pores. This results in a relatively long mean residence time of the percolated water in the depth of 2.20 m (about 7 months).

In the second part, the components of storm runoff were determined using the tracer mass balance. A volume-proportional sampling of rainfall and the runoff at the catchment outlet was performed during five flood events in the summer 1995. The following tracers were used: the isotope $^{18}$O, the ionic substances calcium, chloride, magnesium and silica, as well as the electrical conductivity. A new variant of the mixing calculation using electrical conductivity as tracer was applied. A contribution of the previously stored pre-event water ranging between 50-80 % of the total runoff was computed by use of $^{18}$O. The identification of flowpaths by ions resulted in three components: (1) stored groundwater mobilized during the event, (2) chemically enriched water passing through the soil matrix, and (3) water flowing through the macropores and the drainage network or routed as overland flow. The contributions of these components to the total runoff vary during the flood event.

The results form a contribution to the understanding of the water turnover processes in small hilly prealpine watersheds with porous structures. The developed methodological techniques have to be tested by applications in similar catchments.
Zusammenfassung


Die Resultate können als Beitrag zur Verbesserung der Kenntnisse über die hydrologischen Prozesse in voralpinen hügellen Kleineinzugsgebieten angesehen werden. Die entwickelten methodischen Ansätze sind durch weitere Anwendungen in Einzugsgebieten zu testen.
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Latin symbols

\( a \)  
recharge coefficient [-]

\( A \)  
cross-sectional area normal to flow direction \([\text{L}^2]\)

\( c_{j \text{ fit}} \)  
tracer fitted concentration \([\text{M}\ \text{L}^{-3}\ \text{or a relative expression}]\)

\( c_{j \text{ obs}} \)  
tracer observed concentration \([\text{M}\ \text{L}^{-3}\ \text{or a relative expression}]\)

\( c_{\text{in}} \)  
tracer input concentration \([\text{M}\ \text{L}^{-3}\ \text{or a relative expression}]\)

\( c_n \)  
tracer concentration in the current rainfall (new) water component \([\text{M}\ \text{L}^{-3}\ \text{or a relative expression}]\)

\( c_0 \)  
tracer concentration in the previously stored (old) water component \([\text{M}\ \text{L}^{-3}\ \text{or a relative expression}]\)

\( c_{\text{out}} \)  
tracer output concentration \([\text{M}\ \text{L}^{-3}\ \text{or a relative expression}]\)

\( c_t \)  
tracer concentration in the runoff \([\text{M}\ \text{L}^{-3}\ \text{or a relative expression}]\)

\( C \)  
unspecified concentration variable \([\text{M}\ \text{L}^{-3}\ \text{or a relative expression}]\)

\( C_{\text{in}} \)  
longterm mean tracer input concentration \([\text{M}\ \text{L}^{-3}\ \text{or a relative expression}]\)

\( C_F \)  
concentration in flow mode \([\text{M}\ \text{L}^{-3}\ \text{or a relative expression}]\)

\( C_{FF} \)  
concentration in flow mode resulting from flux injection \([\text{M}\ \text{L}^{-3}\ \text{or a relative expression}]\)

\( C_{\text{out}} \)  
longterm mean tracer output concentration \([\text{M}\ \text{L}^{-3}\ \text{or a relative expression}]\)

\( C_{\text{out}} \)  
constant tracer concentration \([\text{M}\ \text{L}^{-3}\ \text{or a relative expression}]\)

\( C_R \)  
concentration in resident mode \([\text{M}\ \text{L}^{-3}\ \text{or a relative expression}]\)

\( C_{RR} \)  
concentration in resident mode resulting from resident injection \([\text{M}\ \text{L}^{-3}\ \text{or a relative expression}]\)

\( D \)  
dispersion coefficient \([\text{L}^2\ \text{T}^{-1}]\)

\( D/v \)  
dispersion constant \([\text{L}\ \text{T}^{-1}]\)

\( D/vx \)  
dispersion parameter [-]

\( E \)  
water exit age distribution function over an unspecified integration variable [-]

\( g \)  
system response function over an unspecified integration variable [-]

\( GW \)  
groundwater recharge rate obtained by the model BOWAM \([\text{L}]\)

\( h \)  
groundwater depth \([\text{L}]\)

\( H \)  
thickness of saturated aquifer \([\text{L}]\)

\( i \)  
number of month \((1,...,N)\) [-]

\( j \)  
number of observation \((1,...,K)\) [-]

\( J \)  
solute flux density \([\text{M}\ \text{L}^2\ \text{T}^{-1}]\)

\( k \)  
hydraulic conductivity \([\text{L}\ \text{T}^{-1}]\)

\( L \)  
lysimeter outflow rate \([\text{L}]\)

\( m \)  
portion of the component having constant tracer concentration [-]

\( M_0 \)  
mass of tracer \([\text{M}]\)

\( n \)  
effective porosity [-]

\( N \)  
total number of months [-]

\( P \)  
precipitation amount \([\text{L}]\)

\( P_{\text{max}} \)  
maximal rainfall intensity \([\text{L}\ \text{T}^{-1}]\)

\( Pe \)  
Peclet number [-]

\( q \)  
liquid flux density \([\text{L}\ \text{T}^{-1}]\)

\( Q_{\text{max}} \)  
volumetric flow rate of the stormflow peak \([\text{L}^3\ \text{T}^{-1}]\)

\( Q_{\text{min}} \)  
volumetric flow rate before stormflow \([\text{L}^3\ \text{T}^{-1}]\)
\( Q_n \) volumetric flow rate of the current rainfall (new) water component \([L^3 \ T^{-1}]\)

\( Q_o \) volumetric flow rate of the previously stored (old) water component \([L^3 \ T^{-1}]\)

\( Q_t \) volumetric flow rate of the total runoff \([L^3 \ T^{-1}]\)

\( Q \) 1. volumetric flow rate variable \([L^3 \ T^{-1}]\)

2. constant well discharge (Chapter 4.3.3) \([L^3 \ T^{-1}]\)

\( r \) inner well diameter \([L]\)

\( R \) total number of observations \([-]\)

\( REV \) representative elementary volume \([L^3]\)

\( s \) observed drawdown in a well \([L]\)

\( s_c \) corrected drawdown in a well \([L]\)

\( S \) aquifer storativity \([-]\)

\( t \) 1. time variable \([T]\)

2. time since pumping started (Chapter 4.3.3) \([T]\)

\( t' \) unspecified residence time variable \([T]\)

\( T \) transmissivity \([L^2 \ T^{-1}]\)

\( T_a \) air temperature \([^\circ C]\)

\( T_D \) time elapsed between the rainfall centre of gravity and the runoff peak \([T]\)

\( T_m \) mean residence time of water \([T]\)

\( T_Q \) duration of the hydrograph rising limb \([T]\)

\( T_t \) mean residence time of tracer \([T]\)

\( x \) unspecified length variable \([L]\)

\( v \) mean pore water velocity \([L \ T^{-1}]\)

\( V \) unspecified volume variable \([L^3]\)

\( V_m \) volume of mobile water \([L^3]\)

\( V_t \) total volume \([L^3]\)

\( W \) unspecified weighting function \([-]\)

\( W_u \) Theis's well function \([-]\)

**Greek symbols**

\( \alpha, \beta, \gamma \) shape, scale and location parameters of the three-parameter gamma distribution

\( \Gamma() \) Gamma distribution function

\( \delta_{Rhb,Ko,Bc} \) mean monthly \(^{18}O\) concentrations in precipitation at the stations Büel, Konstanz and Bern

\( \delta_{SMOW} \) isotope concentration relative to international standard SMOW

\( \delta(t) \) Dirac delta function for a time variable

\( \Delta s \) drawdown difference in a well per log cycle of time

\( \eta \) ratio of the total volume of the system to the volume with the exponential residence time distribution \([-]\)

\( \lambda \) radioactive decay constant \([T^{-1}]\)

\( \sigma \) criterion of the goodness of fit \([-]\)

**Note:** The quantities \( L, M, \text{ and } T \) refer to length, mass and time, respectively.
1 Introduction

Water may be routed within catchments via different types of flowpaths and physical mechanisms. The knowledge of water fluxes, turnover mechanisms and runoff formation processes is, therefore, an established element of modern catchment hydrology. In addition to the importance in water balance assessment and precipitation-runoff modelling, such investigations are essential for the solution of environmental problems and for water management projects.

A crucial methodological element for solving these problems is the coupled investigation of water and solute fluxes by means of tracing substances. Among a large variety of artificial and natural tracers, environmental isotopes are presumed to offer an important refinement in the knowledge of runoff formation for scales up to a hydrological catchment.

The primary purpose of the present work is to develop a concept of residence time distributions and of water source areas and flowpaths in the small hilly prealpine catchment Rietholzbach in Northeastern Switzerland. The catchment covers an area of 3.18 km² and ranges from 680 to 950 m a.s.l. It is part of the Upper Freshwater Molasse overlaid by Quaternary deposits. The work is based on the use of environmental tracers and divided into two basic steps. The first step is focused on the estimation of mean water residence times using the isotopes $^{18}$O and $^{85}$Kr. The second step treats the determination of runoff components using the isotope $^{18}$O and environmental chemical tracers.

The aim of this chapter is to give a general overview of the topic treated in the present work. Chapter 1.1 presents a short review of studies and concepts of residence time distributions and runoff formation mechanisms in hilly catchments. Chapter 1.2 deals with a review of known methodological approaches. Finally, Chapter 1.3 summarizes the objective of the present study and its interconnection with other currently operated projects.

1.1 Runoff formation in hilly catchments

1.1.1 General

The production of runoff in hilly catchments is still poorly understood. To date, there is no agreement on the role of a variety of suggested mechanisms including preferential macropore flow (Whipkey, 1965; Beven and Germann, 1982), Horton overland flow (Horton, 1933) or various forms of displaced subsurface flow (Hewlett and Hibbert, 1967; Sklash and Parvolden, 1979). For hilly catchments in humid-temperate climates and for porous structures, numerous studies have shown that the stormflow primarily consists of the pre-event water assumed to be subsurface water mobilized in any form from local aquifers. Comprehensive overviews of widely discussed runoff generation concepts on hillslopes are summarized in various theoretical publications (e.g. Kirkby, 1988; Ward and Robinson, 1990) and case studies (e.g. Pearce et al., 1986; Harris et al., 1995). Since the 1960’s, an increased attention has been oriented to the investigation of runoff formation by means of environmental isotopes and chemical tracers. They offered an fundamental methodological improvement in the determination of runoff components (Pinder and Jones, 1969), as well as in the estimation of residence times of waters (Nir, 1964).

Residence times of waters in small porous hilly catchments reach up to several years, depending on the area, as well as on morphological and hydraulic characteristics of the aquifers. Among the very small number of environmental isotope studies presented to
date on water residence times in hilly catchments, Maloszewski et al. (1983) obtained a mean residence time of up to 2.5 years for a groundwater-originated flow in the Lainbach catchment, Southern Germany. Bergmann et al. (1986) calculated a mean water residence time of 2 years at the outflow from the porous-fissured catchment Pöllau/Saifenbach, Southern Austria, and Maloszewski et al. (1992) showed a mean residence time of about 4 years for the porous-karstic basin Wimbach, Southern Germany. In contrast, Pearce et al. (1986) investigated an extremely wet porous hilly catchment Maimai, New Zealand, and reported a mean baseflow residence time of only a few months.

The relatively short residence times of the subsurface water are in agreement with a variety of runoff generation concepts assuming remarkable contributions of the subsurface components to the total outflow during flood events. Most of these concepts were developed by assessment of the analysis of runoff components using the mixing formula (Pinder and Jones, 1969). Pearce et al. (1986) and Sklash et al. (1986) discussed the concept of groundwater ridging which is explained by the conversion of the tension-saturated zone into phreatic water during the rain infiltration (Sklash and Farvolden, 1979). In addition, the rapid infiltration through near-surface pores on the upslope areas having less developed soils leads to a substantial steepening of the hydraulic gradients and, as a consequence, to a mobilization of the previously stored water. For two hilly catchments in the United States, Kennedy et al. (1986) and Bazemore et al. (1994) suggested a concept of a transient saturated zone above the soil-bedrock interface on hillslopes. This mechanism produces a rapid downflow of displaced soil water and can be caused by continuously connected macropores extending from the hillslopes to the stream without any considerable reaction of near-stream groundwater level (e.g. McDonnell, 1990; Mulholland et al., 1990). Kennedy et al. (1986) pointed out that this process is nearly equal to the translatory flow concept introduced in the 1960's by Hewlett and Hibbert (1967). Using a two-tracer hydrograph separation model, Bazemore et al. (1994) illustrated that such a mobilization of pre-event soil water may dominate the flood event especially before and during the peak flow. It is obvious that the application and interpretation of various catchment response types strongly depends on local conditions and on the methodological approaches, on tracing substances and on available additional datasets.

**1.1.2 Swiss prealpine catchments**

Water balance studies of Swiss prealpine catchments located within distinct Tertiary and Quaternary aquifers show high groundwater recharge rates under humid hydroclimatic conditions (e.g. Balderer, 1982; Gronowski and Lang, 1993; Menzel, 1997). Precipitation-runoff modelling studies by use of the models AKWA-M (Fürholz, 1994), TOPMODEL (Jordan, 1992) and BOWAM (Gurtz et al., 1997), as well as the newly developed packages EVA-ETH (Gurtz et al., 1997) and WaSiM-ETH (Schulla, 1997) confirm two characteristics of runoff: firstly, considerable runoff rates produced by heavy rainfall events, secondly, a storage potential of the Tertiary and Quaternary porous aquifers. Using a comparison of water balance in two neighbouring catchments, Balderer (1982) showed that the Tertiary Upper Freshwater Molasse, as well as the Quaternary glacial deposits serve as baseflow reservoirs. This conclusion is in agreement with the postulated hydrogeological system of interconnected aquifer layers (Balderer, 1979, 1983). In addition, the local aquifers serve as an essential water resource (Gronowski and Lang, 1993). The Swiss hilly prealpine catchments can be, therefore, characterized as highly responsive with an important water turnover in the subsurface. One of these catchments is the small catchment Rietholzbach,
established in 1975/76 by the Hydrology Section, Laboratory for Hydraulics, Hydrology and Glaciology, now Department of Geography, ETH Zurich.

An investigation on the water turnover mechanisms in the Rietholzbach catchment was done by use of the linear storage reservoir model DIFGA (Schwarze et al., 1991) which is based on the widely used analysis of the runoff recession curve (summarized e.g. in Tallaksen, 1995). Koenig et al. (1994) and Koenig (1994) applied this approach over the period between 1975-1990 and calculated the balance of four fast and delayed runoff components. Because this concept is based on the temporal resolution of one day, there was no possibility to analyze single events with a duration of several hours. Thus, the resulting storage parameters described the runoff recession over longer periods such as whole months. The storage coefficients obtained cannot be interpreted as mean water residence times. This is due to the fact that they express the intensity of the outflow from the storage reservoir (runoff recession), regardless of the age structure of the outflowing components. Otherwise, the water residence time obtained by means of the environmental tracer dating gives the expected time since the water elements are entered into the reservoir until they leave. According to Bergmann et al. (1986), the storage coefficients represent the "storage energy", but not the "storage capacity", which is characterized by the residence time. A more detailed theoretical discussion on these aspects is reported in Margrita et al. (1984) and Bergmann et al. (1986). To date, the residence times of waters stored within the Swiss prealpine Tertiary and Quaternary sediments have not yet been estimated. Although isotope measurements in the catchment Rietholzbach were performed (Hutterli, 1983), they did not allow a suitable estimation of water residence times because of an insufficiently short input record of isotope concentration in precipitation. Nevertheless, they showed the basic variations of the ¹⁸O concentrations in precipitation and in the stream waters at several sites in the catchment and gave a suitable qualitative background for the present work.

The high amount of fast runoff components obtained by Koenig (1994) and Koenig et al. (1994) might lead to conclusions explaining this phenomenon by fast runoff generation within a developed system of macropores. Moreover, this assumption seemed to be supported by artificial tracer experiments performed in the central part of the Rietholzbach catchment by Burgthaler (1992). They showed a very fast reaction within the unsaturated zone resulting in a fast downflow of the traced water on hillslopes. Further interpretations of these experiments showed, however, that a considerable part of this fast flow is caused by an artificial drainage system localized below the land surface at some places in the catchment. To achieve a better understanding of the flow through the unsaturated zone, an artificial tracer experiment over a period of 16 months was performed in the lysimeter which is installed in the catchment Rietholzbach and filled by a typical soil profile (3.14 m², 2.20 m soil depth). The results obtained by Demuth et al. (1993) proved that the decisive flow process is characterized by a displacement of previously stored water within the pore matrix. It is, therefore, obvious, that the groundwater recharge and runoff formation processes especially in those compartments with more developed deeper soil profiles do not depend only on fast rainfall water flow through macropores (Demuth et al., 1993).

In the present work a concept is developed for residence time distributions and for water source areas and flowpaths in the catchment Rietholzbach. Nevertheless, the results expected here should have a more general significance for the hydrology of small hilly prealpine catchments. Thus, this task is done in two steps and can be, therefore, specified by two groups of relevant questions. The first step, i.e. the development of the spectrum of water residence times, is based on the following questions:
• What are the mean water residence times within the aquifers formed by Freshwater Molasse and Quaternary deposits?
• Is there an agreement between the mean residence time of groundwaters and stream waters under low-flow conditions?
• What are the mean water residence times within hillslope and bottom-valley aquifers?

In addition, the following questions are postulated for the determination of runoff components:
• What are the decisive runoff components generated during summer flood events?
• Is there considerable evidence of a water component generated in the soil during summer flood events?

1.2 Methodology

In general, the questions of water residence times, source areas and flowpaths cannot be successfully tackled by use of hydrological models alone. For example, the linear reservoir models distinguish the runoff components analyzing only the hydrograph falling limb (e.g. Koenig et al., 1994). Some precipitation-runoff models compute the runoff components using parameters which are optimized with respect to the simulation of total runoff. In all the cases the storage parameters cannot be interpreted in terms of residence times because they describe runoff amounts regardless of their age structure (e.g. Margrita et al., 1984; Bergmann et al., 1986). A crucial methodological element for solving these problems is, therefore, the coupled investigation of water and solute fluxes by means of tracing substances.

At present, there is no clear consensus in the literature between numerous terms describing the time-related characteristics of water and tracer flow through hydrological basins. Despite the discussion dealing on the temporal differences in the motion of tracers and of the traced water itself, a number of authors apply different definitions in order to determine the time spent by the water and tracer elements within a storage system. The most common expressions which have to be distinguished in catchments and geological structures are residence time and transit time. In a general overview, Yurtsever and Gat (1981) defined the residence time as the time elapsed since a water element has entered into the system until it leaves at a sampling site. This term is equivalent to the terms water age and travel or arrival time, the latter frequently used in the stochastic approaches (e.g. Dagan, 1989; Dagan et al., 1992; Gelhar, 1986). The terms transit or turnover time, and exit age, characterize the whole time spent by an element between an entry and a natural outflow from the system (Yurtsever and Gat, 1981). The use of these definitions, therefore, depends on the boundary conditions of the investigated storage system. For example, if a subsurface water is sampled at the natural outlet site on the surface, it can be characterized by the term transit time. This occurs in the case of springs or stream waters which have passed through the whole subsurface reservoir. To characterize a groundwater sampled within the aquifer itself (e.g. in a borehole), the term residence time is more suitable. The term residence time is, therefore, more general, even though numerous authors make no difference in the interpretation of both expressions (e.g. Maloszewski and Zuber, 1982).
1.2 Methodology

As constituents of the water molecule, the heavy isotopes of hydrogen and oxygen, i.e. stable oxygen-18 or deuterium and radioactive tritium, are assumed to be suitable tracers in the water cycle (e.g. Moser and Rauert, 1980; Ferronsky and Polyakov, 1982; Mazor, 1991). During the past three decades, known principles of the natural distribution of $^{18}$O together with relatively uncomplicated sampling and measuring procedures made this isotope the most frequently used environmental tracer for the identification of waters on regional scale having short residence times of up to 1-3 years. The isotope $^2$H (deuterium) can be applied in hydrology in the same way, but the measuring procedure is more complicated in comparison to the determination of $^{18}$O. Because the recent tritium concentration in groundwater declines slowly towards the values from the pre-bomb test era in early 1960's, the interest in substances tracing water components of higher ages is directed to the radioactive isotope krypton-85 (Smethie et al., 1992) and to the chlorofluorocarbons (Reilly et al., 1994). In spite of the limitations due to the extremely complicated sampling and measuring procedures and the difficulties in the interpretation of the behaviour of $^{85}$Kr in the unsaturated zone, the $^{85}$Kr method is expected to replace the tritium method (Zuber, 1986).

The deterministic concept of the estimation of water residence times by means of tracer measurements is generally based on the lumped-parameter flow models. They are analytical, steady-state and one-dimensional statements which describe the transformation of a given tracer input concentration into the tracer output concentration within a continuous homogeneous flow system. This relationship is expressed mathematically by a convolution integral over a system response function which characterizes an expected distribution of residence times, the mean residence time being the main model parameter. By the inverse modelling procedure, the measured isotopic concentration record at an outflow site is calculated using the measured concentration record in precipitation and fitted by calibration of model parameters. This approach has been developed mainly in chemical engineering for tracer-related investigations of flowpaths and residence time distributions in industrial reactors (summarized in e.g. Himmelblau and Bischoff, 1968; Levenspiel, 1989) and later discussed as a tool to investigate the water turnover in natural catchments and hydrogeological structures (e.g. Małoszewski and Zuber, 1982; Zuber, 1986). Despite the far-reaching simplification of modelled conditions caused by the steady-state assumption, environmental isotope studies in porous (Małoszewski et al., 1983), porous-fissures (Herrmann et al., 1986b, 1990; Małoszewski et al., 1992) and karstic systems (Rank et al., 1992) as well as in the unsaturated zone (Małoszewski et al., 1995) confirmed a sufficient applicability of the basic concept.

The reliable isotope dating of waters having short residence times by means of lumped-parameter inverse modelling strongly depends on the length and accuracy of the isotope input and output data records, as well as on the available hydrological data which add to the interpretation of obtained results. In the case of the conservative $^{18}$O, the simulation of seasonal concentration variations requires a measured output record of at least 1 year and a measured or extrapolated input record which also characterizes the inclusion of relatively older components during the preceding time. For the extrapolation of local datasets, an international database consisting of longterm records of $^{18}$O, deuterium and tritium concentration in precipitation at a worldwide network of stations exists (Rozanski et al., 1993). In addition, the $^{18}$O input datasets obtained on the land surface have to be weighted by means of groundwater recharge factors. The significance of this weighting is still poorly understood and the discussion on this step is disproportionate to the importance it has (e.g. Małoszewski et al., 1992). This is due to the insufficient use of measured or modelled...
recharge parameters, i.e. measurements in lysimeters or modelling of the soil water balance in catchments (Klotz et al., 1995). Because of the variability of runoff mechanisms in natural catchments, the influence of the weighting techniques on the simulation of output functions may considerably differ. In the case of isotopes such as the radioactive $^{85}$Kr being a dissolved gas, but not a constituent of the water molecule, the main weakness of the interpretation lie in the estimation of the difference between the tracer age and the water age. This is caused by the fact that these substances date the water since the entrance into the saturated zone only (e.g. Cook and Solomon, 1995). It is, therefore, of utmost importance to carry out multi-isotope dating which would cover the whole residence time spectrum of the investigated area and would combine the results obtained by each isotope itself. Graf et al. (1995) interpreted water residence times being mostly longer than 10 years by means of $^{18}$O, tritium and $^{85}$Kr. Because of the difficulties with the interpretation of the current low tritium input activities, however, the application of this combined method for dating of very young waters is questionable.

Unlike the tracing substances for the estimation of water residence times in the subsurface, there is a large variety of elements widely used for tracing of runoff components during a stormflow catchment response. In addition to the stable isotopes, various ions, as well as the electrical conductivity being the sum of dissolved ions, have been taken into account since the 1960's. To express the mixing of the current rainfall water and the displaced subsurface water, Pinder and Jones (1969) introduced the hydrograph deconvolution approach based on the two-component tracer balance. Regardless of the kind of tracers used, the application of this tracer approach in hilly catchments and under humid-temperate climate conditions in most cases confirmed a considerable mobilization of the stored water by flood events. Despite all of these considerations, successful interpretations of a large subsurface contribution during snowmelt events (e.g. Dincer et al., 1970; Martinec, 1975; Herrmann and Stichler, 1980; Rodhe, 1981), as well as of a large rainfall water contribution during flood events in tropical (e.g. Elsenbeer et al., 1994) or deforested Mediterranean (e.g. Travi et al., 1994) catchments are known. The main disadvantage of the hydrograph deconvolution using tracers is that it is practically impossible to apply this method continuously, i.e. not only for selected flood events.

Similar to various terms describing the residence time spent by water and tracer elements in the subsurface, there is no agreement between various terms handling the definitions and the physical significance of runoff components and tracing substances. The fundamental difference between a stable isotope of water and a chemical tracer of water is that the isotopic content changes only as a result of mixing, whereas the chemical concentration in natural streams and subsurface waters depends on a mixture of weathering and leaching processes in the soil and bedrock (Stumm and Morgan, 1981). As a consequence, isotopes trace the source (origin) of water and distinguish "new" (event or current rainfall water) and "old" (pre-event or previously stored water) runoff components (Pilgrim et al., 1979). In contrast, ionic substances being not a part of the water molecule, trace the water flowpaths independent of their origin. To date, numerous flowpath-related components occur in a variety of runoff formation concepts. In general, three basic components are distinguished: firstly, mobilized subsurface water, secondly, current rainfall water passing the soil pathways (generally chemically enriched) and finally, current rainfall water flowing the macropores or routed as overland flow (e.g. Hooper and Shoemaker, 1986; Kennedy et al., 1986; Wels et al., 1991; Pionke et al., 1993).

Most of the ionic substances are involved in complex geochemical or biological interactions. As a consequence, no consensus exists about the most promising geochemical tracer for
1.3 Objective of the present work

The main goal of the present work is to develop a concept of the residence time distribution and of the water origin and flowpaths in the small hilly prealpine catchment Rietholzbach in Northeastern Switzerland. The work is based on the coupled investigation on the water and tracer transport and consists of following tasks:

1. Inverse lumped-parameter modelling of $^{18}$O concentration records in time steps of months over a period of 2.5 years (January, 1994 - June, 1996) and estimation of mean water residence times at the following sites:

- stream water under low-flow conditions at the main catchment runoff gauging site and at the runoff gauging sites of two subcatchments;
- percolated water at the outflow from a 2.20 meter deep lysimeter filled by a typical brown soil layer;

various environments. During the past two decades, the stormflow chemistry, especially of calcium, chloride and silica ions, has attracted an increasing attention with respect to flowpath-related hydrograph deconvolutions (Kennedy et al., 1986; Wels et al., 1991; Pionke et al., 1993; Bazemore et al., 1994, e.g.). Whereas the chloride ions are reported as far-reaching conservative tracer in unsaturated and saturated environments that contain no chlorine mineral as a major constituent (Pionke et al., 1993; Bazemore et al., 1994; Ribolzi et al., 1996), the silica and calcium concentrations are strongly influenced by weathering and dissolution in soils (Kennedy et al., 1986; Wels et al., 1991). In the most recent time, combinations of several geochemically controlled parameters into a single tracer such as the residual alkalinity were introduced (Ribolzi et al., 1996). In order to avoid erroneous conclusions and speculative interpretation of such parameters, however, comprehensive studies on the dissolution kinetics and geochemical equilibria in the subsurface are required. The use of another combined parameter, i.e. the electrical conductivity (sum of dissolved ions), is relatively sparse, even though its continuous measurement in streams does not cause any serious problem (Sklash and Farvolden, 1979; Sklash et al., 1986). The reason is probably similar, i.e. the interpretation of the electrical conductivity records requires parallel measurements of single conservative or non-conservative tracers.

The methodological part of the present work is mainly focussed on the application and development of techniques for the interpretation of the stable isotope $^{18}$O. This tracer plays a crucial role in both main solution steps, i.e. in the estimation of water residence times, as well as in the determination of runoff components, source areas and water flowpaths. In addition, the radioactive isotope $^{85}$Kr and major ions calcium, chloride, magnesium and silica, as well as the electrical conductivity are used. According to the character of the Rietholzbach catchment and to the expected residence times and decisive runoff formation processes, the following methodological questions are specified:

- Is there a possibility to obtain the spectrum of water residence times by means of the $^{18}$O content only?
- How can the $^{18}$O input record be parametrized for purposes of modelling by means of the lumped-parameter approach?
- What are the results of a combined interpretation of water residence times obtained by means of $^{18}$O and $^{85}$Kr values?
- Is there a possibility to obtain the source related, as well as the flowpath-related hydrograph deconvolution by means of $^{18}$O and an additional geochemical tracer?
• groundwater in two boreholes and two captured wells representing both main aquifer types, i.e. the Upper Freshwater Molasse and the Quaternary glacial deposits.

2. Development of methods for extrapolation of the local $^{18}$O input record of 2.5 years (January, 1994 - June, 1996) into the past history and for weighting of this record with respect to the groundwater recharge. The latter is achieved by the use of lysimeter outflow measurements and groundwater recharge modelling (Gurtz et al., 1997).

3. Interpretation of the measured $^{85}$Kr concentration and estimation of the residence time of the relatively oldest groundwaters (from a borehole at a bottom-valley site) in combination with results obtained by the use of $^{18}$O measurements in previous steps.

4. Determination of the contribution of previously stored water to the streamflow by means of stable isotope $^{18}$O content. This type of hydrograph deconvolution is demonstrated by five examples of flood events.

5. Determination of the flowpaths and the timing in the contributions of soil water and groundwater to the streamflow by use of calcium, chloride, magnesium, silica ions, as well as of the electrical conductivity. This type of hydrograph deconvolution is demonstrated by one of the five events analyzed by the use of $^{18}$O content in the previous step.

As mentioned above, these tasks are solved in two basic steps. The first step is focussed on the estimation of mean water residence times using the isotopes $^{18}$O and $^{85}$Kr. The second step treats the determination of runoff components using the isotope $^{18}$O and environmental chemical tracers. Thus, after a brief outline of the investigated catchment (Chapter 2), as well as of the data collection and laboratory measurements (Chapter 3), the tasks enumerated by 1 - 3 are treated in Chapter 4 and those marked by 4 and 5 in Chapter 5.

The present work is incorporated into the group of projects performed in the catchment Rietholzbach within the framework of the long-term research programme HYDREX. It uses some water balance calculations and precipitation-runoff modelling results performed within the recently completed Swiss National Science Foundation Project No. 31 Impacts of climatic variations on the water resources and on the flow regime within the Rhine river basin (Gurtz et al., 1997).

In addition, results and interpretation of the $^{18}$O measurements are used within the currently operated projects Sustainable water management and agriculture in semiarid and arid regions, conducted by the Institute of Hydromechanics and Water Resources Management, ETH Zurich, and Regionalization in Hydrology, conducted by the Technical University Dresden, Germany. The interpretation of the $^{85}$Kr measurement is incorporated into the current project Young groundwaters: age structure, mixing components and other processes, operated by the Physics Institute, University of Bern.

To date, a general overview of the $^{18}$O measurements in the catchment Rietholzbach in the period 1994-1995, including estimations of residence times in surface waters and lysimeter, is given in Vitvar and Balderer (1997). Some aspects on the interconnections between the subsurface and surface water under low-flow conditions are discussed in Vitvar (1997).
2 Catchment description

The Rietholzbach catchment (Figure 2.1) is a small hilly prealpine basin in the middle part of the Thur river, canton of St. Gallen, Northeastern Switzerland, which is one of the major contributor to the prealpine part of the Rhine basin. The catchment area of 3.18 km² running west to east is sparsely populated and is primarily used as pasture land. For hydrological purposes, the catchment can be regarded as a representative basin for the prealpine and lower alpine regions of Switzerland (e.g. Lang and Grebner, 1984; Gurtz et al., 1997; Menzel, 1997). Basic geographical and land-use characteristics of the catchment are listed in Table 2.1.

The geology of the catchment is characterized by the Tertiary deposits of the Upper Freshwater Molasse which belong to the sedimentation of the nearly horizontal stratified Hörnli-Fan Deposits "Hörnlschuttfächer" particularly covering the prealpine parts of Northeastern Switzerland (e.g. Hantke, 1967; Hottinger et al., 1970; Balderer, 1979, 1983; Bürgisser, 1981). It is composed of consolidated clastic sediments such as conglomerates "Nagelfluh", sandstones, layers of marls and banks of freshwater limestone. In the flatter parts of the catchment valley there are also Pleistocene non-consolidated sandy and silty gravel pockets which represent Würm moraines originating from periodic movements of glaciers (e.g. Bürgisser, 1981; Krays and Keller, 1994). The conglomerates, sandstones and the Quaternary glacial deposits can be particularly regarded as groundwater aquifers with medium to high hydraulical conductivities and relatively large storage capacities. Unlike the lower catchment area close to the outlet, the Quaternary deposits are distributed in the upper catchment area directly along the Rietholzbach itself and may play an important role in the turnover of water originating on the surrounding slopes. The portion
Table 2.1: Basic geographical characteristics of the Rietholzbach catchment. After Koenig (1994).

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>area</td>
<td>3.18 km²</td>
</tr>
<tr>
<td>maximal altitude</td>
<td>938 m a.s.l.</td>
</tr>
<tr>
<td>outlet altitude</td>
<td>681 m a.s.l.</td>
</tr>
<tr>
<td>mean altitude</td>
<td>796 m a.s.l.</td>
</tr>
<tr>
<td>mean slope</td>
<td>12.5°</td>
</tr>
</tbody>
</table>

*land use:*
- grassland: 67%
- forest: 25%
- wet areas: 4%
- bushes: 2%
- roads: 2%

The heterogeneity of parent rock types and relief produce a large variety of soil types. Germann (1981) distinguished among 8 different soil types which can be summarized in a group of relatively less permeable gley soils (42% of the catchment area) and a group of relatively more permeable brown soils and regosols (58% of the catchment area). The typical values of hydraulic conductivity range between $1.0 \times 10^{-5}$ m s⁻¹ and $5.0 \times 10^{-4}$ m s⁻¹ with a mean being $1.8 \times 10^{-4}$ m s⁻¹ (Germann, 1981). Gley soils are located in the lower catchment parts, whereas brown soils and regosols are distributed on hillslopes, as well as...
Figure 2.2: View of the Rietholzbach catchment. Top: The upper catchment part with the highest point of the catchment St. Iddaburg. Bottom: The catchment outlet Rietholz within a gorge formed by the hard Oehninger-Layers conglomerates.
on hilltops at the periphery of the catchment. Accordingly to the catchment morphology, the decisive portion of brown soils and regosole types can be identified particularly on the slopes in the northeastern catchment part. Based on soil moisture measurements at some sites in various depths up to 50 cm, Menzel (1997) demonstrated differences between the velocity of moisture fronts movement within the cited soil types. The more permeable soil types are expected to have a developed system of macropores. Nevertheless, as shown by the artificial tracer experiment performed in the 2.20 m deep lysimeter by Demuth et al. (1993), such a macropore system alone cannot explain the vertical water flow through a deeper soil profile. Other field investigations (Germann, 1981) and analysis of borehole profiles (Chapter 4.3.3) proved that the soil depth is strongly variable and ranges between less than 50 cm on sharp slopes oriented to the north up to about 2 m in more flat catchment parts. These observations confirm the expected relatively rapid infiltration through the less developed soil layers on hillslopes accompanied with the mobilization and displacement of stored water. The water balance calculation for the lysimeter, as well as tracer experiments, provided the mean volumetric water content within a typical brown soil profile of about 25 % (Demuth et al., 1993).

The evolution of the dominant dairy farming in the whole prealpine region of Switzerland has lead to a vegetation cover which is primarily composed of grassland. This type of land use is accompanied by a network of private drainage systems. As shown e.g. in Burgthaler (1992), the fast drainage downflow might play a role in the evaluation of water movement in the unsaturated zone on hillslopes. The water supply of the sparse farm houses is obtained mostly by private wells.

The water balance of the Rietholzbach catchment is typical of the prealpine humid climate. The average annual values for the period 1975 - 1990 are summarized in Table 2.3.
The hydrological research basin Rietholzbach was established and equipped in 1975/76 by the Laboratory for Hydraulics, Hydrology and Glaciology, now Hydrology Section, Department of Geography, ETH Zurich, within the framework of the long-term research programme HYDREX. This project is focussed on the investigation of the water balance and hydrological processes such as runoff formation, soil water recharge and evapotranspiration with respect to the climatic conditions in the prealpine region. Moreover, the catchment is included into the group of test catchments organized by the Swiss National Hydrological and Geological Survey Bern. The aim of these test catchments is to investigate natural and man-influenced runoff regimes and to characterize the regime types of Swiss basins (Landeshydrologie und -geologie, 1992).

Table 2.3: Average annual water balance of the Rietholzbach catchment for the period 1975 - 1990, after Koenig et al. (1994).

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precipitation</td>
<td>1600 mm</td>
</tr>
<tr>
<td>Runoff</td>
<td>1046 mm</td>
</tr>
<tr>
<td>Evapotranspiration</td>
<td>554 mm</td>
</tr>
</tbody>
</table>
3 Data collection

The experimental part of the present work is based on the use of permanently measured hydrological and meteorological parameters in the Rietholzbach catchment and on our own experimental programme. The latter consists of water sampling, isotopical and chemical measurements and aquifer tests.

The basic permanent measurements of hydrological and meteorological parameters in the catchment Rietholzbach have been conducted since 1975 (Lang and Grebner, 1984). The meteorological parameters are collected at the station Büel, which is located in the representative central part of the catchment (Figure 3.1). The runoff from the catchment is registered at the mean gauging site Mosnang (681 m a.s.l.) established in 1975 by the Swiss National Hydrological and Geological Survey Bern (Landeshydrologie und -geologie, 1992). The weighing lysimeter located at the station Büel serves for measurements of water percolation. Since 1994, the standard programme has been extended and includes also runoff measurements at the outlets from the subcatchments Oberer Rietholzbach and Huwilerbach, as well as measurements of groundwater levels in the boreholes B1, B2 and B3.

Some remarks on the permanent measurements of relevant meteorological and hydrological data are given in Chapter 3.1. Chapter 3.2 treats the probe sampling methodology and Chapter 3.3 briefly describes the laboratory measurements.

![Figure 3.1: Sampling sites in the Rietholzbach catchment. The map is based on the 25 m resolution digital elevation model (Bundesamt für Landestopographie, 1996).](image)
3.1 Permanent meteorological and hydrological measurements

Among the permanently measured meteorological parameters at the station Büel, two parameters are of particular interest for purposes of the present work: firstly, the precipitation, and secondly, the air temperature. Both parameters are registered by standard operational instruments with temporal resolution of 5 minutes.

- Air temperature is measured by PT 100 temperature sensors installed in a wooden screen (Stevenson type).
- Precipitation is registered by an automatic precipitation gauge RG 200 (Joss-Tognini gauge) installed in a standard height of 1.5 m above the land surface. The data are corrected with respect to the kind of precipitation, as well as to the wind velocity. The correction parameters are listed in Gurtz et al. (1997).

In addition, the station Büel is equipped with instruments collecting data on the following meteorological parameters:

- relative air humidity,
- wind velocity,
- global radiation.

The above parameters are registered with high temporal resolution up to 15 seconds. The specification of the instruments can be found e.g. in Koenig (1994) and Menzel (1997).

The stream water runoff at the mean runoff gauging site Mosnang is registered by an electrical signal from a pressure transducer. The recorded water levels are collected in form of runoff rates. Since May 1995, the water electrical conductivity has been registered by a WTW LF95 electrode. The water levels at the runoff gauging sites of the subcatchments, Oberer Rietholzbach and Huwilerbach, are registered by a pressure sonde and converted into flow rates. Runoff data are available with temporal resolution of 5 minutes.

The weighing lysimeter on the area of the station Büel has the diameter of 2 m and depth of 2.20 m yielding a total volume of 6.9 m³. The lysimeter column is filled with a typical braunerde profile which is representative of this locality. The amount of percolation water passing through the lysimeter layer into the depth of 2.20 m is registered hourly by the mass difference, as well as by a tipping bucket having a volume of 50 cm³. The water outflow is collected in a barrel where the samples are taken.

The groundwater boreholes B1, B2 and B3 form a profile across the central part of the Rietholzbach catchment and are close to the meteorological station Büel. The borehole B1 is equipped with a sensor monitoring the groundwater levels in a temporal resolution of 5 minutes. The groundwater levels in the boreholes B2 and B3 were measured weekly (1995) and two-weekly (since 1996) by a portable sounding lead SEBA KLL. Besides the groundwater levels, electrical conductivity and groundwater temperature are measured on-line with a portable electrode WTW LF91. The pumping tests were carried out using a borehole pump of type GRUNDFOS MP1.

The automatically collected hydrological and meteorological data from the Rietholzbach catchment are regularly transferred using a phone connection to a database system operated by the Hydrology Section, Department of Geography, ETH Zurich (Lang and Grebner, 1984; Koenig, 1994).

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1 Wissenschaftlich-Technische Werkstätten GmbH, Dr.-Karl-Slevogt-Str. 1, D-82362 Weilheim, Germany
2 POLAR AG, Mess- und Ortungstechnik, CH-6274 Eschenbach, Switzerland
3.2 Probe sampling

The sampling campaign was organized in two basic groups with respect to the two main objectives of the present work. The first group consists of routine sampling to obtain $^{18}$O records in precipitation (input function), as well as at various outlet sites (output functions). In addition, a groundwater sampling campaign to determine the $^{85}$Kr concentration was carried out in July, 1996. The second group consists of the automatic sampling of rainfall and stream water during selected flood events to estimate the runoff contributions using $^{18}$O and chemical tracers.

**Routine sampling.** The sampling for $^{18}$O analysis was carried out over the period 1994-1996. A volume of 100-200 ml was sampled. The localities, periods and intervals of this sampling are summarized in Table 3.3 (see also Figure 3.1).

<table>
<thead>
<tr>
<th>Water</th>
<th>Locality</th>
<th>Sampling period</th>
<th>Sampling interval</th>
</tr>
</thead>
<tbody>
<tr>
<td>precipitation</td>
<td>Büel</td>
<td>1994-1996</td>
<td>month</td>
</tr>
<tr>
<td>lysimeter outflow</td>
<td>Büel</td>
<td>1994-1996</td>
<td>week 2 weeks</td>
</tr>
<tr>
<td>stream water</td>
<td>Mosnang</td>
<td>1994-1996</td>
<td>week/day 2 weeks</td>
</tr>
<tr>
<td></td>
<td>Oberer Rietholzbach</td>
<td>1994-1996</td>
<td>week 2 weeks</td>
</tr>
<tr>
<td></td>
<td>Huwilerbach</td>
<td>1994-1996</td>
<td>week 2 weeks</td>
</tr>
<tr>
<td>groundwater</td>
<td>B1, B2, B3</td>
<td>1995-1996</td>
<td>week 2 weeks</td>
</tr>
<tr>
<td></td>
<td>Farm house-well</td>
<td>1994-1996</td>
<td>week 2 weeks</td>
</tr>
<tr>
<td></td>
<td>Trough</td>
<td>1994-1996</td>
<td>week 2 weeks</td>
</tr>
</tbody>
</table>

The following details on the sampling are denoted:

- The precipitation water registered by the tipping bucket of the Joss-Tognini gauge RG200 was conducted through a hose into a closed bottle located below the gauge. To avoid the evapotranspiration of the stored rainwater, the bottle was embedded into the ground.

- The lysimeter outflow water was taken from the barrel collecting the water that had passed through the lysimeter layer. While the amounts of the outflowing water are registered continuously, it was possible to calculate weighted mean $^{18}$O contents for longer periods such as whole months.

- Between April and December 1995, daily samples of the stream water at the main runoff gauging site Mosnang were collected using an automatic sampler ISCO 1680. The aim was to distinguish the $^{18}$O content under various runoff conditions. Only a selection could be analysed for $^{18}$O due to the limited capacity of the mass spectrometry equipment.

- The groundwater sampling from the boreholes B1, B2 and B3, as well as from the artificial farm house-well and trough, was taken accompanied with groundwater level (in the boreholes only), electrical conductivity and temperature measurements.

**Sampling related to selected flood events.** During the spring and summer period 1995, an automatic sequential volume-proportional sampling on five flood events was performed in order to determine the runoff components using $^{18}$O, electrical conductivity and

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$^{3}$ISCO Environmental Division, 531 Westgate Blvd., Lincoln, NE 68528-1586, USA
3.2 Probe sampling

major ions. This sampling resulted in rainfall water samples collected at the station Büel and in stream water samples collected at the main runoff gauging site Mosnang (see also Figure 3.1). In total, samples of five complete flood events and two additional rainfall events were collected and analyzed. The sampling programme is summarized in Table 3.2.

Table 3.2: Outline of the automatic sampling related to selected flood events in the summer 1995.

<table>
<thead>
<tr>
<th>Event</th>
<th>Rainfall sampling</th>
<th>Runoff sampling</th>
<th>Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Site</td>
<td>Samples</td>
<td>Site</td>
</tr>
<tr>
<td>July 11-13</td>
<td>Büel</td>
<td>10</td>
<td>Mosnang</td>
</tr>
<tr>
<td>July 15-16</td>
<td>Büel</td>
<td>7</td>
<td>Mosnang</td>
</tr>
<tr>
<td>August 7-8</td>
<td>Büel</td>
<td>10</td>
<td>Mosnang</td>
</tr>
<tr>
<td>August 8-10</td>
<td>Büel</td>
<td>5</td>
<td>Mosnang</td>
</tr>
<tr>
<td>September 9-10</td>
<td>Büel</td>
<td>3</td>
<td>Mosnang</td>
</tr>
<tr>
<td>April, 25-26</td>
<td>Büel</td>
<td>12</td>
<td>-</td>
</tr>
<tr>
<td>June 10-11</td>
<td>Büel</td>
<td>8</td>
<td>-</td>
</tr>
</tbody>
</table>

The sampling equipment was installed in collaboration with the Institute of Hydrology and Meteorology, Technical University Dresden, Germany, and can be described as follows:

- For the collection of the precipitation water, a sampling construction consisting of a standard precipitation Hellmann gauge connected with a pumping system was used. The precipitation water level within the rain gauge is registered by a liquid level sampler actuator ISCO 1640 which regulates the sampling frequency. After the registration of every 3 mm of precipitation, the whole content of the gauge is automatically pumped out and collected by a programmable portable sampler ISCO 3700. Thus, a rainfall event of a total amount of 30 mm is collected in a consecutive sequence of 10 samples. The capacity of this sampler covers 24 bottles. On-site sampling reports and program information can be transferred to a personal computer using the software package SampLink. The measurements of electrical conductivity in the precipitation water were carried out in situ using the portable electrode WTW LF91.

- For the collection of the stream water, sampling system consisting of a portable flow meter ISCO 3220 on-line with a programmable portable sampler ISCO 3700 was used. By evidence of water levels using a pressure sonde, the flow meter regulates the start time and the frequency of the sampling. Thus, an initial water level can be set for every expected flood event. After this water level has been reached, the sampling follows volume-proportionally throughout the whole event. Like the precipitation water sampling, the capacity of the sampler is 24 bottles. The flow measurement and sampling results can be transferred to a personal computer and evaluated using the packages FlowLink and SampLink, respectively.

The quality of the automatic sampling generally depends on the estimation and programming two basic parameters: firstly, the initial sampling water level, secondly, the runoff volume per sample (sampling frequency). The parameters have to be estimated before each event. Thus, only selected events could be successfully sampled (Table 3.2).

Sampling for $^{85}$Kr measurements. Evaluations of $^{18}$O data from the groundwater in the borehole B1 over the year 1995 have shown that the mean residence time of this
relatively oldest water cannot be estimated by means of $^{18}$O alone. Thus, a sampling campaign for a measurement of $^{85}$Kr concentration in a groundwater sample from this borehole was carried out in July, 1996. The campaign was performed in collaboration with the Physics Institute, University of Bern.

The low-level measurement of $^{85}$Kr in natural water samples requires a complicated large-volume sampling based on a gas extraction. The groundwater was pumped during two hours with a pumping rate of 13 l/min through a closed tank equipped with a set of jets. Due to a spreading of inflowing water in the jets, 10 l gases were evolved from the water and stored in a closed bottle under the pressure of 2.5 atmosphere. The extraction procedure has to be done under vacuum conditions in order to avoid an exchange with the atmospheric air.

![Figure 3.2: View of the gas extraction device used for the measurement of $^{85}$Kr in the groundwater in the borehole B1 (left). The device essentially consists of a closed tank with a set of jets (middle-right) and closed bottles containing the stored gases (right). The equipment was developed by the Physics Institute, University of Bern.](image)

The whole sampling and extraction device was developed by the Physics Institute, University of Bern, and is described in more details elsewhere (Loosli and Oeschger, 1978; Kropf, 1996).

### 3.3 Laboratory measurements

The laboratory measurements used for purposes of this work essentially consist of mass spectrometry isotope measurements of $^{18}$O and $^{85}$Kr contents in water samples, as well as
of measurements of major ion concentrations. The measurements of the $^{18}$O content were carried out at the Stable Isotope Laboratory of the Geological Institute, ETH Zurich, the measurement of $^{85}$Kr at the Low-Level-Laboratory of the Physical Institute, University of Bern, and the measurements of major ions in the Central Laboratory of the Federal Institute of Forest, Snow and Landscape Research in Birmensdorf, Switzerland.

### 3.3.1 Mass spectrometry measurements of $^{18}$O

The measurements of $^{18}$O content in water samples were performed in a CO$_2$ - H$_2$O equilibration device on-line with a gas source mass spectrometer OPTIMA (Figure 3.3). Stable isotope ratios are obtained in the form of relative $\delta$-values by comparison of the isotopic composition of an unknown gas (sample) with that of a gas of known composition (reference gas) being an intermediate standard. Finally, the values are related to the international standard established as Standard Mean Ocean Water SMOW (e.g. Craig, 1961; Gonfiantini, 1978)

$$\delta_{SMOW} = \left( \frac{R_x}{R_{SMOW}} - 1 \right) \times 1000$$ (3.1)

where $R_x$ and $R_{SMOW}$ are the ratios between the rare ($^{18}$O) and common ($^{16}$O) isotopic species in the sample and in the standard, respectively. The delta values are expressed in units of parts per thousands ($\%o$ or per mil SMOW).

![Figure 3.3: Block diagram of a CO$_2$ - H$_2$O equilibration device connected with a mass spectrometer. Modified after Fortier (1994).](image)

The CO$_2$ - H$_2$O equilibration device consists of a set of 24 glass reaction vessels arranged in four banks of six and connected to a manifold through a capillary tube and valve assembly. The valves can be controlled individually for isolating leaks or simultaneously for pump down and introduction of reactant gas CO$_2$. For each vessel, 2 ml of water sample are required. The preparation time for one run with 24 samples is approximately 1 hour. The time of isotopic exchange (fractionation) of the oxygen in the sample with oxygen of known isotopic composition in CO$_2$ under the temperature of 25 °C is set to 4 hours.

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$^{4}$VG ISOTECH, Aston Way, Middlewich, Cheshire, CW10 0HT England
Afterwards the sample gas is separately introduced into the spectrometer. Several aspects of the CO$_2$ - H$_2$O exchange processes including random and systematic laboratory errors are discussed elsewhere (Bottinga and Craig, 1969; Richet et al., 1977; Brenninkmeijer et al., 1983; Fortier, 1994).

A mass spectrometer is an instrument designed to separate charged atoms and molecules based on their masses and their motions in magnetic fields (Faure, 1986). The OPTIMA mass spectrometer has electromagnets which allow the magnetic field and the acceleration potential to be changed for measuring different masses. The spectrometer consists essentially of four separate sections:

- The dual inlet system consists of two identical halves and a changeover valve which enables the sequential introduction of the sample and the reference gas into the source analyzer part. Since the quality of the spectrometer depends partially on gas flow rates and ion beam intensities, the inlet pressures of these two gases are set equal. This is reached by use of two variable volume reservoirs (bellows) which are used to modify the pressure of the gas to be introduced into the source via a capillary tube.

- The source is a small chamber where the gas is ionized by collision with electrons produced by a heated filament. The produced positive ions are accelerated by a high voltage electric field and focussed before they enter the flight tube.

- The flight tube forms an arc of a circle and is set in a magnetic field which deflects the ions depending on their mass and velocity. By adjusting the acceleration voltage in the source and the intensity of the magnetic field it is possible to measure different masses with the same collector.

- The triple collector consists of three Faraday cups which collect the ions. The incoming ions produce a current proportional to their number and hence to the partial pressure of the corresponding isotopic species in the sample gas.

Figure 3.4 demonstrates the CO$_2$ - H$_2$O equilibration device and the mass spectrometer operated in the Stable Isotope Laboratory of the Geological Institute, ETH Zurich.

The analysis carried out by the OPTIMA mass spectrometer produce raw delta values (so-called error rejected delta) related to the laboratory working standard. Therefore, the following additional conversion and correction steps have to be applied to obtain the final values:

- Instrumental corrections (Mook and Grootes, 1973);
- Conversion of raw $\delta$ values to the international standard SMOW (Friedman and O’Neil, 1977);
- Craig correction of $\delta$ values (Craig, 1957);
- Normalization of values on the scale between SMOW and a second international reference standard called “Standard Light Atlantic Precipitation SLAP” (Coplen, 1988).

The standard deviation of final $\delta$ values is $\pm 0.1$ $\%$ SMOW.

### 3.3.2 Mass spectrometry measurement of $^{85}$Kr

The determination of the $^{85}$Kr content in the water sample was carried out using an experimental procedure which is under continuous development at the Physics Institute, University of Berne (Loosli and Oeschger, 1978). It consists basically of three steps.
3.3 Laboratory measurements

- Separation of krypton from the extracted gases using distillation, gas-chromatography and chemical procedures.
- Determination of $^{85}$Kr radioactivity using low-level proportional counting procedure.
- Determination of the $^{85}$Kr content in the counter using a mass spectrometer.

The resulting $^{85}$Kr concentration of the sample, i.e. the specific $^{85}$Kr activity, is obtained by relating the radioactivity measured by the low-level counting system to the volume of krypton present in the sample. It is expressed in units dpm/cc Kr, which is the number of $^{85}$Kr disintegrations per minute related to cm$^3$ krypton (e.g. Smethie et al., 1992).

Using the described procedure, one sample can be prepared and measured within one week. Most of the time is devoted to the counting. The low-level counting procedure is under continuous improvement. Since the $^{85}$Kr measurement was performed in collaboration and is not a direct part of our own programme, no more detailed remarks concerning the procedures are given.

3.3.3 Measurements of major ions

The measurements of major ions were performed in two groups.
Table 3.3: Errors of measurements of selected major ions, Central Laboratory of the Federal Institute of Snow, Forest and Landscape, Birmensdorf.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Standard deviation [mg/l]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium</td>
<td>± 0.18</td>
</tr>
<tr>
<td>Chloride</td>
<td>± 0.01</td>
</tr>
<tr>
<td>Magnesium</td>
<td>± 0.05</td>
</tr>
<tr>
<td>Silica</td>
<td>± 0.02</td>
</tr>
</tbody>
</table>

- The anion contents were determined by the Ion Chromatography method using the chromatograph DIONEX DX-100.
- The cation contents were determined using the Inductively Coupled Plasma-Mass Spectrometry method using the mass spectrometer ELAN 5000A.

The errors of measurement are listed in Table 3.3. Since the results are not obtained by our own measurements, no more detailed notes on the instruments are given.

\(^5\)Dionex AG, Olten, Switzerland
4 Analysis of water residence times

The estimation of water residence times in natural catchments cannot be performed by use of hydrological data alone. Among numerous studies, Margrita et al. (1984) and Bergmann et al. (1986) confirmed that the storage constants frequently obtained in hydrological linear reservoir models cannot be fairly interpreted in terms of residence times. Thus, the water dating requires the use of elements directly tracing the water particles. As constituents of water cycle, environmental isotopes are an established tool for solving questions of water residence times in a large variety of hydrological systems.

The aim of this chapter is to develop a concept of water-residence-time distribution for the typical aquifers as well as for the soil storage reservoir in the prealpine catchment Rietholzbach. This goal can be achieved by evaluating the $^{18}$O and $^{85}$Kr isotope records for the period 1994 - 1996 at various sites using the inverse lumped-parameter flow modelling approach.

The application of the lumped-parameter flow approach in catchments generally deals with the transfer of a tracer concentration record in precipitation (input function) into a tracer concentration at an outflow site (output function) using a system response function. The important background of the lumped-parameter flow approach is presented in Chapter 4.1. Chapter 4.2 deals with the $^{18}$O and $^{85}$Kr isotope input functions used in the present study. Finally, Chapter 4.3 shows the modelling results discussed afterwards in Chapter 4.4.

4.1 Description and discussion of the lumped-parameter flow approach

This chapter is divided into three parts. Some general remarks are given in Chapter 4.1.1. Chapters 4.1.2 and 4.1.3 are dedicated to the discussion of the model variants used in this study.

4.1.1 General

The basic elements of the lumped-parameter model approach are the input and output tracer concentrations and the system response function. Thus, general remarks on the tracer concentration modes and on the derivation of the response function are given below.

Notes on tracer concentration modes. Solving of tracer transport in one-dimensional form requires a cross sectional concentration averaging over a representative elementary volume. In general, this averaging can be performed in one of two ways depicted in Figure 4.1. Whereas the resident concentration $C_R$ can be regarded as the tracer mass per unit volume of tracer solution, the flux concentration $C_F$ is the concentration passing through a cross section per unit time. Thus, the representative elementary volume $REV$ for the resident concentration $C_R$ is defined as the cross sectional area $A$ of the flow multiplied by a unit distance $\Delta x$ and the $REV$ of the flux concentration $C_F$, is defined by the tracer volumetrical flow rate $Q$ flowing in one time unit $\Delta t$. Kreft and Zuber (1978) pointed out that the differences in observed concentrations result not only from the measurement within the system itself (detection mode), but they also depend on how the tracer is injected into the system (injection mode). Hence, four theoretical combinations of concentration concepts can be distinguished as shown in the case of non-dispersive flow through parallel vessels (Levenspiel and Turner, 1970), capillaries (Gardner et al.,
FIGURE 4.1: Sketch of two concentration modes used in the one-dimensional flow and transport approach. Performed after the description in Maloszewski and Zuber (1982) and Zuber (1986).

Notes on the system response function. Under steady-state conditions, the turnover time $T_m$ of mobile water flowing with a rate $Q$ through the volume $V_m$ is defined as

$$ T_m = \frac{V_m}{Q} \quad (4.1) $$

Rearranging of equation (4.1) in form of a distribution of residence times of water elements which entered the system at a given real time $t=0$ leads to the expression

$$ T_m = \int_0^\infty t \ E(t) \ dt \quad (4.2) $$

where $E(t)$ means the exit-age distribution of water having a property

$$ \int_0^\infty E(t) \ dt = 1 \quad (4.3) $$

Similarly, the expression of the mean residence time of a conservative tracer $T_t$ in terms of unspecified concentrations $C(t)$ observed at the measurement point as a result of an entrance into the system at the real time $t=0$

$$ T_t = \frac{\int_0^\infty t \ C(t) \ dt}{\int_0^\infty C(t) \ dt} \quad (4.4) $$

1973) and in the case of the advective-dispersive flow (Kreft and Zuber, 1978; Parker and van Genuchten, 1984). Considering that environmental isotopes are injected and transported proportionally to the flow by nature itself, the concentration mode for natural hydrological systems is assumed to be of type $C_{FF}$. A more detailed discussion of the concentration concepts and its consequences related to the system response function can be found elsewhere (e.g. Zuber, 1986).
can be rewritten in form of tracer residence time distribution

\[ T_t = \int_0^\infty t \, g(t) \, dt \]  

(4.5)

where the function \( g(t) \) is analogically to equation (4.3) normalized to

\[ \int_0^\infty g(t) \, dt = 1 \]  

(4.6)

It is obvious that if the residence time distribution of tracer \( g(t) \) is identical with the residence time distribution of traced water \( E(t) \), both the mean residence times of tracer \( T_t \) and of water \( T_m \) are equal. Like the differences between the modes of tracer concentrations, the distinction between the residence times of tracer and water is an essential point in the discussion on the theory and practice of the tracer methods. In terms of the concentration modes defined above, theoretical studies (Kreft and Zuber, 1978; Maloszewski and Zuber, 1982; Zuber, 1986) confirmed that \( T_t \) is equal to \( T_m \) only if a conservative, non-delayed tracer is injected and sampled in the flux mode \( C_{FF} \). Considering the two isotopes used in the present study, the stable isotope \(^{18}\)O as a constituent of the water molecule, satisfies all mentioned conditions and can be, therefore, assumed to be an "ideal" tracer. The isotope \(^{85}\)Kr, however, does not behave conservatively because of two reasons: firstly, due to its radioactive decay during the transport, secondly, due its movement through the unsaturated zone by diffusion. The radioactive decay itself is integrated into equation (4.4) using a correction factor \( \exp(-\lambda t) \) where \( \lambda \) is the decay constant. This factor converts the observed concentrations into the concentrations which would be observed for a non-decaying tracer. Thus, in the case of an application of the radioactive tritium being a constituent of the water molecule, this procedure would reestablish the equality between the residence times \( T_m \) and \( T_t \). However, the diffusion of gaseous \(^{85}\)Kr results in the \(^{85}\)Kr age having to be interpreted as the time estimated since the entrance of water into the saturated zone only. This mean residence time of \(^{85}\)Kr \( (T_t) \) is, therefore, not equal to the mean residence time of water \( (T_m) \). Although this aspect has recently attracted much attention in the hydrological application of gaseous tracers, such as \(^{85}\)Kr itself or of the group of chlorofluorocarbons (e.g. Cook and Solomon, 1995), the interpretation of the differences between both residence times \( T_m \) and \( T_t \) is still poorly understood.

For exactly defined initial and boundary conditions, the function \( g(t) \) is usually derived theoretically or by artificial tracer experiments using the mass balance

\[ g(t) = \frac{C(t)Q}{M_0} \]  

(4.7)

where \( M_0 \) is the total mass of tracer. In complex systems on the regional scale however, the function \( g(t) \) has to be defined as a model concept which characterizes an expected distribution of flowpaths within the system and, therefore, an expected residence time distribution. Since the environmental isotopes are injected rather continuously instead of being an instantaneous pulse at the time \( t=0 \), the unspecified time variable \( t \) changes to the residence time variable \( t' \). Thus, the convolution of tracer input \( c_{in} \) to tracer output \( c_{out} \) leads to the general expression (for derivation see e.g. in Haitjema, 1995)

\[ c_{out}(t) = \int_0^\infty c_{in}(t - t') \, g(t') \, \exp(-\lambda t') \, dt' \]  

(4.8)
Here, the residence time distribution function $g(t')$ is generally called weighting function or system response function. The decay rate $\lambda$ for a radioactive tracer is calculated as

$$\lambda = \frac{\ln 2}{\tau} \quad (4.9)$$

where $\tau$ is the half life of the tracer. Thus, $\lambda = 0$ in the case of stable isotopes and $\lambda = 0.0646$ in the case of the radioactive $^{85}$Kr having a half life 10.76 years. The system response function $g(t')$ expresses the model concepts using the mean residence time $T_t$ as the main parameter. In the case of conservative stable $^{18}$O, $T_t$ is assumed to be equal to the mean residence time of water $T_m$. The number of additional parameters depends on the boundary conditions of a given concept and on the volumetric proportions between applied response types. Combinations of more concepts (i.e. of more response functions) to describe one aquifer are also possible. To date, the problem of combined lumped-parameter flow models for applications in natural basins has been treated rather theoretically in the literature (Maloszewski and Zuber, 1982; Richter et al., 1993). Although the practical use of various model combinations might lead to better simulation of experimental data, the estimation of proportions between the single models introduces additional parameters which have an unreliable physical significance under natural conditions.

The general mathematical relationship for the system response function has the form of three-parameter gamma distribution which is given by the equation below, after Amin and Campana (1996)

$$g(t') = \frac{\exp \frac{\gamma - t'}{\beta} - 1}{\beta^\alpha \Gamma(\alpha)} (t' - \gamma)^{\alpha-1} \quad (4.10)$$

where $\beta$ and $\gamma$ mean the scale and location parameters, respectively, while $\alpha$ is the shape parameter and $\Gamma(\alpha)$ is the gamma function. Setting of $\alpha=1$ leads to concepts describing the flowpaths by combinations of perfect mixing and non-mixing "piston flow" without the consideration of dispersion processes (Chapter 4.1.2). Otherwise, the use of values $\alpha$ between 0 and 1 describes the so-called partial mixing (Amin and Campana, 1996) which can be physically explained by the advection-dispersion theory (Chapter 4.1.3).

### 4.1.2 Concepts without dispersion

Assuming the flow and transport concepts without the dispersion, the equation (4.10) becomes a reduced form

$$g(t') = \frac{\exp \frac{\gamma - t'}{\beta}}{\beta} \quad (4.11)$$

with parameters $\beta$ and $\gamma$ defined as

$$\beta = \frac{T_m}{\eta} \quad (4.12)$$

and

$$\gamma = T_m \left(1 - \frac{1}{\eta}\right) \quad (4.13)$$
where $\eta$ is the dimensionless ratio of the total volume of the system to the volume with the perfect mixing and $T_m$ is the mean water residence time. Introduction of equations (4.12) and (4.13) into equation (4.11) leads to the expression

$$g(t') = \frac{\eta}{T_m} \exp \left( -\frac{\eta t'}{T_m} + \eta - 1 \right)$$

which is mathematically equivalent to the two-parameter exponential-piston flow model (Wolf and Resnick, 1963) consisting of a well-mixed exponential model connected in series with a piston-flow model. As defined by equation (4.13), the additional parameter $\eta$ expresses the ratio $V_T/V_E$ of the total volume $V_T$ and the volume $V_E$ occupied by the exponential mixing type. Thus, the equation (4.14) is valid for the segment of residence times defined as

$$t' > T_m(1 - \frac{1}{\eta})$$

The segment of shorter residence times defined as

$$t' \leq T_m(1 - \frac{1}{\eta})$$

is assumed to characterize elements that are moved by the piston-flow so that

$$g(t') = 0$$

Figure 4.2 shows the relationship between the parameter $\eta$ and the relative segment $d = t'/T_m$ of residence times which satisfy the equation (4.15). The physical significance of this relationship is the exclusion of water elements having residence times between 0 and $t'/T_m$ from the current mixing at the outlet of the investigated storage system. For the interpretation of residence times in hilly prealpine catchments, it should be assumed that the parameter $d$ and $\eta$ increase with the increasing role of deeper Molasse groundwaters displaced by lateral movement on hillslopes and contributing to the creek baseflow. Otherwise, the parameter $d$ and $\eta$ should decrease with the prevailing role of shallow aquifer fluxes close to the bottom-valley parts, i.e. for example in upper flatter parts of the catchment Rietholzbach formed by glacial deposits.

The one-parameter boundary cases of this combined model can be derived by changing the value of the parameter $\eta$ in equation (4.14). Hence substituting $\eta = 1$ expresses the exponential model or well-mixed model with the weighting function

$$g(t') = \frac{1}{T_m} \exp \left( -\frac{t'}{T_m} \right)$$

and with only the parameter $T_m$ being the mean residence time. The exponential form of the residence time distribution means that the young components receive an exponentially heavier weight. This mixing concept generally corresponds (Eriksson, 1958) to a situation of decreasing hydraulic conductivity with the aquifer depth and frequently occurs in runoff generation routines of precipitation-runoff models. Although the general presumption of the complete mixing along all flowpaths seems to be unrealistic, the true significance of the expression 4.16 is that the mixing may occur at the sampling site only without the complete mixing in aquifer. As mentioned above, the exponential type of mixing is expected to occur in shallow groundwater aquifers with a recharge area where the amount of recharge close to the drainage prevails over that at a larger distance (Zuber, 1986).
Finally, letting \( \eta \to \infty \) leads to a pure piston flow model (Kaufman and Libby, 1953) characterized by the equation

\[
g(t') = \delta(t' - T_m)
\]

(4.17)

with \( \delta \) being the Dirac delta function and only with the parameter \( T_m \). This boundary does not assume any mixing of water elements so that there are no flow lines with different residence times. It is obvious that the practical applicability of this model is rather limited to cases with flow in clearly defined industrial systems. Despite the approximate description of the water motion in some very old confined deep aquifers (Andrews et al., 1993), there is no example of a successful use of this concept alone for dating of shallow groundwaters in natural basins. Nevertheless, in order to describe residence time distributions of water elements moved by displacement of previously stored water within the unsaturated zone, as well as within the saturated zone on hillslopes, the piston flow statement is assumed to be an important component of the partial mixing exponential-piston flow model (equation 4.14).

### 4.1.3 Concepts with dispersion

The advection-dispersion concept is a generally accepted and widely used model of a continuous flow with partial mixing. Like the group of models discussed in Chapter 4.1.2, the dispersion statement has been developed mainly in chemical engineering for solving problems such as flow in pipelines (Taylor, 1953, 1954), chemical exchange columns (Danckwerts, 1953) or industrial vessels (Himmelblau and Bischoff, 1968; Niemi, 1977). The spreading of a homogeneous distribution of a tracer in a flowing fluid is due to a complex phenomena which is in the literature generally called hydrodynamic dispersion. In a fundamental work, Bear (1972) discusses the two basic processes of the hydrodynamic dispersion in porous systems, i.e., the mechanical dispersion and the molecular diffusion. Whereas the latter results from tracer concentration gradients in the liquid phase, the mechanical dispersion can be regarded as a consequence of inhomogeneities on microscopic (variations of pore geometry) or macroscopic (variations in permeabilities along flow paths) scale, respectively.

**Figure 4.2:** Relationship between the parameters \( d \) and \( \eta \) in the combined exponential-piston flow model.
The one-dimensional advection-dispersion concept for conservative tracers can be characterized by the following mass balance, written in form of a continuity equation according to the Fickian law (Parker and van Genuchten, 1984)

\[ \frac{\partial(C \theta)}{\partial t} = \frac{\partial J}{\partial x} \]  

(4.18)

with \( \theta \) being the volumetric water content, \( C \) being the tracer concentration and \( J \) being the tracer flux density. \( J \) can be expressed as

\[ J = qC - D \theta \frac{\partial C}{\partial x} \]  

(4.19)

where \( q \) is the liquid flux density and \( D \) the dispersion coefficient.

Combining and rearranging equations (4.18) and (4.19) yields the general one-dimensional convection-dispersion equation

\[ \frac{\partial C}{\partial t} + \frac{\partial}{\partial x} \left( v \frac{\partial C}{\partial x} \right) = D \frac{\partial^2 C}{\partial x^2} \]

(4.20)

where \( v \) is the mean pore water velocity.

The physical significance of terms describing the hydrodynamic dispersion depends on the on the boundary conditions and the scale of the system where the residence time is estimated. In the Fickian approximation, dispersion due to the three-dimensional variations in the velocity field is cross-sectionally averaged into an effective dispersion coefficient defined by Taylor (1954) as longitudinal dispersion coefficient \( D \). Division of \( D \) by the mean pore water velocity \( v \) leads to the dispersion constant or dispersivity \( D/v \) (Taylor, 1954). Many studies in capillaries (Saffman, 1959), as well as in river channels (Day, 1975) and granular deposits (DeJong, 1958), have shown a distinct scaling effect of the dispersivity, i.e. the dispersivity increases nearly linearly with distance traveled in the system.

A compilation of tracer experiments conducted both in field scale and laboratory scale shows that the dispersivity increases nearly linearly and seemingly limitlessly with the scale of the experiment, regardless of the type of media traversed (Neuman, 1990). Using a stochastic probabilistic distribution of the velocity field, Sposito et al. (1986) considers the scaling effect as the result of continual exposure of the tracer to increasingly large velocity variations in the flow domain. With the increasing scale towards the field conditions in natural catchments, the dispersivity reaches an apparent quantity which depends mainly on the distribution of residence times, and is practically order of magnitudes larger than the dispersion parameter resulting from the hydrodynamic dispersion itself (Zuber, 1986). As the injection of environmental isotopes is extended over the whole recharge area and does not exist only at \( x = 0 \), the apparent dispersion constant is expected to be on the order of the length of the recharge zone measured along the flowpaths.

Solving the equation (4.20) for purposes of lumped-parameter modelling requires an integral dispersion characteristic parameter in the system response function \( g(t') \). This quantity has the form of a dimensionless apparent dispersion parameter \( D/\nu x \) expressing the relative relationship between the dispersion and advection motion within the system. The dispersion parameter is reciprocal to the Peclet number \( Pe \) commonly used in chemical engineering.

The form of the dispersion model response function depends on the concentration mode (Chapter 4.1.1) assumed for solving equation (4.20). In two theoretical papers, Kreft
and Zuber (1978) and Parker and van Genuchten (1984) treat the derivation for both the injection and detection sampling modes (Chapter 4.1.1) for all combinations of the residence \( C_R \) and flux \( C_F \) concentration modes. Since the concentration of environmental isotopes in natural waters is regarded to be of the type \( C_{PF} \) in terms of Chapter 4.1.1, the boundary conditions for a pulse injection \( \delta(t) \) and detection in fluid with flow rate \( Q \) over the area \( A \) at place \( x \) and time \( t \) are defined

\[
C_F(0, t) = \frac{A}{Q} \delta(t)
\]

and for \( x > 0 \)

\[
C_F(x, 0) = 0
\]

with

\[
\lim_{x \to \infty} C_F(x, t) = 0
\]

According to several independently obtained solutions (e.g. Lenda and Zuber, 1970), Kreft and Zuber (1978) stated the equation for the above defined conditions in the form

\[
C_{PF}(x, t) = \frac{A}{Q \sqrt{(4\pi D t^3)}} \exp \left( -\frac{(x - vt)^2}{4Dt} \right)
\]

(4.21)

In addition, Kreft and Zuber (1978) proved that this solution can only be directly used in the form of a system response function and inserted into equation (4.8). Thus, rearrangement of the equation (4.21) leads to the expression for the system response function containing the residence time variable \( t' \), as well as the mean residence time \( T_m \) and the apparent dispersion parameter \( D/vx \) or \( 1/Pe \), respectively (e.g. Maloszewski and Zuber, 1982)

\[
g(t') = \left( 4\pi \frac{D}{vx T_m} \right)^{-\frac{1}{2}} \exp \left( -\left(1 - \frac{t'}{T_m} \right)^2 \frac{vx T_m}{4D T} \right)
\]

(4.22)

Otherwise, the solution of the equation (4.20), as reported e.g. by Crank (1957) under boundary conditions defined for resident injection and sampling modes \( C_{RR} \), cannot be directly used for the system response function. Kreft and Zuber (1978) showed that the solutions for both the concentration modes \( C_{PF} \) (equation 4.22) and \( C_{RR} \) differ by the dispersion parameter so that the discrepancy between the interpretation of the concentration modes in the advection-dispersion approach increases with the apparent dispersivity. As reported again in Kreft and Zuber (1978), some of the earlier works (e.g. the first application of the dispersion model in the groundwater hydrology by Nir, 1964) did not account for these differences. For the modelling of highly dispersive systems, it is, therefore, of crucial importance to properly distinguish the boundary conditions.

In a similar matter to the parameter \( \eta \) in equation (4.14), the apparent dispersion parameter \( D/vx \) determines the proportion between the advection motion and dispersion by mixing. The increase in the dispersion parameter leads to residence time distributions similar to those defined by the pure exponential model. In contrast, the decrease of the dispersion parameter, i.e., the prevailing role of advection, means a distribution nearly equivalent to the pure piston flow statement.

4.2 Description and parametrization of the isotope input functions

The length and accuracy of the record of isotope concentration in precipitation or in the air (i.e. the input function) is an essential starting point in hydrological applications
of the environmental isotopes. For isotopes being constituents of the water molecule, the
International Atomic Energy Agency (IAEA) in cooperation with the World Meteorological
Organization (WMO) is conducting a worldwide survey of $^{18}$O, deuterium, and tritium
content in precipitation. The programme was initiated in 1958, and, since 1961, more
than 500 meteorological stations in 93 countries have been collecting monthly precipitation
samples for the IAEA/WMO Global Network of Isotopes in Precipitation GNIP (Rozanski
et al., 1993; Yurtsever, 1993). The main initial objective was the systematic collection of
basic data on isotope content of precipitation and, consequently, to provide basic isotope
data for the use of environmental isotopes in hydrological investigations. All data from the
GNIP database are offered on a WWW-server. Unlike this considerably developed base,
the network of stations regularly collecting the $^{85}$Kr data records is very sparse because
of a complicated measurement of $^{85}$Kr in the air. Therefore, no internationally conducted
data base containing $^{85}$Kr input data exists until now.

The goal of this chapter is to construct $^{18}$O and $^{85}$Kr input functions for their use in the
lumped-parameter inverse simulation of the $^{18}$O and $^{85}$Kr output functions in the catch¬
ment Rietholzbach. Some general remarks on the $^{18}$O in precipitations are given in chapter
4.2.1. Chapter 4.2.2 discusses the local $^{18}$O input function measured during 30 months
between January, 1994 and June, 1996. Chapter 4.2.3 deals with the parametrization of
this function for the purpose of the lumped-parameter modelling. Finally, Chapter 4.2.4
briefly treats the $^{85}$Kr input function.

### 4.2.1 General remarks on the $^{18}$O input function

A water molecule may be composed of two stable hydrogen isotopes ($^1$H and $^2$H) and
three isotopes of oxygen ($^{16}$O, $^{17}$O and $^{18}$O), which are the most useful for hydrological
purposes. The common molecule is $^1$H$_2^{16}$O and two rare species are $^1$H$^2$H$^{16}$O and $^1$H$_2^{18}$O.
Due to the different atomic weights, the water molecules are divided into light molecules,
such as $^1$H$_2^{16}$O, and heavy molecules, such as $^1$H$^2$H$^{16}$O and $^1$H$_2^{18}$O. In natural waters,
the relative amount (isotopic abundance) of water molecules containing the heavy isotope
$^{18}$O is approximately 0.2 % (e.g. Faure, 1986; Mazor, 1991).

The $^{18}$O content in precipitation water can be regarded as a result of fractionation of
the isotopic species of water molecules. From the meteorological and hydrological point of
view, the fractionation means changes of isotopic concentration caused by phase transitions
of water molecules. This phenomenon is explained by a lower saturation vapor pressures for
the heavy molecule $^1$H$_2^{18}$O than for the common molecule $^1$H$_2^{16}$O. As a consequence, when
water evaporates from the surface of the ocean, the water vapor is enriched in the common
specie $^{16}$O, and when raindrops are formed in a cloud by condensation of water vapor, the
liquid phase is enriched in the heavy specie $^{18}$O. Dansgaard (1954, 1964) described the
stable isotope fractionation in water molecules during phase transitions by the Rayleigh
distillation equation with a temperature-dependent fractionation factor which expresses
the relation between the $^{18}$O content in the enriched fraction and in the depleted fraction.

Various experiments have shown that the temperature dependence of the fractionation
factor is nonlinear and may be described using a more complicated polynomial function
(Ferronsky and Polyakov, 1982). Since this temperature dependence is indirect, the cooling
processes during the condensation cause a depletion of $^{18}$O content in the condensate
and lead to the so-called temperature effect of the isotopic composition of precipitation.

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6 http://www.iaea.or.at/programs/ri/gnip/gnipmain.htm
Although the temperature effect can be regarded as the most important factor, evaluations of large datasets have shown that there are also other effects which reflect the differences in the source and genesis of precipitation and in the geographical conditions of a given region. The observed depletion of $^{18}$O content in precipitation with increasing precipitation amount, geographical latitude, altitude and distance from the ocean were established as amount, latitude, altitude and continental effects (e.g. Siegenthaler and Oeschger, 1980; Mazor, 1991). The interaction of this phenomena is extremely complex and has not been fully explained.

4.2.2 Discussion of the local $^{18}$O input function

Figure 4.3 presents the measured monthly $\delta^{18}$O values in precipitation at the hydrometeorological station Büel for the period of 30 months between January, 1994, and June, 1996. The measured $^{18}$O concentration cycles are almost parallel to the observed seasonal temperature cycles. The most pronounced temperature deviations during March 1994, February 1995 and October 1995 are well indicated by the relative $^{18}$O enrichment in precipitation. The relationship between $^{18}$O content in precipitation and the air temperature yields a temperature coefficient for seasonal $\delta^{18}$O variations of 0.41%o SMOW per 1 °C. Siegenthaler and Oeschger (1980) evaluated similar relationships for datasets based on measurements at some Swiss stations and obtained temperature coefficients between $\delta^{18}$O values of 0.35 %o SMOW (Bern) and 0.55 %o SMOW (Guttannen) per 1 °C. It should be pointed out that this seasonal relationship cannot be identified with the relationship plotting longterm mean values of $^{18}$O against the longterm mean air temperature at different stations. The latter was established by Dansgaard (1964) using datasets from IAEA/WMO stations on the northern hemisphere and can be characterized by a temperature coefficient of 0.7 %o SMOW per 1 °C. Thus, the expression of Dansgaard reflects isotopical variations under completely different climatic conditions, whereas the relationship between the monthly air temperature and $^{18}$O content in precipitation at one station reflects strongly seasonal isotopical variations (e.g. Siegenthaler and Oeschger, 1980; Mazor, 1991). According to the Rayleigh distillation assumption (Dansgaard, 1964), the condensation temperature should be considered as the critical temperature which drives the fractionation processes in the clouds. Furthermore, the changes in the isotopic composition of the precipitation water caused by evaporation in the atmosphere could be taken into account. Nevertheless, such observations are rarely available so that the air temperature on the surface is the most used value. For the present study, the mean monthly air temperature was calculated as a mean temperature of the days with more than 1 mm precipitation. A comparison of the $\delta^{18}$O-temperature relationships by using the mean monthly air temperatures of all the days (Figure 4.4) versus where only the days with more than 1 mm precipitation were used (Figure 4.3) showed that there is no difference in the quality of the regression. However, it can be seen that the $\delta^{18}$O values plotted against the temperature on days with precipitation shows a very good correlation especially in the case of summer months with high temperatures. This can be explained by the strong dependence of the summer precipitations on local convective storms where the isotopical composition of the precipitation water is formed under local temperature conditions. In the case of frontal precipitation situations occurring mostly during the spring and the autumn, different origin of transported vapour masses might cause more considerable deviations in the observed values from the regression line.

As denoted in Chapter 2, the elevation difference in the Rietholzbach catchment is about
FIGURE 4.3: The monthly measured $\delta^{18}O$ values of precipitation, station Büel; period January, 1994 - June, 1996. The air temperature is calculated as monthly mean values using the days with more than 1 mm precipitation.
Figure 4.4: The monthly measured $\delta^{18}O$ values of precipitation, station Büel; period January, 1994 - June, 1996. The air temperature is calculated as mean monthly values using all days.
4.2 Description and parametrization of the isotope input functions

300 m. The station Büel is located on the altitude of 755 m a.s.l., close to the mean catchment altitude of 796 m a.s.l. Therefore, it can be assumed that the $^{18}$O concentration in precipitation at the station Büel is representative for the whole catchment. No significant amount effect on the monthly $^{18}$O content in precipitation from the station Büel occurs as demonstrated in Figure 4.5. It is obvious that in the case of monthly values at one station, the seasonal temperature effect limits the influence of the amount effect. According to Rozanski et al. (1982), a clear amount effect can be rather observed either by comparison of long-term mean values from many stations on large scale or by evaluation of successive $^{18}$O content in precipitation during a single rain event. The latter will be treated in Chapter 5.

4.2.3 Parametrization of the local $^{18}$O input function

To investigate the transfer of $^{18}$O signal between the input in precipitations and output from a storage system, two conditions have to be met for the local input function:

- The local $^{18}$O input function has to be sufficiently long since the simulation of the output function also requires input data from the past history representing components with higher residence time.

- The local input function has to be parametrized by use of recharge weighting factors so that the weight of the current input is determined by its real recharge into the storage system. Thus, the modelled flow satisfies the steady-state assumption of the lumped-parameter flow approach.

Unfortunately, the parametrization procedures in both steps described above are rarely handled in the literature. The main reason for this might be that some studies only worked with the sinusoidal approximation of the cyclical $^{18}$O input functions (e.g. Pearce et al., 1986).
Extrapolation of the local $^{18}$O input function. The role of the extrapolation generally decreases with the length of the measured local input function and increases with the increasing mean residence time. Some of the small number of known studies use nearby stations with available data to simply connect the records (e.g. Małoszewski et al., 1983, 1992). Graf et al. (1995) extrapolated the input function using known temperature records and applied the local relationship between the temperature and isotopic content in precipitation. Although the latter seems to be widely applicable, considerable errors may occur in cases where there is a weak temperature dependence. In the present study, a method adopting available data from nearby stations and applying a correction factor was used. A general evaluation of the influence of several extrapolation methods to the estimation of residence times is important. However, such a sensitivity study has not yet been provided. The local $^{18}$O input function from the station Büel covers a period of 30 months from January, 1994 until June, 1996. To extrapolate this record for the period before our own measurements, available data from nearby Swiss and German stations (Figure 4.6) were investigated. Figure 4.7 shows the monthly $^{18}$O input function from the station Büel, as well as from two IAEA/WMO stations in Konstanz and Bern, and from two additional stations in Vaduz and Buchs-Suhr of the Swiss National Hydrological and Geological Survey for the period between 1992 and 1995. All the stations show similar variations in monthly $^{18}$O content in precipitation over this period. Some deviations in the case of the Vaduz station might be explained by the location in the Rhine valley where frequent winter temperature inversions are common (Schotterer et al., 1995). Because of the length of the measured records, the IAEA/WMO stations in Konstanz (data since 1981) and Bern (data since 1978) were chosen for the extrapolation of the Büel record since 1981. Data from the other mentioned stations are available since 1992 only. In the first step, a mean

Figure 4.6: Map of Switzerland with the location (points) of the Rietholzbach catchment, as well as of the nearby stations Bern, Buchs-Suhr, Konstanz and Vaduz with available data of $^{18}$O content in precipitation. The coordinates are given in kilometers.
4.2 Description and parametrization of the isotope input functions

Figure 4.7: The monthly $^{18}O$ input function; station Büel and four stations close to the Rietholzbach catchment, period 1992 - 1995. Plotted using data from the Swiss National Hydrological and Geological Survey, Bern.

Figure 4.8: Measured and parametrized local monthly $^{18}O$ input function, station Büel; period 1994. The parametrization was performed by use of values from IAEA/WMO stations in Bern and Konstanz and of an elevation parameter.
value from both stations for each month was calculated. In the second step, an elevation correction was performed using a correction factor including the elevation dependence of $^{18}$O in precipitation. As described above, the depletion of $^{18}$O content with increasing altitude is one of the consequences of isotope fractionation in the condensation phase of rain water during an orographic ascent of air masses. The elevation dependence of $^{18}$O content in precipitation is a spatially and temporally variable phenomenon which can be approximately determined by longterm profile observations. To date, there are no isotope measurements from a profile of precipitation stations in Northeastern Switzerland. Nevertheless, longterm observations in the Hasli Valley near Bern performed by the Physics Institute of the University Bern at three IAEA/WMO stations Meiringen, Guttanen and Grimsel (Siegenthaler and Oeschger, 1980; Pearson et al., 1991; Schotterer et al., 1995) established a gradient of $\delta^{18}$O values of precipitation of about 0.22 $\%$o SMOW for 100 m a.s.l. difference in elevation. Using this value as a parameter, the monthly $^{18}$O input function for the Rietholzbach basin for the period before 1994 is

$$\delta_{Rhb} = \frac{\delta_{Ko} + \delta_{Be}}{2} - 0.7$$

(4.23)

Hence, the coefficient 0.7 represents the elevation difference of about 300 m a.s.l. between the cited stations in Konstanz (407 m a.s.l.), Bern (511 m a.s.l.) and Bül (755 m a.s.l.) and $\delta_{Ko}$, $\delta_{Be}$ and $\delta_{Rhb}$ represent the monthly $\delta^{18}$O values of precipitation at these stations. Figure 4.8 shows the comparison of parametrized values with observed values at the station Bül for the calibration year 1994. Despite the slight systematic overestimation of the parametrized values at the beginning of summer, the procedure produced results in a good agreement between the observed values and the parametrized values. Thus, the combination of the measured values for the period between January, 1994 and June, 1996 with values obtained by the equation (4.23) for the period since July, 1981 until December, 1993 yields the raw unweighted local $^{18}$O input function.

**Weighting of the local $^{18}$O input function.** The raw unweighted input function provides the isotopic precipitation composition at the surface, which is independent on the precipitation amount and on the net precipitation portion which contributes to the water turnover in the subsurface. Therefore, a weighting of the input function has to be provided. If considered for stable isotopes, i.e. without the radioactive decay term, the basic equation (4.8) becomes

$$c_{out}(t) = \frac{\int_0^\infty W(t-t') c_i(t-t') g(t') dt'}{\int_0^\infty W(t-t') g(t') dt'}$$

(4.24)

with the unweighted input concentration $c_i$ and a weighting parameter $W$.

For weighting of a cyclical input function, Bergmann et al. (1986) proposed a general formula

$$c_{in} = \frac{\sum_{i=1}^N a_i P_i}{N} (c_i - C_{in}) + C_{in}$$

(4.25)

where $c_{in}$ and $c_i$ represent the parametrized and the measured monthly isotope concentration in the $i$-th month, respectively, $N$ is the number of months for which the isotope input record is parametrized, $a_i$ and $P_i$ are an unspecified recharge parameter and the precipitation amount in the $i$-th month, respectively. Considering the whole input function
4.2 Description and parametrization of the isotope input functions

For the period between July, 1981 - June, 1996, the value $N$ is equal to 180 so that the values of $i$ range from 1 to 180. $C_{in}$ means the longterm mean isotope input concentration calculated as

$$C_{in} = \frac{\sum_{i=1}^{N} a_i P_i C_i}{\sum_{i=1}^{N} a_i P_i} \quad (4.26)$$

The physical significance of the equations (4.25) and (4.26) is the redistribution of the monthly $^{18}$O input values around the longterm mean which depends on two parameters:

- the recharge amount itself
- the difference between the unweighted concentration and the longterm mean.

It appears that the potential differences between the unweighted and weighted values increase with increasing difference between the unweighted input function and the longterm mean. Therefore, all unweighted concentrations close to the mean remain nearly equal regardless of the recharge amount. In contrast, the weight of the concentrations differing strongly from the mean is considerably affected by the recharge amounts. As a consequence, a negligible recharge amount related to the above-average or sub-average input values sets these values to nearly equal to the mean regardless of the difference between the unweighted input and the mean.

Up to now, several approaches have been performed in order to express a reliable form of the recharge parameter $a_i$. Three groups of methods are discussed below.

- **Weighting by precipitation amounts only**, i.e. setting $a_i$ in equations (4.25) and (4.26) equal to 1 (Pearce et al., 1986). As no temporal differences in the recharge amounts are assumed, this approach obviously neglects the evapotranspiration losses, thus, overestimating the role of rainfall in summer months while underestimating the winter recharge due to snowmelt. Unfortunately, Pearce et al. (1986) handled the input function with respect to its amplitude only and did not investigate how the input function is affected by this parametrization for each time step. Figure 4.9 shows the application of this approach for the $^{18}$O input function of the station Büel. It appears that the concentrations in summer months mostly remain unaffected, except for values from extremely dry months including for example the October 1995. According to the equations (4.25) and (4.26), the small precipitation amount neglects the role of the input and causes the parametrized values in these periods closer towards the longterm mean weighted value (Figure 4.9). Otherwise, the concentrations in winter months are generally more affected because of the low precipitation amounts. The weakness of the weighting by precipitation due to the neglect of the evapotranspiration losses and of the winter and spring recharge is, therefore, confirmed.

- **Weighting by recharge parameter as a function of precipitation amount.** Stewart and McDonnell (1991) divided weekly precipitation amounts into three categories ranging between a fully infiltrated precipitation and precipitation without any infiltration to evaluate short water residence times in shallow unsaturated zone. Depending on this criterion, the input function consists of fully weighted, semi-weighted and non weighted segments. Similar to the approach described above, this procedure does not consider real outflow amounts and cannot determine the real input weight for the given time step.
• Weighting by a recharge parameter which expresses the relationship between the groundwater recharge in winter and summer season (e.g. Bergmann et al., 1986; Herrmann et al., 1986b; Maloszewski et al., 1992). This relationship can be derived either by comparison of isotope input values and the mean isotope output value as proposed in an approximative method of Grabczak et al. (1984), or by simple comparison of runoff coefficients obtained separately for winter and summer months. Although the latter considers temporal recharge variations, the averaging over the whole season still leads to a considerable simplification. Moreover, the interpretation of groundwater recharge in terms of infiltration parameters defined as discharge-precipitation relationship leads to an input overestimation in periods with high surface runoff amounts. Concerning the approach based on the method proposed by Grabczak et al. (1984), the weighting of the input function uses a winter-summer recharge relationship obtained by means of the longterm mean of the input function itself, so that the weighting parameter cannot be regarded as fully independent. A more detailed discussion on these aspects is published in Bergmann et al. (1986) and Maloszewski et al. (1992).

For the purpose of the present work, a modified weighting approach was developed. It is based on monthly weighting of the isotope input function by an independent groundwater recharge variable. Two variables were applied: firstly, the monthly measured lysimeter outflow rates in the depth of 2.20 meter; secondly, the monthly groundwater recharge obtained using the soil water balance model BOWAM.

• Lysimeter outflow rates. If assumed that the lysimeter outflow rates \( L_i \) in \( i \)-th month can be regarded as monthly contribution from the precipitation to the subsurface water turnover, the recharge parameter \( a_i \) in equations (4.25) and (4.26) becomes to \( a_i = L_i/P_i \), so that equations (4.25) and (4.26) are rewritten as

\[
c_i = \frac{N L_i}{\sum_{i=1}^{N} L_i} (c_i - C_{in}) + C_{in}
\]

and

\[
C_{in} = \frac{\sum_{i=1}^{N} L_i c_i}{\sum_{i=1}^{N} L_i}
\]

In a similar manner to Figure 4.9, Figure 4.10 shows the results of the parametrization using the lysimeter outflow rates for the local \(^{18}\text{O}\) input function at the station Büel. It appears here, that there is a number of values particularly related to summer months where the groundwater recharge is low. As a consequence, although the unweighted input concentrations might be high, the low recharge rates causes a limited weight of these values in the whole input function.

Finally, Figure 4.11 compares the results of the two weighting procedures presented above for the \(^{18}\text{O}\) input function at the station Büel. Again, the main differences are observed. In contrast to the weighting by use of precipitation amounts, the weighting by use of the lysimeter outflow rates expresses more realistically the limited role of the summer recharge and the importance of the recharge during the winter and spring months. This conclusion is confirmed by the Table 4.1 where the mean \(^{18}\text{O}\) concentrations in precipitation obtained using the cited weighting
Weighting by precipitation amounts

Figure 4.9: Weighting of the monthly $^{18}\text{O}$ input function from the station Büel, period July, 1981 - June, 1996, using the precipitation amounts. Top: Plot of the monthly records. Bottom: Relationship between the raw and weighted values including the average of weighted values, as well as the 1:1 line.
Figure 4.10: Weighting of the monthly $^{18}$O input function from the station Büel, period July, 1981 - June, 1996, using the lysimeter outflow rates. Top: Plot of the monthly records. Bottom: Relationship between the raw and weighted values including the average of weighted values, as well as the 1:1 line.
4.2 Description and parametrization of the isotope input functions

Figure 4.11: Relationship between the monthly $^{18}$O input values weighted by use of lysimeter outflow rates and precipitation amounts at the station Büel over the period July, 1981 - June, 1996.

Techniques are listed. As mentioned above, the weighting by precipitation amounts tends to give higher concentrations during summer months, resulting in a higher mean concentration in comparison with the unweighted function. Otherwise, the weighting using the lysimeter outflow results in a lower mean $^{18}$O input concentration.

Table 4.1: Mean monthly $^{18}$O content in precipitation obtained by assessment of different weighting methods. Station Büel, period July, 1981 - June, 1996.

<table>
<thead>
<tr>
<th>Weighting Method</th>
<th>$^{18}$O [%o SMOW]</th>
</tr>
</thead>
<tbody>
<tr>
<td>No weighting</td>
<td>-10.58</td>
</tr>
<tr>
<td>Precipitation amounts</td>
<td>-10.38</td>
</tr>
<tr>
<td>Lysimeter outflow rates</td>
<td>-11.14</td>
</tr>
</tbody>
</table>

- **Soil water balance model BOWAM.** Among the various soil water balance models, the model BOWAM allows the process-related simulation of the soil water balance inclusive of the infiltration, percolation, evapotranspiration, changes in soil moisture, formation of overland flow, interflow, and groundwater recharge (Peschke *et al.*, 1986). This model is based on the two-step infiltration concept developed by Peschke (1977). During an unsaturated period without overland flow the entire rain water infiltrates and produces a new distribution of soil moisture. In the case of high precipitation intensities the soil surface is saturated, followed by a recession phase during which a surface runoff occurs, as well as groundwater recharge GW. The procedure is coupled with an evapotranspiration submodel (Peschke, 1987).

Within the framework of the NFP-31 project *Impacts of climatic variations on the water resources and on the flow regime within the Rhine river basin* an application
of the model BOWAM in the Rietholzbach catchment was carried out (Gurtz et al., 1997). It appears that the obtained monthly groundwater recharge amounts \( GW \) are smaller than the lysimeter outflow rates \( L \) because the latter represents all the infiltrated components, whereas the groundwater recharge amounts indicate the inflow into the saturated zone only. According to equations (4.27) and (4.28), the monthly weighted input function using the groundwater recharge parameter \( GW \) can be written in the form

\[
\bar{c}_{in} = \frac{N\sum_{i=1}^{N} GW_i}{N} (c_i - C_{in}) + C_{in} \quad \text{(4.29)}
\]

and

\[
C_{in} = \frac{\sum_{i=1}^{N} GW_i c_i}{\sum_{i=1}^{N} GW_i} \quad \text{(4.30)}
\]

Figure 4.12 shows the comparison of the weighting of the \( ^{18}O \) input function for the years 1994 and 1995 using different weighting methods. It appears that the monthly values weighted by the parameter \( L \) and \( GW \) are in good agreement, although the physical significance of these parameters is not equal. Whereas the high summer precipitation amounts cause high input \( ^{18}O \) content, the evapotranspiration losses and the overland or macropore outflow lead to relatively lower weight in the \( ^{18}O \) input function. A good example for this effect is observed during the extremely dry month of October 1995, with 3.1 mm precipitation and negligible lysimeter outflow and groundwater recharge. Even though the original \( \delta^{18}O \) value of precipitation is very high (~6.75 %SMOW), the weighted one reaches values close to the longterm mean input being -10.38 %SMOW (Table 4.1).

In contrast to the lysimeter outflow data the weighting procedure has not been performed for the complete \( ^{18}O \) input function because the modelled groundwater recharge data do not cover the whole period until the summer 1996. Thus, the computation of the \( ^{18}O \) output functions was carried out by the input function weighted using equations (4.27) and (4.28).

### 4.2.4 General remarks and discussion of the \( ^{85}Kr \) input function

\( ^{85}Kr \) is a radioactive inert gas with a half life of 10.76 years. The natural level of \( ^{85}K \) activity in the atmosphere is conditioned by the reaction \( ^{84}Kr(n,\gamma)^{85}Kr \) in which the secondary neutrons of the cosmic rays take part. The production of some additional amounts of \( ^{85}K \) isotope occurs in the course of spontaneous fission of uranium and thorium nuclei (Ferronsky and Polyakov, 1982). During the past four decades, the development of the nuclear industry results in a considerable release of technogenic krypton into the atmosphere because of the fission of uranium and plutonium. The decisive sources of technogenic \( ^{85}Kr \) to the atmosphere are nuclear-weapon testing and nuclear reactors used for both commercial energy production and plutonium-weapon production. In nuclear reactors, the \( ^{85}Kr \) produced is retained in the fuel rods so that the reprocessing of these fuel rods lead to the release of \( ^{85}Kr \) into the atmosphere (Smethie et al., 1992). As the fuel reprocessing is mostly conducted in the industrially developed countries, most \( ^{85}Kr \) enters
Different weighting methods

\[ \text{\deltatwO (per mil SMOW)} \]

\[ \text{\deltatwO weight, lysim. outflow (per mil SMOW)} \]

**Figure 4.12:** Weighting of the monthly $^{18}$O input function from the station Büel, period 1994 - 1995, using various weighting methods. Top: Plot of the monthly records. Bottom: Relationship between values weighted by the lysimeter outflow rates, as well as by the groundwater recharge rates obtained by the model BOWAM (regression coefficient = 0.86).
the Northern Hemisphere. The observed $^{85}$Kr specific activity in the Southern Hemisphere is approximately 20% lower because of slow atmospheric mixing across the Intertropical Convergence Zone (e.g. Rozanski, 1979).

Unlike the stable isotopes of the water molecule and the radioactive tritium, the density of stations with available records of $^{85}$Kr content in the air is very sparse. Thus, a comprehensive description of all the factors controlling the distribution of $^{85}$Kr in the atmosphere is not available. Despite the coupled modelling studies on the large-scale mixing of atmospheric gases (e.g. Weiss et al., 1984), there is only a very small number of works dealing with the variations of $^{85}$Kr content on smaller scales.

Because the local $^{85}$Kr input record was not feasible to obtain in the catchment Rietholzbach, data from nearby stations were investigated. The closest non-alpine station is situated at the Schauinsland Hill near Freiburg im Breisgau, Southern Germany, at a distance of about 120 km from the catchment Rietholzbach. Here the weekly measurements of the $^{85}$Kr in the air are operated by the German Federal Institute of Radiation Protection, Freiburg im Breisgau. The $^{85}$Kr input function used from this station covers the period between January, 1990 and September, 1996 and is shown in Figure 4.13.

4.3 Description and simulation of the isotope output functions

Mixing processes within a storage system of the catchment lead to a transfer of the isotope input into the isotope output at the storage outlet. In order to estimate the mean water residence time using the lumped-parameter flow approach, the best fit of the measured output record is computed.

The aim of this chapter is to simulate the measured $^{18}$O and $^{85}$Kr output functions and to calculate the mean water residence times in the typical aquifers and soil storage reservoirs of the prealpine catchment Rietholzbach. As stated in previous Chapter 4.2, the compu-
4.3 Description and simulation of the isotope output functions

description is based on the following two input functions: firstly, the local $^{18}$O input function of the station Büel for the period between July, 1981 - June, 1996, weighted by use of the lysimeter outflow rates, and secondly, the $^{85}$Kr input function of the station Schauinsland, Germany, for the period January, 1990 - September, 1996. According to the description of the field sampling set-up, $^{18}$O output functions at the following sites were analyzed:

- Stream water from the whole Rietholzbach catchment represented by main runoff gauging site Mosnang.
- Stream water from two subcatchments Oberer Rietholzbach and Huwilerbach in the upper part of the Rietholzbach catchment represented by two runoff gauging sites close to the hydrometeorological station Büel.
- Percolated water flowing out from a 2.20 km deep soil layer in the lysimeter located within the hydrometeorological station Büel.
- Groundwater in three boreholes which form a profile across the valley, close to the hydrometeorological station Büel, with different types, i.e.:
  1. Aquifer on the hillslope site oriented to the south, represented by the borehole B3;
  2. Aquifer on the hillslope site oriented to the north, represented by the borehole B2;
  3. Aquifer represented by the borehole B1, close to the hydrometeorological station Büel.
- Groundwater in two captured wells, both close to the hydrometeorological station Büel, i.e.:
  1. Groundwater in the "Farm house-well";
  2. Groundwater in the well "Trough".

The length of these $^{18}$O output functions reaches up to 3 years over the period 1994 - 1996. Concerning the $^{85}$Kr measurement, the simulation of the output function is based on one measurement carried out for the groundwater in the borehole B1 in July, 1996. Here no sufficient dating using $^{18}$O only was obtained.

The simulations were performed mostly by use of software packages FLOWPC ⁷ and MULTIS ⁸. They are dedicated to simulating the isotopic transport using a variety of lumped-parameter flow models. The computation by means of the $^{85}$Kr measurement was carried out by Norbert Mattle, Physics Institute, University of Bern, within the framework of the project Young groundwaters: age structure, mixing components and other processes. The degree of fit was controlled by the σ-criterion in form

$$\sigma = \sqrt{\frac{\sum_{j=1}^{R} (c_{j\, obs} - c_{j\, fit})^2}{R}}$$

(4.31)

where $c_{j\, obs}$ and $c_{j\, fit}$ are the measured and the fitted concentrations, respectively, and $R$ is the number of observations.

⁷GSF-Forschungszentrum, Institut für Hydrologie, Ingolstädter Landstraße 1, D-85764 Ober-)schießheim, Germany

⁸International Atomic Energy Agency, Section of Isotope Hydrology, Wagramerstraße 5, P.O. Box 100, A-1400 Vienna, Austria
This chapter is divided into three parts. Chapter 4.3.1 deals with the baseflow component of stream waters, Chapter 4.3.2 handles the soil water percolated through the lysimeter layer and Chapter 4.3.3 treats the groundwaters.

4.3.1 Stream waters

Three runoff gauging stations were chosen for the sampling. In addition to the main runoff gauging station Mosnang, samples from two stations representing the subcatchments, Huwilerbach and Oberer Rietholzbach, were taken into account in order to investigate the mean water residence times of water, particularly those which pass through the Quaternary deposits in the upper part of the catchment.

Figure 4.14 presents the $^{18}O$ output functions for the stream water from Rietholzbach at three runoff gauging sites: main catchment runoff gauging site Rietholzbach and the runoff gauging sites of the subcatchments, Oberer Rietholzbach and Huwilerbach. The data records show a cyclic behaviour of $^{18}O$ content with a damping of the amplitude and with a clear influence of current precipitation water. The latter can be detected by separate notation of values measured on instantaneous samples related to stormflow situations. In the case of summer stormflow, the $^{18}O$ concentrations are higher due to isotopically more enriched precipitation, whereas winter precipitation including snow are depleted in $^{18}O$ and causes distinct concentration deviations in the creek water towards low values. It is assumed that these values express the influence of current water components passing the macropores, the drainage network or routed as overland flow. Using artificial tracer experiments, Burgthaler (1992) has shown that the mean residence time of such components in the Rietholzbach catchment ranges between few hours to several days. This phenomenon causes extremely high short-time variations in $^{18}O$ concentrations in the stream water up to a difference of 3 % SMOW in the $\delta$-values. Thus, for the purpose of the dating, the resulting output function is divided into a component related to the baseflow and a component with high short-term variations of isotope concentration due to short rainfall and flood events. If the stream water would be sampled continuously and volume-proportionally in longterm series, the output function would be simulated as representative of the whole stream runoff (Maloszewski et al., 1983; Herrmann et al., 1986b). In the case of instantaneous sampling, the values related to flood events are filtered out by means of runoff data. Thus, values marked by circles in Figure 4.14 represent a runoff higher than the mean runoff of the given month and the separated output function marked by stars was simulated as a steady-state baseflow component. This filtering of $^{18}O$ output functions of stream waters was introduced by Pearce et al. (1986).

Figure 4.15 shows the results of the simulations by use of lumped-parameter flow models for the stream water sampled at three outlets. The best fits were found for parameters summarized in Table 4.2.

Although the calibration of parameters was performed individually for both model concepts used (i.e. the variant with dispersion, equation 4.22, and the variant without dispersion, equations 4.14 and 4.16), the best fitting results are reached for an identical mean residence time. In all the cases presented here, the models based on the exponential type of mixing sufficiently simulate the experimental output function with respect to its amplitude, as well as to its phase shift. It can be seen, however, that especially in the case of highly dispersive storage systems such as the glacial deposits forming an essential part of the subcatchments Huwilerbach and Oberer Rietholzbach, the simulated output function obtained by the dispersion model is slightly delayed in comparison with
Figure 4.14: The $^{18}$O output functions for the stream water from three runoff gauging stations; period 1994 - 1996. The filtering of values related to stormflow situations was performed by means of runoff data.
Figure 4.15: Simulation of $^{18}O$ output functions for the baseflow component of the stream water from three runoff gauging stations; period January, 1994 - June, 1996. The best fits are reached by use of the combined exponential-piston flow model and the dispersion model for the mean water residence time 12.5 months (catchment Rietholzbach) and 24.5 months (subcatchments Huwilerbach and Oberer Rietholzbach), respectively.
4.3 Description and simulation of the isotope output functions

The interpretation of the residence times obtained and of the simulations leads to the following simplified conclusions:

- The mean residence time of the baseflow determined at the outlets from both subcatchments Oberer Rietholzbach and Huwilerbach is influenced by efficient mixing within the aquifer formed by Quaternary glacial deposits and is larger than the mean residence time of the baseflow from the whole catchment Rietholzbach. It is, therefore, expected that there are faster hillslope fluxes originating particularly in the Molasse layers on the slopes oriented to the north and having considerably smaller residence times. The influence of the Quaternary deposits might be, therefore, compensated so that the mean water residence time within the whole catchment (determined for samples at the catchment outlet) remains for about 1 year. These questions have to be solved in combination with the estimations of the mean residence times of groundwaters (Vitvar, 1997).

- The fitting of the $^{18}O$ output functions for both subcatchments shows a higher agreement for the use of the exponential model in comparison with the dispersion concept. It is obvious that the modelled residence time distribution, i.e. a theoretical full mixing at the outlet from the subsurface, satisfies more realistically the efficient mixing within the Quaternary layers. Regardless of the apparent dispersion parameter, the advection-dispersion concept still assumes a contribution of water motion caused by advection, so that the computation of a full water mixing within the cited aquifers using this concept is not possible. This aspect may be treated in more details by means of the analysis of the residence time distribution functions of the model concepts used here (Chapter 4.4).

- The fitting by use of the parametrized local $^{18}O$ input function produces good results for all the computed $^{18}O$ output functions. The length of the output functions is sufficient and reaches up to 3 years, so that more than two cycles of seasonal variations of isotopic concentrations could be modelled.

- The comparison of mean water residence times obtained in the Rietholzbach catchment with results of some studies carried out in hilly catchments shows a good agreement. Among the very limited number of such studies existing to date, the modelling of the $^{18}O$, deuterium and tritium output functions of the baseflow component in the porous Lainbach catchment (Małoszewski et al., 1983) or in the porous-fissured catchments Lange Bramke (Herrmann et al., 1986a,b) or Wimbach (Małoszewski et al., 1992), results in residence times of up to 4 years. For a

<table>
<thead>
<tr>
<th>Locality</th>
<th>Model</th>
<th>$T_m$ [months]</th>
<th>$D/vx$ [-]</th>
<th>$\eta$ [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>catchment</td>
<td>dispersion</td>
<td>12.5</td>
<td>0.7</td>
<td>-</td>
</tr>
<tr>
<td>Rietholzbach</td>
<td>exponential/piston flow</td>
<td>12.5</td>
<td>- 1.05</td>
<td>-</td>
</tr>
<tr>
<td>subcatchment</td>
<td>dispersion</td>
<td>24.5</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td>Oberer Rietholzbach</td>
<td>exponential</td>
<td>24.5</td>
<td>- 1.0</td>
<td>-</td>
</tr>
<tr>
<td>subcatchment</td>
<td>dispersion</td>
<td>24.5</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td>Huwilerbach</td>
<td>exponential</td>
<td>24.5</td>
<td>- 1.0</td>
<td>-</td>
</tr>
</tbody>
</table>
relatively larger (58.3 km²) porous-fissured catchment Pöllau/Seifenbach, Austria, (Bergmann et al., 1986), the calculated mean water residence time of 23 months is relatively short, but this result is valid for the whole catchment outflow and not for the baseflow component only. It is, therefore, obvious that all these results cannot be generalized or directly transferred to other catchments, but they have to be interpreted in strong relation to the catchment characteristics, as well as to the model parameters used.

All the conclusions denoted here will be discussed in more detail in Chapter 4.4.

4.3.2 Soil water in the lysimeter

The estimation of the mean residence time of water percolated through the lysimeter layer gives essential insights into the groundwater recharge mechanisms, as well as into the vertical flow and transport behaviour within the unsaturated zone. Moreover, the lysimeter in the Rietholzbach catchment serves as a representative "subcatchment" for studies on water balance components, especially the evapotranspiration (e.g. Menzel, 1997).

In the present study, the following aspects are of particular interest:

• The lysimeter outflow amounts are used as recharge rates for the weighting of the monthly 18O input function as described in Chapter 4.2.3.

• The mean residence time of water percolated through the lysimeter is used in the combined 18O and 85Kr interpretation of the residence time of groundwater in the borehole B1 as described in Chapter 4.3.3.

Unlike the saturated zone, the modelling of vertical flow and transport through the lysimeter has to deal with some special aspects. Two tasks are of particular interest and are shortly discussed here: firstly, the existence of the mobile and immobile water components within the soil layer, and secondly, the existence of components having a stable isotopic content.

• Existence of mobile and immobile components. Investigating the vertical flow through the unsaturated zone, several authors have shown that only a part of the water volume, i.e. the mobile water, participates in the motion, whereas a second volume portion remains stagnant. This is due to the local inhomogeneities in the distribution of pores within the unsaturated environment, in many cases known as the concept of dead-end pores (Coats and Smith, 1964; DeSmedt and Wierenga, 1979). The unsaturated zone is, therefore, regarded as a double porosity medium with mobile and immobile water components and with water and tracer transfer between these phases. The distribution of stagnant components is difficult to distinguish experimentally. Solutions performed by means of a two-phase transport model using a double porosity dispersion model either under variable flow conditions (DeSmedt et al., 1986; Maciejewski, 1993; Klotz et al., 1995) or under the steady-state assumption (Klotz et al., 1988) have shown that the increased number of additional parameters, i.e. the relationship between mobile and immobile water content and the transfer coefficient of tracer exchange between mobile and immobile water phases, cannot be properly interpreted. Since the application of the double-porosity approach assumes a tracer exchange between mobile and immobile phases, the mean residence time obtained has to be regarded as the residence times of tracer and not the residence time of the flowing water. Nevertheless, comparative studies performed in column experiments (DeSmedt et al., 1986), as well as in
lysimeters (Klotz et al., 1995) and in double-porosity fissured media (Maloszewski and Zuber, 1985), showed that the discrepancy between these residence times for values greater than 1 week is practically negligible. Investigations in large refuse lysimeters performed by Maloszewski et al. (1995) confirmed these assumptions and showed a very good accuracy of modelling $^{18}$O output functions by use of the two-parameter dispersion model (equation 4.22).

- Existence of components having a constant isotopic content. The artificial tracer experiment performed in the lysimeter in the Rietholzbach catchment by Demuth et al. (1993) showed that the tracer break-through curve over a period of 16 months is not ideal because of an extremely slow decrease of tracer concentrations at the end of the experiment. Demuth et al. (1993) explained this phenomenon by a tailing effect, which is similar to the concept of mobile and immobile components, but does not assume any fully immobile phase. The delay is caused by slow outflow of components passing the micromatrix instead of the displacement in larger pores. Large precipitation obviously leads to the displacement of previously stored water from the pores, as well as to the inflow of the rest of this water into the micromatrix. This micromatrix water might be regarded as a well-mixed component having a constant tracer content under steady-state conditions.

To express the above mentioned delayed component in the sense of the lumped-parameter flow approach, the equation (4.8) is rewritten in the form

$$c_{\text{out}}(t) = \int_0^\infty m \overline{C}_{\text{out}} + (1 - m) c_{\text{in}}(t-t') g(t') \exp(-\lambda t') \, dt'$$

(4.32)

where $m$ is the volume proportion of the component having a constant tracer content $C_{\text{out}}$. The value of the $C_{\text{out}}$ was calculated as the weighted mean of the monthly $^{18}$O concentrations in precipitation related to the months with lysimeter outflow rates higher than 200 mm (Table 4.3). According to longterm observations, the highest lysimeter outflow rates mainly occur in winter months, i.e. the micromatrix recharge is dominated by isotopically lighter water. Thus, this component plays an essential role in the summer outflow during dry periods. The weighted mean $^{18}$O concentration $\overline{C}_{\text{out}}$ is, therefore, -11.4 $\%_{\text{SMOW}}$. In a preceding work, Vitvar and Balderer (1997) applied the equation (4.32) separately for the years 1994 and 1995 considering $C_{\text{out}}$ being the mean $^{18}$O concentration of the isotopically lighter water flowing out in summer months.

Figure 4.16 presents the $^{18}$O output function for the lysimeter outflow as well as the results of their simulation. It is obvious that the outflowing water contains a considerable portion of displaced water. The output function has a phase shift of about one half year, i.e. the winter outflow mainly contains isotopically heavier water infiltrated during the summer season, and the summer outflow consists of isotopically lighter water components infiltrated in winter. The simulation was performed using the monthly weighted output function and is depicted again in Figure 4.16. The best fits were reached by use of parameters listed in Table 4.4. The simulations were computed by use of the modified convolution equation (4.32) and two model concepts (equations 4.22 and 4.14).

The results are summarized as follows:

- The simulation of the $^{18}$O output function confirmed the results obtained by the artificial tracer experiment performed by Demuth et al. (1993), who calculated the mean water residence time of 204 days using the dispersion model (equation 4.22).
Figure 4.16: The $^{18}$O output function of the water flowing out from the lysimeter layer in the depth of 2.20 m; hydrometeorological station Bäel, period 1994 - 1996. Top: Plot of the output function based on weekly (1994 - 1995) and two-weekly (1996) measurements. Bottom: Simulation of the output function for the same period expressed in monthly weighted values. The best fits are reached by use of the combined exponential-piston flow model and the dispersion model for the mean water residence time 7.3 months (exponential-piston flow model) and 7 months (dispersion model), respectively.
with a dispersion parameter \( D/v_x = 0.05 \). Despite the additional parameters \( m \) and \( \bar{C}_{out} \), the other parameters used in the present work are close to those used by Demuth et al. (1993). Among the extremely sparse number of works dealing with the lumped-parameter applications of stable isotopes in lysimeters, similar mean residence times between 18 and 28 weeks of water flowing out from 2 m deep columns filled by the Bavarian prealpine sandy soils were obtained (Klotz et al., 1995). Investigations on the residence times within refuse lysimeters (Maloszewski et al., 1995) showed considerably higher mean water residence times up to several years because of the compaction and layering of the refuse material.

- The computation using the modified convolution equation (4.32) overcame the problem concerning the slow micromatrix component observed by Demuth et al. (1993). Moreover, the parameters \( m \) and \( \bar{C}_{out} \) permitted the calculation of the lysimeter \(^{18}O\) balance having the form

\[
(1 - m) C_{in} + m \bar{C}_{out} = C_{out}
\]  

(4.33)

where the mean input concentration \( C_{in} \) is defined by the equation (4.28) and the \( C_{out} \) expresses the mean weighted output concentration. The calculation for the period 1994 - 1995 yielded \( C_{in} = -10.62 \% \) SMOW and \( C_{out} = -10.91 \% \) SMOW. Putting these values into equation (4.33) together with \( m = 0.4 \) and \( \bar{C}_{out} = -11.4 \) satisfies the balance.
Like the results presented in the previous Chapter 4.3.1, the conclusions stated here will be discussed in more details in Chapter 4.4.

4.3.3 Groundwaters

The equipment for studying the groundwater component in the present study consists of three boreholes and two captured wells.

Before the boreholes were maintained, private farm house-wells have been the only source for sampling groundwater in the Rietholzbach catchment. However, due to the intensive use for agricultural purposes and as drinking water, the groundwater regime of these wells cannot be regarded as being natural.

Three groundwater boreholes B1, B2 and B3 were installed in December, 1994. They form a profile throughout the central part of the catchment. The aim was to obtain data describing the natural groundwater regime for incorporating the groundwater component into the process studies on the interactions between the surface water and the shallow groundwater. In order to quantify the main hydraulic profile parameters of the aquifers, pumping tests on the boreholes were carried out.

Notes on the groundwater regime. Combining the interpretation of measurements of groundwater levels and temperatures (Figure 4.17) and of groundwater electrical conductivities (Figure 4.18) in the boreholes, the following characteristics of the groundwater regime can be derived:

- The groundwater depth in the borehole B2 is shallower in comparison with those in the boreholes B1 and B3 so that the groundwater temperatures in the borehole B2 show the relatively largest variations. The variability in electrical conductivity values in the borehole B2 is also larger, whereas the minimal values reach the level of about 200-300 $\mu$S/cm. This fact demonstrates the influence of rapid infiltration of the rainfall water from the land surface. This can be regarded as a typical characteristic of the groundwater regime with a less efficient water mixing on the slopes oriented to the north having less developed soils.

- The groundwater level in the borehole B3 shows large variations particularly due to the considerable drawdown during dry periods. A variation of electrical conductivities between 500 and 700 $\mu$S/cm shows a more efficient mixing of water components in comparison with the borehole B2. This might be explained by the more developed soils on the slopes oriented to the south and, as a consequence, by deeper depth of the groundwater table.

- The groundwater regime in the borehole B1 is an example of a buffering effect of the layers of glacial deposits on the valley level. Although the records of the groundwater levels and, consequently, of the groundwater temperatures are similar to those of the borehole B3, the efficient mixing of components originating from the slopes leads to a steady record of groundwater conductivities. Thus, such a type of groundwater can be regarded as a low flow reservoir with high expected values of water residence times.

Notes on the pumping tests. Single-well tests were carried out in June-July, 1997, on the boreholes B1, B2 and B3. The numerical evaluation (software package SATEM
4.3 Description and simulation of the isotope output functions

Figure 4.17: Groundwater levels and temperatures in the boreholes B1, B2 and B3; period 1995 - 1996, based on weekly (1995) and two-weekly (1996) measurements.
Figure 4.18: Relationship between electrical conductivity and groundwater depth in the boreholes B1, B2 and B3; period 1995 - 1996, based on weekly (1995) and two-weekly (1996) measurements.
4.3 Description and simulation of the isotope output functions

9) was performed using hydraulic approaches for the groundwater flow towards a well within an unconfined aquifer under unsteady-state flow conditions (e.g. Kruseman and de Ridder, 1970). The general formula for unsteady-state flow introduces the time factor and the aquifer storativity and was derived by Theis (1935) from the analogy between the groundwater flow and the conduction of heat in the form

\[ s = \frac{Q}{4\pi kH} \int_{u}^{\infty} e^{-y} dy = \frac{Q}{4\pi kH} W(u) \]  (4.34)

with

\[ u = \frac{r^2 S}{4kHt} \]  (4.35)

where \( k \) and \( S \) are the hydraulic parameters conductivity and storativity, \( H \) is the aquifer thickness, \( Q \) the constant well discharge, \( s \) the drawdown, \( t \) the time since pumping started and \( r \) is the inner well diameter. The exponential integral \( W(u) \) is generally read as Theis's well function. From the equation (4.34) it can be seen that after a sufficiently long pumping time, the terms beyond \( \ln u \) in the series become so small that they can be neglected and the well function exhibits a straight line segment. Thus, for this straight-line segment, Cooper and Jacob (1946) introduced an approximation of equation (4.34)

\[ s = \frac{Q}{4\pi kH} \log \frac{2.25 kHt}{r^2 S} \]  (4.36)

If the slope of this straight-line segment is expressed as the drawdown difference \( \Delta s \) per log cycle of time, rearranging equation (4.36) gives the expression of the hydraulic conductivity

\[ kH = \frac{2.30 Q}{4\pi \Delta s} \]  (4.37)

Finally, if the straight line is extended until it intercepts the time axis where \( s = 0 \), the interception point has the coordinates \( s = 0 \) and \( t = t_0 \). Substituting these values into equation (4.36) gives the expression of the aquifer storativity

\[ S = \frac{2.25 kHt_0}{r^2} \]  (4.38)

In order to avoid possible misinterpretations resulting from various departures from the described theory under field conditions, the following aspects were taken into account in the present study.

- The measured drawdowns in tests described here are large in comparison with the initial saturated thickness of the aquifer. As a consequence, the condition of an approximately horizontal flow towards the well in an unconfined aquifer is not satisfied. Thus, the use of equations given above is based on corrected drawdown values \( s_c \) obtained by the expression of Jacob (1944).

\[ s_c = s - \frac{s^2}{2H} \]  (4.39)
Table 4.5: Hydraulic profile parameters of the aquifer derived from pumping tests on the boreholes B1, B2 and B3.

<table>
<thead>
<tr>
<th>Borehole</th>
<th>Altitude [m]</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$k$ [m s$^{-1}$]</td>
</tr>
<tr>
<td>B1</td>
<td>754</td>
<td>$1.2 \times 10^{-4}$</td>
</tr>
<tr>
<td>B2</td>
<td>758</td>
<td>$3.6 \times 10^{-6}$</td>
</tr>
<tr>
<td>B3</td>
<td>767</td>
<td>$1.3 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

The measured drawdowns show an effect of so-called delayed yield caused by a time lag between the elastic response of the unconfined aquifer and the downward movement of the watertable due to gravity drainage (e.g. Kruseman and de Ridder, 1970). The latter phenomenon leads to flat segments of time-drawdown curves as demonstrated in Figure 4.19. As a consequence, only the relatively steep segments are relevant for the numerical evaluation.

Figure 4.19: Time-drawdown diagram of pumping tests under unsteady-state conditions performed on the boreholes B1, B2 and B3.

The results of the pumping tests are summarized in Figure 4.19 and Table 4.5.

Estimation of water residence times by use of $^{18}$O. Figure 4.20 presents the $^{18}$O output functions for the subsurface waters from the boreholes B1, B2 and B3. Unlike the $^{18}$O output functions in the stream waters presented in Figure 4.14 and according to the above described characteristics of the groundwater regime, the following two phenomena can be detected:

1. No variations of $^{18}$O content occur in the groundwater from the borehole B1. This fact indicates a generally well mixed water having a mean residence time which cannot be identified by means of the $^{18}$O isotope alone.
2. An effect of the irrigation water introduced into the borehole B3 during the drilling work on December 6th, 1994. Hence, this irrigation water taken from the creek influenced the isotopic composition of the groundwater so that the natural form of groundwater isotopic variations was established in the summer 1995.

In the case of the boreholes B2 and B3, the data show a cyclic variations of $^{18}$O content with a damping of the amplitude in comparison with the amplitude of the input function. In the case of the borehole B2, an influence of rapidly infiltrated water from the land surface can be detected. Similar to the output functions for surface water (Figure 4.14), a filtering of values representing this fast infiltration through the unsaturated zone was carried out. Thus, $^{18}$O values related to samples having the electrical conductivity lower than 500 $\mu$S/cm are marked by circles in Figure 4.20. The values marked by stars indicate the output function of the groundwater what is not affected by rapid rainfall infiltration. This function is simulated by lumped-parameter flow approach. Figure 4.21 shows the results of the simulations for the boreholes B2 and B3 (equations 4.22 and 4.14). The best fits were found for parameters summarized in Table 4.6.

### Table 4.6: Results of the simulations of the $^{18}$O output functions for the groundwater in the boreholes B2 and B3; period January, 1994 - June, 1996.

<table>
<thead>
<tr>
<th>Borehole</th>
<th>Model</th>
<th>$T_c$ [months]</th>
<th>$D/\nu x$ [-]</th>
<th>$\eta$ [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>B2</td>
<td>dispersion</td>
<td>9</td>
<td>0.8</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>exponential/piston flow</td>
<td>9</td>
<td>-</td>
<td>1.1</td>
</tr>
<tr>
<td>B3</td>
<td>dispersion</td>
<td>12.5</td>
<td>0.7</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>exponential/piston flow</td>
<td>12.5</td>
<td>-</td>
<td>1.05</td>
</tr>
</tbody>
</table>

The results of the simulations for both captured wells, as well as their simulations. The parameters of the best fits obtained are summarized in Table 4.7.

### Table 4.7: Results of the simulations of the $^{18}$O output functions for the groundwater in the captured wells over the period January, 1994 - June, 1996.

<table>
<thead>
<tr>
<th>Locality</th>
<th>Model</th>
<th>$T_c$ [months]</th>
<th>$D/\nu x$ [-]</th>
<th>$\eta$ [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>House well</td>
<td>dispersion</td>
<td>12.5</td>
<td>0.7</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>exponential/piston flow</td>
<td>12.5</td>
<td>-</td>
<td>1.05</td>
</tr>
<tr>
<td>Trough</td>
<td>dispersion</td>
<td>24.5</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>exponential</td>
<td>24.5</td>
<td>-</td>
<td>1.0</td>
</tr>
</tbody>
</table>

The results can be briefly interpreted as follows:

- The spectrum of the residence times of water within the analyzed aquifers is close to that obtained for the stream waters. The groundwater located particularly within the molasse aquifers below the hillslopes oriented to the south (Borehole B3, Farm-house well) indicate a residence time of 12.5 months which is identical with that of the surface baseflow at the catchment outlet. The groundwater located particularly within the aquifer consisting of the Quaternary deposits (the well "Trough") indicate a residence time of 24.5 months which is
FIGURE 4.20: The $^{18}$O output functions for the groundwater in three boreholes B1, B2 and B3; period 1994 - 1996. In the case of the borehole B2, the filtering of components related to fast precipitation infiltration was performed by means of groundwater electrical conductivities.
4.3 Description and simulation of the isotope output functions 63

Borehole B2

\[ \delta^{18} \text{O (per mil SMOW)} \]

-8
-9
-10
-11
-12
-13
-14


measured values
 dispersion model
 exp/piston-flow model

Borehole B3

\[ \delta^{18} \text{O (per mil SMOW)} \]

-8
-9
-10
-11
-12
-13
-14


measured values
 dispersion model
 exp/piston-flow model

\textbf{FIGURE 4.21: Simulation of}^{18}\text{O output functions for the groundwater from the boreholes B2 and B3, period January, 1994 - June, 1996. The best fits are reached by use of the combined exponential-piston flow model and the dispersion model for the mean water residence time 9 months (borehole B2) and 12.5 months (borehole B3), respectively.}
Figure 4.22: Simulation of $^{18}O$ output functions for the groundwater from the captured wells over the period January, 1994 - June, 1996. The best fits are reached by use of the combined exponential-piston flow model and the dispersion model for the mean water residence time 12.5 months (House-well) and 24.5 months (Trough), respectively.
in agreement with the estimated residence times for the surface baseflow at the subcatchment outlets Huwilerbach and Oberer Rietholzbach. The groundwater originating on the hillslopes oriented to the north represented by the borehole B2 seems to accelerate the circulation as the aquifer is relatively shallow and is affected by rapid macropore infiltration. Besides the estimated residence times, a good agreement between the other fitting parameters of the output functions of the stream waters and groundwaters was found. This indicates an efficient interconnection between the groundwater circulation and the outflowing stream water.

- The results of the groundwater dating by use of $^{18}$O are consistent with the results of the measurements of groundwater level, temperatures, and electrical conductivities, as well as by the pumping tests. The pumping tests particularly on the borehole B1 showed relatively high hydraulic conductivity and aquifer storativity values which potentially lead to an efficient mixing within the aquifer. Furthermore, the measurements of groundwater electrical conductivity in the borehole B2 distinguished samples affected by rapid rainfall water infiltration. Like the separation of the surface water samples using the runoff data, the filtering of these rapid components is necessary to obtain output functions nearly representing the steady-state flow conditions.

- It can be concluded that the relatively steady $^{18}$O content in the well-mixed groundwater in the borehole B1 (of about -10.6 %o SMOW, Figure 4.20) represents the mean isotope composition of mixed waters stored in the catchment (Vitvar and Balderer, 1997). When assuming the weighted $^{18}$O input into the catchment $C_{in} = -10.62$ %o SMOW (weighting by the lysimeter outflow rates, equation 4.28) for the period between July, 1992 and June, 1996, it appears that both values are nearly equal. Moreover, this mean value is nearly equal to the mean $^{18}$O concentration in the stream water at the catchment outlet Rietholz under low-flow conditions (Figure 4.14). This fact confirms that the whole volume of water stored in the catchment can be generally regarded to be mobile, i.e. there are no significant stagnant components with a significantly different isotope composition. This balance is not achieved for the case of vertical fluxes within the lysimeter Büel (equation 4.33) where a well-mixed micromatrix component exists. In contrast, for small lysimeters with relatively fast water fluxes (and without such micromatrix component), the balance may be also equal (Klotz et al., 1995).

In addition, the calculated balance of the mean weighted $^{18}$O input and the mean output indicates that there is no significant change of the $^{18}$O content as a result of evaporation in the unsaturated zone (i.e. an $^{18}$O enrichment in the remained water during the phase translation). This conclusion was also found for other very young groundwaters in catchments located in the same climatic region (e.g. Maloszewski et al., 1992). Nevertheless, the isotopic enrichment of the soil water generally exists (at least at selected sites in the catchment), even though its consequence for the isotope balance of the whole catchment, as well as for the lumped-parameter modelling of the $^{18}$O output functions, may be negligible (e.g. very slight $^{18}$O enrichment of water with a long residence time in the upper part of a lysimeter, Maloszewski et al., 1995).

Estimation of water residence times using $^{18}$O and $^{85}$Kr. The measured $^{18}$O output function for the groundwater in the borehole B1 (Figure 4.20) showed neither significant seasonal variations, nor significant trends. Considering the results of simulations presented above, it can be expected that the groundwater represented by the borehole B1 has a
residence time higher than 2 years. Thus, the dating by use of $^{85}$Kr was carried out. Figure 4.23 shows the simulation of the $^{85}$Kr output function in monthly steps for the period between January, 1995 - September, 1996. The best fits (equations 4.22 and 4.14) are obtained using parameters listed in Table 4.8. Because the $^{85}$Kr passes the unsaturated zone by gaseous diffusion and not in dissolved form, the gas $^{85}$Kr dates the groundwaters since their entrance into the saturated zone only. It appears, therefore, that the estimated mean groundwater residence time of 18 months has to be regarded as the residence time within the saturated zone only. In terms of Chapter 1.2, the residence time of water $T_m$ is not equal to this residence time $T_t$ of the tracer $^{85}$Kr. In order to calculate the whole residence time for both the saturated and unsaturated zone, the time spent within the unsaturated zone has to be added. The quantification of this delay of gaseous tracers within the unsaturated zone is still poorly understood. Cook and Solomon (1995) stated that the delay depends on a variety of factors, such as the water content and the depth of the unsaturated profile, as well as the gas dispersion coefficient.

In this study, the estimation of the mean groundwater residence time in the borehole B1 was performed by adding the mean residence time obtained using $^{85}$Kr for the saturated zone (18 months) and of the mean residence time obtained using $^{18}$O in the lysimeter.

![Figure 4.23: Simulation of the $^{85}$Kr output function for the groundwater in the borehole B1. The best fit using the exponential/piston-flow model and the dispersion model was reached for the mean $^{85}$Kr residence time of 18 months. Computed by Norbert Mattel, Physics Institute, University of Bern.](image)

| Table 4.8: Results of the simulations of the $^{85}$Kr output functions for the groundwater in the borehole B1 over the period January, 1995 - September, 1996. |
|---|---|---|---|
| **Borehole** | **Model** | **Fitting parameters** |
| | | $T_t$ [months] | $D/\nu x$ [-] | $\eta$ [-] |
| B1 | dispersion | 18 | 1.0 | - |
| | exponential/piston flow | 18 | - | 1.5 |
4.4 Discussion of the results

The aim of this section is to summarize and to discuss the results obtained so far in this chapter. The discussion is organized according to the questions postulated in Chapter 1.

- What are the mean water residence times within the aquifers formed by Freshwater Molasse and Quaternary deposits?

The mean residence times of waters obtained above cover a spectrum reaching up to 2.1 years. The upper area Oberer Rietholzbach is characterized by a good mixing in the Quaternary deposits complex that yields a mean residence time of 24.5 months. For the whole catchment, the lower mean water residence time of 12.5 months was obtained. This spectrum of residence times is formed by a large variety of factors where the relatively fast groundwater fluxes on hillslopes and the efficient mixing within the bottom-valley area of the Quaternary sediments are of particular importance. This spectrum generally confirms the hypothesis on the generally short expected water residence times. The influence of the mixing efficiency on the spectrum of groundwater residence times is also common under more complex geological conditions. For the porous-fissured basin Lange Bramke, Lower Saxonia, Germany, Herrmann et al. (1986a,b) reported that the porous aquifer in the bottom-valley region of this very small catchment (0.76 km²) yields a mean water residence time of about 4 months. This value seems to be short in comparison with the mean residence time of 18 months obtained using the $^{85}$Kr for the groundwater in the borehole B1 representing the Quaternary sediments layer in the catchment Rietholzbach. Nevertheless, this discrepancy can be easily explained by the differences in the area of both the aquifers. Groundwater dating in some porous-fissured catchment structures showed that the relatively higher values of water residence times occur within the fissured parts of aquifers, as proved by Herrmann et al. (1986b, 1990) for quarzites or by Maloszewski et al. (1992) for fractured limestones.

- Is there an agreement between the mean residence time of groundwaters and stream waters under low-flow conditions?

The measured $^{18}$O output functions have shown that there is an agreement between the composition of surface water from a runoff gauging station and of groundwater from relevant aquifers. Thus, the computation of the output functions of groundwaters and surface waters by use of identical parameters yielded identical residence times. Vitvar
(1997) showed the interconnections between the stream water at the catchment outlet and the aquifer represented by the borehole B3 on the slope oriented to the south, as well as by the nearby farm-house well, determined the mean water residence time of 12.5 months. On the other hand, similar interconnections occur between the creek water at the outlet from the subcatchment Oberer Rietholzbach and Huwilerbach and the aquifer represented e.g. by the well "Trough" determining the mean residence time of 24.5 months. This fact confirms that the aquifers on the hillslopes oriented to the south are critical for the supply of the baseflow in the creek at the catchment outlet. In a study utilizing the parallel measurements of the isotopic content of stream waters and groundwaters, Pearce et al. (1986) showed similar phenomena in the catchment Maimai, New Zealand, although the mean residence time of the baseflow and of the interconnected aquifer in their extremely small (4 ha) hilly catchment ranges up to 4 months only.

- What are the mean water residence times within hillslope and bottom-valley aquifers?

The assymetry in the geomorphology of the catchment Rietholzbach (Chapter 2) plays an important role for the evaluation of the contributions of aquifers to the baseflow in the creek. This assymetry results in essential differences between the hillslopes oriented to the north and those oriented to the south with respect to the depth of the soil horizon and of the groundwater table, as well as to the hydraulic aquifer parameters. The groundwater stored in aquifers on the hillslopes oriented to the south apparently represents the main groundwater contribution to the stream under low flow conditions. The groundwater fluxes on the slopes oriented to the north, represented by the borehole B2, obviously have an acceleration effect, whereas the effect of the Quaternary sediments serves as a buffer. The role of the fast fluxes on the slopes oriented to the north is supported by fast recharge of the shallow aquifers from the land surface. Whereas this factor remarkably affects the $^{18}O$ output function of the groundwater borehole B2, the $^{18}O$ output functions of the aquifers on the hillslopes oriented to the south, i.e. of those represented by the borehole B3 or the captured wells, does not show a similar phenomenon. Thus, the concept discussed here seems to explain realistically the postulated spectrum of mean water residence times up to 2.1 years.

- Is there a possibility to obtain the spectrum of water residence times in a small hilly prealpine catchment by means of the $^{18}O$ only?

According to the hypothesis postulated in Chapter 1, the measurements of the $^{18}O$ records at various outlet sites have shown sufficiently developed seasonal variations of isotopic content. This fact is caused by the relatively fast reactions of aquifers and of the unsaturated zone in the highly responsive hilly environment. The analyzed $^{18}O$ output functions show a variety of amplitudes ranging between 1 % SMOW for waters characterizing the mixing within the Quaternary deposits and 3 % SMOW for the vertically percolated water through the lysimeter profile. The well-mixed groundwater in the borehole B1 does not show any significant variation of the $^{18}O$ concentrations. In this case the estimation of the mean water residence time by use of $^{18}O$ alone was, therefore, not possible.

All the simulations of the $^{18}O$ output functions performed in monthly steps using the lumped-parameter inverse modelling showed a good agreement between the measured and fitted values. The best computation results were obtained using the two-parameter concepts. Although Richter et al. (1993) proved that a combination of more than two single models, especially in heterogeneous structures, can improve the degree of fit, the number of fitting parameters increases according to the number of integrated partial models and, therefore, the additional parameters decrease the physical significance.
4.4 Discussion of the results

Another way to verify the results lies in the comparison of computations obtained using two different two-parameter concepts, i.e., one variant without the dispersion and one based on the advection-dispersion concept. Figure 4.24 shows the comparison of system response functions used in this work for simulations of three \(^18\)O output functions. The system response functions of the exponential-piston flow model and the dispersion model show a very good agreement supported by the performed simulations. The comparison of the system response function of the exponential model and the dispersion model depicted below demonstrates why there is a difference in the simulations using these two concepts. In contrast to the exponential concept, the advection-dispersion concept never assumes a full mixing, i.e., a portion of residence times theoretically being equal to zero. Analyzing the statistical moments of the system response functions, Maloszewski and Zuber (1982) and Zuber (1986) stated that the best agreement of the dispersion model with the exponential model may be obtained for the apparent dispersion parameters \(D/vx\) larger than 0.5. This conclusion is essential for calibrating the parameters because Maloszewski et al. (1992) has shown that the dispersion model may also produce a sufficiently good fit using considerably lower dispersivities and higher mean residence times in comparison with those obtained by the exponential model. In order to avoid such misinterpretations, the control of the agreement between two system response functions obtained independently for the simulation of one output function seems to be of great importance.

As noted in Chapter 4.1.3, the dispersion parameter used in the lumped-parameter approach on a larger scale is an apparent quantity representing the heterogeneity of residence times instead of the proper dispersivity of the subsurface material. In the case of the lysimeter, however, the parameter \(D/vx\) can be treated in the sense of effective dispersion because the constant length variable \(x\) is known. On the other hand, this fact may present some limits of the lumped-parameter approach for applications in vertical columns. The varying water content within the soil layer depending on the amount of percolated water, as well as the interactions between the mobile and immobile components, produce changes of the soil dispersivity, which is under steady-state conditions assumed to be constant. This phenomenon appears particularly on relatively small scales, such as lysimeter columns, and might cause some discrepancies between the measured and computed output functions, even though the mean water residence time was approximately estimated (Vitvar and Balderer, 1997). Nevertheless, Klotz et al. (1995) reported that the numerical modelling using the dispersion model under variable flow conditions does not offer an essential refinement. Thus, the modelling of isotopic transport through lysimeters still remains a poorly understood topic.

- How can the \(^18\)O input record be parametrized for purposes of modelling by means of the lumped-parameter approach?

The parametrization of the \(^18\)O input function was performed in two steps, i.e., the extrapolation of the local input function in the preceding history and the weighting using a recharge parameter. It was shown that it is possible to complete the measured monthly \(^18\)O record using input functions from the stations Bern and Konstanz for the period since July, 1981. During the calibration year 1994, the input function obtained by this approach is in good agreement with observed local Rietholzbach values. According to the relatively short water residence times obtained, it is obvious that the input concentrations in the period before 1990 plays a very limited role. The weighting of the input values using the lysimeter outflow rate (equations 4.27 and 4.28) permitted performance of all the presented simulations. Figures 4.25 and 4.26 show the comparison of the simulations carried out by use of weighted and non-weighted input functions.
Figure 4.24: Residence time distribution function for the mean water residence times of 9 months (example the borehole B2), 12.5 months (example baseflow from the whole Rietholzbach catchment) and 24.5 months (example baseflow from the subcatchment Oberer Rietholzbach), respectively.
FIGURE 4.25: Comparison of the simulations of the $^{18}$O output functions performed using the parametrized input function, as well as the input function without any parametrization; period January, 1994 - June, 1996: Simulation of the baseflow isotope record at the main runoff gauging site Mosnang, computed by use of the exponential-piston flow model for the mean water residence time of 12.5 months. Bottom: Simulation of the baseflow isotope record at the gauging site Oberer Rietholzbach, computed by use of the exponential-piston flow model for the mean water residence time of 24.5 months.
Figure 4.26: Comparison of the simulations of the $^{18}$O output functions performed using the parametrized input function, as well as the input function without any parametrization; period January, 1994 - June, 1996. Top: Simulation of the groundwater isotope record in the borehole B2, computed by use of the exponential-piston flow model for the mean water residence time of 9 months. Bottom: Simulation of the lysimeter outflow isotope record, computed by use of the exponential-piston flow model for the mean water residence time of 7.3 months.
4.4 Discussion of the results

It appears that the weighting essentially improves the quality of all the fits because the use of the non-weighted function overestimates the role of the isotopically heavier summer input. As a consequence, the computed output functions remain above the measured records. It might be questionable why this approach works using recharge quantities containing the pure groundwater recharge, as well as the components which would flow outside the lysimeter, as lateral fluxes only. Nevertheless, the critical factor controlling the weighting is not the recharge amount itself, but the relative variations. This hypothesis was confirmed using the groundwater recharge factors obtained by assessment of the groundwater recharge model BOWAM. It can be, therefore, stated that the groundwater recharge modelling may cause similar weighting effects to those provided by use of lysimeter outflow amounts. This task seems to be of particular importance for natural catchments or hydrogeological structures where no lysimeter investigations are performed. Unfortunately, the problem of extrapolation and weighting of isotopic input functions is generally rarely treated in the literature. Although some works (e.g. Klotz et al., 1995) reported losses of simulation quality due to the underestimation of the input weighting, no sensitivity studies on this topic exist.

- What are the results of a combined interpretation of water residence times obtained by means of $^{18}$O and $^{85}$Kr?

The mean residence time of 2.1 years obtained by the combined interpretation of the $^{18}$O-residence time for the unsaturated zone and the $^{85}$Kr-residence time for the saturated zone seems to be realistic because of the estimation of both residence times using two different lumped-parameter model concepts. Moreover, the water residence times obtained by computations of the $^{18}$O output functions at various outlet sites indicate that the mean residence time of the relatively oldest groundwater should be longer than 2 years, even though it is not realistic to expect any considerably higher value. Possible errors may occur because the $^{85}$Kr output function is based on one measurement only. In addition, the estimation of the water residence time within the unsaturated zone is strongly limited to the lysimeter site, i.e. it is assumed that the vertical percolation through the lysimeter profile is representative for the vertical infiltration through the entire unsaturated zone overlaying the aquifer. This question may be tackled by further evaluations of tritium records carried out within the framework of the project Young groundwaters: age structure, mixing components and other processes, currently conducted by the Physics Institute, University of Bern.
5 Analysis of runoff components

The developed concept of the water residence times (Chapter 4) describes the interactions between the subsurface waters and the stream waters in the hilly catchment Rietholzbach under steady-state conditions. Nevertheless, the runoff generation processes during flood events are strongly variable and lead to contributions of various runoff components to the total outflow from the catchment. Like the groundwater residence times, the source areas and flowpaths of these components cannot be fairly determined by use of hydrological models alone. In the precipitation-runoff models the composition of the hydrograph is computed using estimated and optimized parameters. In contrast, the environmental tracer methods permit the direct identification of the components and controlling processes.

The aim of this chapter is to determine runoff components contributing to the single flow events in the catchment Rietholzbach. The results are interpreted with respect to the concept of the water-residence-time spectrum developed in the previous Chapter 4. Some general remarks on the approach based on the mixing formula are given in Chapter 5.1. Chapter 5.2 deals with the hydrograph deconvolutions of five flood events using $^{18}O$ and chemical tracers. Finally, the results are discussed in Chapter 5.3.

5.1 Description and discussion of the mixing approach

The deconvolution of a hydrograph from tracer data is equivalent to solving for each outlet sampling time a mass balance equation for the water and tracer fluxes in the stream. Assuming that two flow systems contribute to outlet discharge, the contributions of the previously stored water can be expressed as

$$\frac{Q_o}{Q_t} = \frac{c_t - c_n}{c_o - c_n}$$  (5.1)

and those of the current rainfall water in the form

$$\frac{Q_n}{Q_t} = \frac{c_t - c_o}{c_n - c_o}$$  (5.2)

where $Q$ means the discharge rate and $c$ the tracer concentration in total runoff ($t$), in the previously stored ("old") water ($o$) and in the current rainfall ("new") water ($n$), respectively. This equation was introduced by Pinder and Jones (1969) for a variety of chemical tracers to separate storm hydrographs for three small watersheds in United States. In order to clarify possible misinterpretations of the equations (5.1) and (5.2), Sklash and Farvolden (1979) outlined two important aspects which have to be discussed especially when using stable isotopes as tracers: firstly, the existence of distinguishable isotope content in the current rainfall water and in the previously stored water, and secondly, the existence of an uniform isotope content of both components throughout the event.

- Existence of distinguishable isotope composition of the current rainfall water and of the previously stored water. As discussed in Chapter 4.2.2, the fractionation of stable isotopes in natural waters is determined primarily by the temperature at which the water condenses. A favorable condition for hydrograph separation exists, therefore, in the case of summer storms with isotopically heavy precipitations.
To express the concentration \( c_0 \), the pre-event concentration of the stream water is assumed to represent the isotope content in the pre-event water. In order to avoid misinterpretations of this pre-event water composition, the knowledge of the seasonal \( ^{18}O \) variations in the stream water under low-flow conditions is important (Figure 4.14).

- Existence of an uniform isotope content of both the components throughout the event. Besides the variations in the isotopic composition of precipitation over long periods (Chapter 4.2), variations over short periods and at individual locations occur. Analyzing fractionally collected rainwater, Ambach et al. (1975) and Heathcote and Lloyd (1986) showed that storm rainfall isotopic content may vary on a time scale between hours and a few days, without any seasonal dependence or any clear relationship with daily mean temperatures. These variations are owing to the raining out of a cell, i.e. to the preferential fall of isotopically heavier water drops, and to the cell structure of the precipitation field. The latter is determined by the evolution of the precipitation field, which cause non-equilibrium fractionation conditions, i.e. in this case kinetic isotope effects are assumed to dominate (e.g. Dansgaard, 1964; Ambach et al., 1975).

In order to overcome this problem, McDonnell et al. (1990) proposed a group of methods for weighting of a fractionally collected variable \( ^{18}O \) input. However, this approach is applicable only when the flood event occurs nearly at the same time as the rainfall event. Some studies in such extremely responsive catchments showed plausible hydrograph separations with intrastorm \( ^{18}O \) variations in the rainfall reaching up to 4 % SMOW (McDonnell et al., 1990; Pionke et al., 1993; Ribolzi et al., 1996).

Unlike the isotope content, the concentration of dissolved ionic substances in rainwater and in the stored water in the catchment is generally considerably different. Even though intrastorm variations in chemical composition of the rainfall occur, they do not play a key role when considering remarkably higher concentrations in streams and subsurface waters.

The role of the circumstances for hydrograph separation denoted by Sklash and Farvolden (1979) is documented in Figure 5.1 showing two rain events with different isotopic variations, collected at the meteorological station Biel in the catchment Rietholzbach. The event from April 25-26, 1995 shows a slight \( ^{18}O \) variation oscillating around -11 % SMOW. Although this slight variation would yield a representative mean, the use of this mean in the mixing equation (5.1) remains impossible because the \( ^{18}O \) content in the stream pre-event water has nearly the same concentration. Thus, the first above mentioned condition is not met. In contrast, the event from June 10-11, 1995 is an example showing a large \( ^{18}O \) variation caused obviously by the preferential outraining of isotopically heavier drops. The considerable intrastorm variation reaching up to 6 % SMOW limits the application of the mixing approach for two reasons: firstly, because of the large variation itself, and secondly, because of the fact that the record of \( ^{18}O \) content in precipitation crosses the \( ^{18}O \) content observed in the stream water.

5.2 Separation of runoff contributions using environmental tracers

During the summer season 1995, five flood events were analyzed with respect to the determination of runoff contributions of the previously stored water and of the current rainwater. Four of these events were analyzed using one tracer only, i.e. the stable isotope \( ^{18}O \).
Figure 5.1: Example of two rain events which do not allow to perform the separation of runoff components using the $^{18}$O as a tracer; station Büel. Top: The measured $^{18}$O content in precipitations varies between -9 and -11% SMOW, i.e. the input concentrations do not clearly differ from the concentrations in the stream water. Bottom: The large temporal variation of $^{18}$O content between -8 and -14% SMOW does not approach a representative mean input concentration.
This two-component hydrograph deconvolution is discussed in Chapter 5.2.1. In addition, the hydrograph of the event from July 15-16, 1995, was deconvoluted into flowpath-related components using the \( ^{18} \text{O} \) and two additional tracers, electrical conductivity and chloride ions. This task is discussed in Chapter 5.2.2.

### 5.2.1 Source-related separation

Tables 5.1 shows up the basic rainfall characteristics of the five analyzed summer flood events. All these events were caused by convective rainfalls having high amounts of \( P \) up to 30 mm and high intensities of \( P_{\text{max}} \) up to 1 mm/min. The duration of the events \( T_D \) is mostly short. In comparison with the pre-event runoff rates \( Q_{\text{min}} \), the peak runoff rates \( Q_{\text{max}} \) are highly variable and range up to 1951 l/s for the July 11-13 event. The time interval \( T_P \) represents the time elapsed between the centre of gravity of the rainfall event and the time interval \( T_Q \) expresses the time elapsed during the hydrograph rising, i.e. between the \( Q_{\text{min}} \) and \( Q_{\text{max}} \).

#### Table 5.1: Rainfall characteristics of the flood events from the summer season 1995, analyzed using \( ^{18} \text{O} \) as a tracer; station Büel.

<table>
<thead>
<tr>
<th>Event</th>
<th>( P ) [mm]</th>
<th>( P_{\text{max}} ) mm/min</th>
<th>( T_D ) [min]</th>
<th>( T_P ) [min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>July 11-13</td>
<td>30.8</td>
<td>6.3</td>
<td>205</td>
<td>30</td>
</tr>
<tr>
<td>July 15-16</td>
<td>22.7</td>
<td>3.4</td>
<td>100</td>
<td>50</td>
</tr>
<tr>
<td>August 7-8</td>
<td>31.2</td>
<td>4.5</td>
<td>145</td>
<td>40</td>
</tr>
<tr>
<td>August 8-10</td>
<td>15.1</td>
<td>1.3</td>
<td>600</td>
<td>70</td>
</tr>
<tr>
<td>September 9-10</td>
<td>9.2</td>
<td>0.6</td>
<td>255</td>
<td>150</td>
</tr>
</tbody>
</table>

#### Table 5.2: Runoff characteristics of the flood events from the summer season 1995, analyzed using \( ^{18} \text{O} \) as a tracer; main runoff gauging site Mosnang.

<table>
<thead>
<tr>
<th>Event</th>
<th>( Q_{\text{min}} ) [l/s]</th>
<th>( Q_{\text{max}} ) [l/s]</th>
<th>( T_Q ) [min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>July 11-13</td>
<td>15</td>
<td>1951</td>
<td>45</td>
</tr>
<tr>
<td>July 15-16</td>
<td>33</td>
<td>1111</td>
<td>70</td>
</tr>
<tr>
<td>August 7-8</td>
<td>11</td>
<td>1186</td>
<td>85</td>
</tr>
<tr>
<td>August 8-10</td>
<td>29</td>
<td>177</td>
<td>110</td>
</tr>
<tr>
<td>September 9-10</td>
<td>44</td>
<td>326</td>
<td>220</td>
</tr>
</tbody>
</table>

The comparison of the time intervals \( T_P \) and \( T_D \) indicates that the critical part of the rainfall event occurred before the middle of the hydrograph rising was reached. The delay of the runoff peak in comparison with the rainfall gravity centre indicates the essential role of subsurface components in the runoff formation.

Table 5.3 shows the \( ^{18} \text{O} \) concentrations applied in the computations using equations (5.1) and (5.2). All of the analyzed floods are related to summer events. Therefore, the differences in \( ^{18} \text{O} \) content between the rainfall water and the prestorm water in the stream are sufficiently large and reach up to 5 % SMOW. The timing between the rainfall and
Table 5.3: $^{18}O$ concentrations in rainfall and pre-event stream water related to the analyzed flood events from the summer season 1995.

<table>
<thead>
<tr>
<th>Event</th>
<th>$^{18}O$ [%o SMOW]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>rainfall</td>
</tr>
<tr>
<td>July 11-13</td>
<td>-5.76</td>
</tr>
<tr>
<td>July 15-16</td>
<td>-6.52</td>
</tr>
<tr>
<td>August 7-8</td>
<td>-6.89</td>
</tr>
<tr>
<td>August 8-10</td>
<td>-7.67</td>
</tr>
<tr>
<td>September 9-10</td>
<td>-7.28</td>
</tr>
</tbody>
</table>

the runoff reaction results in the critical part of the rainfall having fallen before the first sample of the rising limb of the stream runoff could be taken. The $^{18}O$ content in the rainfall water is, therefore, represented by the bulk mean of samples sequentially collected for every 3 mm of rainfall (Chapter 3). In this case, the alternative weighting methods proposed by McDonnell et al. (1990) were not applicable. Figures 5.2 - 5.6 present the results of the two-component hydrograph deconvolutions using $^{18}O$ and also show other data records related to the analyzed events. The results are summarized as follows (Vitvar and Balderer, 1997):

- Water present from previous rainfall events volumetrically substantially contributes to the outflow response to the rainfall. The main discharge peak is accompanied by the maximal runoff of old water (contribution of about 50% in all the analyzed cases). After the outflow peak, a mixing of old water with current rainfall water can be identified. The high calculated amount of the previously stored components is in agreement with the most accepted concept which assumes a considerable mobilization of the previously stored water (summarized e.g. in Hooper and Shoemaker, 1986; Pearce et al., 1986; Turner et al., 1987; Ribolzi et al., 1996). The current rainfall water contributes to the stream runoff especially in the form of flow through drainage channel network (Burghthaler, 1992) and partially in the form of direct flow of the rainfall water in the stream. Nevertheless, the separation of pre-event and event water components does not provide the determination of the flowpaths, i.e. the specification of runoff generation mechanisms within the saturated zone and within the soil.

- During the storm flow, an increase of groundwater level in the near-stream borehole B1 can be observed. The rise of the groundwater level starts simultaneously with the hydrograph rising limb. In contrast, the lysimeter outflow remains negligible and does not show any increase during the event. The lysimeter outflow is generally delayed because the vertical flow through macropores is very limited within the lysimeter layer (Demuth et al., 1993). The reaction of the lysimeter is delayed depending on a variety of factors, especially on the pre-event soil humidity and the rainfall intensity (Koenig, 1994; Gurtz et al., 1997). This indicates that the groundwater recharge is immediately affected by an increasing subsurface hydraulic gradient towards the stream. It is, therefore, impossible to describe the runoff generation only by the soil water flow in the transient saturated zone on hillslopes (McDonnell, 1990; Mulholland et al., 1990). Similar interconnections between stream runoff and groundwater level in a near-stream borehole were reported e.g. by Sklash and Farvolden (1979) for two small porous catchments in Canada.
5.2 Separation of runoff contributions using environmental tracers

Figure 5.2: Two-component analysis of runoff components of the flood event from July 11-13, 1995, at the main runoff gauging site Mosnang using the $^{18}O$ as a tracer. The following parameters are depicted: precipitation, total runoff and the stored water component obtained by $^{18}O$ (top), records of $^{18}O$ and electrical conductivity in the stream water (middle) and records of the groundwater depth and lysimeter outflow (bottom).
Figure 5.3: Two-component analysis of runoff components of the flood event from July 15-16, 1995, at the main runoff gauging site Mosnang using the $^{18}$O as a tracer. The following parameters are depicted: precipitation, total runoff and the stored water component obtained by $^{18}$O (top), records of $^{18}$O and electrical conductivity in the stream water (middle) and records of the groundwater depth and lysimeter outflow (bottom).
5.2 Separation of runoff contributions using environmental tracers

Figure 5.4: Two-component analysis of runoff components of the flood event from August 7-8, 1995, at the main runoff gauging site Mosnang using the $^{18}$O as a tracer. The following parameters are depicted: precipitation, total runoff and the stored water component obtained by $^{18}$O (top), records of $^{18}$O and electrical conductivity in the stream water (middle) and records of the groundwater depth and lysimeter outflow (bottom).
Figure 5.5: Two-component analysis of runoff components of the flood event from August 8-10, 1995, at the main runoff gauging site Mosnang using the $^{18}$O as a tracer. The following parameters are depicted: precipitation, total runoff and the stored water component obtained by $^{18}$O (top), records of $^{18}$O and electrical conductivity in the stream water (middle) and records of the groundwater depth and lysimeter outflow (bottom).
5.2 Separation of runoff contributions using environmental tracers

Figure 5.6: Two-component analysis of runoff components of the flood event from September 9-10, 1995, at the main runoff gauging site Mosnang using the $^{18}$O as a tracer. The following parameters are depicted: precipitation, total runoff and the stored water component obtained by $^{18}$O (top), records of $^{18}$O and electrical conductivity in the stream water (middle) and records of the groundwater depth and lysimeter outflow (bottom).
The plot of electrical conductivity values shows a difference in conductivity values before and after the flood event. An increase of ionic content occurs owing to the rapid leaching of presumably calcite and silicate minerals with which the infiltrating water comes in contact. The subsurface runoff contains, therefore, a component of soil water which moves laterally along the slopes (Kennedy et al., 1986; Bazemore et al., 1994). It should be pointed out that there is no evidence in the literature on such behaviour of electrical conductivity records in streams. Sklash and Farvolden (1979) and Sklash et al. (1986) showed that although the concentration of selected ions after the runoff peak exceeds the pre-event values, the electrical conductivity reaches nearly exactly the pre-event level.

A more detailed discussion on the source areas-related separation will be given in Chapter 5.3.

5.2.2 Flowpath-related separation

Like the separation using 18O, the hydrograph deconvolution using chemical tracers is based on the mixing equations (5.1) and (5.2). Figure 5.7 shows the concentrations of selected tracers in precipitation fractionally collected after the fall of every 3 mm at the station Büel. The 18O content is high due to the fractionation during high summer temperatures. The low concentrations of other substances decrease during the event because of the outraining of isotopically heavier drops in the initial intensive rainfall phase.

Figure 5.8 shows the relationship between the stream runoff and the content of two tracers in the stream water during the flood event. In the case of 18O, the highest content is related to the highest runoff and decreases with the falling limb of the flood towards the pre-event level. The electrical conductivity, showing a dilution during the peak runoff phase, increases since the start of the falling limb and exceeds the pre-event level. This indicates that at least a part of the runoff recession is characterized by leaching and dissolution of ionic constituents of the soil, i.e. that the concentration of some ions is not controlled by a single equilibrium reaction only (Stumm and Morgan, 1981; Wels et al., 1991).

Figure 5.9 shows the record of the stream runoff and the concentrations of magnesium and chloride ions. Both tracers show a dilution caused by the current rainfall water and an increase after the runoff peak. They are generally assumed to be suitable conservative substances for tracing runoff generation processes in small watersheds (e.g. Wels et al., 1991; Pionke et al., 1993). Nevertheless, the dilution is more efficient in the case of magnesium ions than in the case of chloride ions. Dissolution investigations within a column of podzolic soil performed by Wels et al. (1991) showed small changes in magnesium concentrations of the leachate (despite the application of large volumes of water). Similarly, chloride ions are essentially non-reactive, and no known geologic sources exist in the catchment Rietholzbach. Though, chloride was reported to be subject to non-specific adsorption (Bazemore et al., 1994), so that a potential mixing of event and pre-event components in a desorption of chloride from soils.

Figure 5.10 demonstrates the record of the stream runoff and the concentrations of weathering products silica and calcium ions. Unlike the nearly conservative behaviour of magnesium and chloride ions, the calcium and silica concentrations in the stream are obtained from fast continuous leaching of minerals, as observed in a variety of catchments in porous sediment structures (e.g. Kennedy et al., 1986; Wels et al., 1991; Pionke et al., 1993). It is obvious that the high absolute amounts of especially these substances in the Rietholzbach
Figure 5.7: Measured content of the tracers calcium and $^{18}O$ (top), as well as chloride and electrical conductivity (middle) in precipitation. Bottom: the precipitation record. Station Büel, rainfall event from July 15, 1995.
Figure 5.8: Relationship between the stream water runoff and two tracer contents in the stream water: $^{18}O$ (top) and electrical conductivity (bottom); main runoff gauging site Mosnang, flood event from July 15-16, 1995.
5.2 Separation of runoff contributions using environmental tracers

Figure 5.9: Runoff record of the flood event from July 15-16, 1995, and the stream water concentrations records of the magnesium (top) and chloride (bottom) ions; main runoff gauging site Mosnang. The tracer concentrations are marked by stars.
stream water control the increase of electrical conductivity (Figures 5.3 and 5.8). Whereas in the case of the silica ions a small dilution during the runoff peak occurs, the calcium does not undergo any dilution and shows increasing concentrations after the mean runoff peak.

Figures 5.11 and 5.12 summarize the above presented records. Figure 5.11 illustrates the relationship between the stream runoff and the concentrations of analyzed tracers, as well as the groundwater level in the borehole B1. The comparison of all the measured values against the stream runoff suggests that the main phase of the groundwater recharge in the near-stream aquifer follows the main contribution of soil water enriched by silica and calcium ions into the stream. This fact supports the evidence of the relatively rapid lateral runoff component which is activated within the soil, probably in the form of a transient saturated zone (e.g. Kennedy et al., 1986; Bazemore et al., 1994). Figure 5.12 illustrates the relationship between the contents of the isotope $^{18}$O and the chloride and silica ions throughout the flood event. The relation between $^{18}$O and chloride ions, i.e. between two tracers assumed to be conservative, is very close. In contrast, nonconservative silica ions lead to a weak relation against the conservative $^{18}$O.

The quantification of the runoff components related to their flowpaths was based on an identical approach as that related to their origin, i.e. equations (5.1) and (5.2) were applied. Table 5.4 summarizes the mean tracer contents in rainfall, as well as the initial tracer contents in the pre-event streamwater. Besides the isotope $^{18}$O, magnesium and chloride ions, as well as the electrical conductivity, were used. In order to perform the computation using the electrical conductivity, a modification of the mixing approach (equations 5.1 and 5.2) was applied. It is based on the use of two different electrical conductivity values $c_0$ for the subsurface stored water. Figure 5.11 demonstrates that the most diluted water occurs in the stream before the main runoff peak $Q_{\text{max}}$. Thus, assuming this threshold runoff value $Q_t=900 \text{ l/s}$ (Figure 5.11), the first part of the event is separated using the pre-event conductivity value $c_0=470 \text{ } \mu \text{S/cm}$ (Table 5.4, Figures 5.3, 5.8) and the second part is separated using the conductivity value $c_0=518 \text{ } \mu \text{S/cm}$ occurring after the event (Figures 5.3, 5.8).

### Table 5.4: Tracer contents used for the flowpath-related hydrograph deconvolution, flood event from July 15-16, 1995.

<table>
<thead>
<tr>
<th>Tracing substance</th>
<th>Tracer content in rainfall</th>
<th>Tracer content in pre-event water</th>
</tr>
</thead>
<tbody>
<tr>
<td>el. conductivity $[\mu \text{S/cm}]$</td>
<td>10</td>
<td>470</td>
</tr>
<tr>
<td>chloride [mg/l]</td>
<td>0.41</td>
<td>3.20</td>
</tr>
<tr>
<td>magnesium [mg/l]</td>
<td>0.07</td>
<td>16.51</td>
</tr>
<tr>
<td>$\delta^{18}$O [%o SMOW]</td>
<td>-6.52</td>
<td>-10.40</td>
</tr>
</tbody>
</table>

Figures 5.13 and 5.14 show the computation results for the deconvolutions using magnesium and chloride ions. Figure 5.15 presents the separation using the electrical conductivity.

The results are interpreted as follows:

- The comparison of separations performed in Chapters 5.2.1 and 5.2.2 show that the prevailing part of the hydrograph rising limb is simultaneously accompanied by the expulsion of the stored subsurface water (groundwater and soil water), i.e. there is
5.2 Separation of runoff contributions using environmental tracers

Figure 5.10: Runoff record of the flood event from July 15-16, 1995, and the stream water concentrations records of the silica (top) and calcium (bottom) ions; main runoff gauging site Mosnang. The tracer concentrations are marked by stars.
Figure 5.11: Relationship between the creek water runoff rates and the following parameters: chloride and magnesium (top) and silica and calcium concentrations in the creek water (middle) at the main runoff gauging site Mosnang, as well as the groundwater depth in the borehole B1 at the station Büel (bottom), for the flood event from July 15-16, 1995.
5.2 Separation of runoff contributions using environmental tracers

Figure 5.12: Relationship between the contents of $^{18}$O and the chloride (top) and silica (bottom) ions in the stream water during the flood event from July 15-16, 1995, at the main runoff gauging station Mosnang.
Figure 5.13: Analysis of runoff components of the flood event from July 15-16, 1995, at the main runoff gauging site Mosnang using the $^{18}O$ and magnesium ions as tracers. Top: Total runoff and subsurface runoff components obtained by use of the $^{18}O$ and magnesium ions. Bottom: Relationship between the subsurface runoff components obtained by the $^{18}O$ and magnesium ions.
5.2 Separation of runoff contributions using environmental tracers

**Figure 5.14:** Analysis of runoff components of the flood event from July 15-16, 1995, at the main runoff gauging site Mosnang using the $^{18}O$ and chloride ions as tracers. Top: Total runoff and subsurface runoff components obtained by use of the $^{18}O$ and chloride ions. Bottom: Relationship between the subsurface runoff components obtained by the $^{18}O$ and chloride ions.
Figure 5.15: Analysis of runoff components of the flood event from July 15-16, 1995, at the main runoff gauging site Moosnang using the $^{18}O$ and electrical conductivity as tracers. Top: Total runoff and subsurface runoff components obtained by use of the $^{18}O$ and electrical conductivity. Bottom: Relationship between the subsurface runoff components obtained by the $^{18}O$ and the electrical conductivity.
5.3 Discussion of the results

a similarity to the concept of the groundwater ridging (e.g. Sklash and Farvolden, 1979). In addition, the rising limb is accompanied by a relatively slight rise of groundwater levels. This mechanism may be explained by the fast infiltration on hillslopes. These mechanisms lead to the increasing steepening of the hydraulic gradient in aquifers and to the water displacement. The increasing ionic concentrations (especially those of silica and calcium) after the peak indicate an influence of leaching reactions of rainfall water with the subsurface material with which this water came in contact. As a consequence, the subsurface outflow during and after the peak also consists of a soil water component which had rapidly passed the soil pores and contributes to the stormflow without any mixing with the groundwater. The main outwashing phase is then followed by the increased groundwater recharge due to the increased hydraulic conductivity of the soil pores.

The above described processes can be compared to several concepts investigated to date in similar catchments. The increase in the hydraulic gradient in aquifers satisfies the assumption of the groundwater ridging (e.g. Sklash and Farvolden, 1979; Sklash et al., 1986; Pionke et al., 1993), although the displacement of the previously stored water may be supported by a relatively fast infiltration through shallow soils on hillslopes (and not only by the activation of the phreatic water; more detailed discussion in Chapter 5.3). The outwashing of chemically enriched soil water towards the stream may occur according to the threshold activation of a transient saturated zone above the soil-bedrock interface on hillslopes (McDonnell, 1990; Mulholland et al., 1990; Bazemore et al., 1994, e.g.). In contrast to the concept of Bazemore et al. (1994) stated in a forested catchment, however, the activation of the unsaturated zone in the Rietholzbach catchment follows the mobilization of the groundwater. Similar timing, i.e. the primary groundwater mobilization, was reported e.g. by Pionke et al. (1993) for a small porous hilly catchment in the United States. Nevertheless, the increase in the groundwater contribution in the latter study does not occur simultaneously with the hydrograph rising limb.

- The measured records of ionic concentrations permitted the use of the stream water electrical conductivity (sum of all dissolved solids) as a tracer in equations (5.1) and (5.2), even though the conductivity value after the event exceeds the pre-event level. Using the presented modification, the hydrograph deconvolution was possible (Figure 5.15) and showed contributions which are nearly equal to those obtained using the conservative tracers $^{18}$O (Figure 5.3) and magnesium (Figure 5.13). It can be, therefore, stated that the electrical conductivity and magnesium potentially substitute the $^{18}$O as conservative tracer for source area-related (i.e. event and pre-event) runoff components. This should be tested and verified on other events.

A more detailed discussion follows in Chapter 5.3.

5.3 Discussion of the results

The aim of this chapter was to distinguish the runoff components contributing to the flood events in the catchment Rietholzbach. The separation of these components was carried out in two steps: firstly, the source-related previously stored (pre-event) and the current (event) rainfall water components, and secondly, the pathways-related components were considered. The results are discussed according to the questions stated in Chapter 1.

- What are the decisive runoff components generated during summer flood events? Is there considerable evidence of a transitory soil water component?
The critical component consists of water which has passed in any form through the subsurface. The most important part of this contribution is the pre-event water stored within the catchment. The volume portion of between 50% (in the peak) and 80% (during the falling limb) of the total runoff is in agreement with the concept assuming the increasing steepening of the hydraulic gradient in aquifers and the expulsion of the previously stored (i.e. pre-event or "old") groundwater. Nevertheless, the interpretation of the timing between the contributions of the expelled water and the current water passing the soil matrix in various parts of the catchment remains questionable. This is mainly because of the differences in the groundwater residence times in the catchment, especially when considering the local differences between the hillslopes oriented to the north and those oriented to the south or the differences between the main aquifer types (see Chapter 4.3.3). Thus, although the groundwater borehole B1 can be regarded as representative for the near-stream catchment part, the interactions between the fluxes in the unsaturated and in the saturated zone may differ depending on the local conditions. Firstly, the expected mechanisms on the catchment hillslopes oriented to the north should be considered. Table 5.5 compares the $^{18}$O values of the groundwater in the boreholes B1, B2 and B3 for the days July 11 and July 14, 1995, i.e. before and after the flood event on July 11-13.

<table>
<thead>
<tr>
<th>Locality</th>
<th>July 11</th>
<th></th>
<th>July 14</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta^{18}$O</td>
<td>cond.</td>
<td>$h$</td>
<td>$\delta^{18}$O</td>
<td>cond.</td>
</tr>
<tr>
<td>B1</td>
<td>-10.54</td>
<td>638</td>
<td>430</td>
<td>-10.63</td>
<td>635</td>
</tr>
<tr>
<td>B2</td>
<td>-10.53</td>
<td>612</td>
<td>222</td>
<td>-8.38</td>
<td>375</td>
</tr>
<tr>
<td>B3</td>
<td>-10.62</td>
<td>628</td>
<td>439</td>
<td>-10.32</td>
<td>630</td>
</tr>
</tbody>
</table>

The values indicate that the groundwater in the borehole B2 is strongly influenced by the rainfall water rapidly infiltrating into the aquifer. In addition, this shallow groundwater shows a relatively poor mixing, i.e. the isotope content after the rainfall event remains affected by the higher isotope values of the infiltrated water. It can be, therefore, assumed that the storm runoff contribution from this type of subsurface environment is essentially influenced by fast fluxes within the soil. In contrast, the groundwater in the borehole B3 seems to be more efficiently mixed (similar electrical conductivity values on the both days), although the groundwater level increase is nearly equal to that measured in the borehole B2. The groundwater level in the borehole B1 (Figure 5.2) increases during the flood event due to the steepening of the hydraulic gradient and to the recharge from the soil, but the latter prevails during and after the runoff peak (Table 5.5). The mixing within the Quaternary aquifer leads to a decrease in groundwater levels towards the pre-event depth.

- Is there a possibility to obtain a flowpath-related hydrograph deconvolution by means of $^{18}$O and a geochemical tracer?

The obtained results show that the stable isotope $^{18}$O and chloride ions can be used as tracers for the determination of source area-related and flowpath-related runoff components. The hydrograph deconvolution using $^{18}$O and chloride ions gives the timing between the stored water mobilization (obtained from $^{18}$O) and the chemically
enriched water passing through the soil matrix (obtained from chloride ions). In terms of water source areas, the "old" component obtained by chloride ions also contains a portion of the event "new" water, which is chemically enriched because of the reaction with the soil material. Thus, this component cannot be obtained using $^{18}$O as a part of the previously stored "old" water (Hooper and Shoemaker, 1986).

The hydrograph deconvolution using the electrical conductivity (Figure 5.15) should be verified and supported by more detailed geochemical investigations. The most serious problem here is the estimation of the runoff $Q_t$ where the two conductivity values $c_0$ in equation (5.1) have to be changed. In the present work, this estimate was obtained using the stream chemistry records of the most important major ions. It would be, therefore, desirable to develop a more general approach which would estimate this parameter without the measurement of ionic constituents.
6 Conclusions and outlook

6.1 Conclusions

In the present work a concept of the groundwater residence-time-distribution and water-source areas and flowpaths in the hilly prealpine catchment Rietholzbach in Northeastern Switzerland was developed. The study was based on the use of environmental tracers and divided into two basic parts. The first step focussed on the estimation and interpretation of mean water residence times using the environmental isotopes $^{18}$O and $^{85}$Kr. The second part treated the determination and interpretation of runoff components using the isotope $^{18}$O and environmental chemical tracers.

In the first part, the mean water residence times were estimated using the inverse lumped-parameter simulation of $^{18}$O output functions under quasi steady-state conditions between January, 1994 and June, 1996. Comprehensive measurements of $^{18}$O content in precipitation and at various outlet sites were carried out. The dating of the oldest groundwater component to be more than 2 years was accomplished using $^{85}$Kr. New approaches for parametrization of the $^{18}$O input function were developed. They consist of two techniques: (1) an extrapolation of the local input function using nearby IAEA/WMO stations Konstanz and Bern, and (2) weighting its significance using percolation amounts in a lysimeter. The computations were performed for three groups of water: (1) for stream waters at three runoff gauging sites, (2) for water percolated throughout the soil in the lysimeter, and (3) for shallow groundwaters in boreholes and captured wells representing the basic types of aquifers. To accurately access the residence times of the groundwaters, subsequent investigations on the natural groundwater regime, as well as pumping tests on the boreholes, were performed. The results yielded a spectrum of mean water residence times of up to 2.1 years. This conclusion is realistic and in agreement with other investigations carried out by using isotope dating in relatively similar hilly catchments (e.g. Maloszewski et al., 1983; Stichler and Herrmann, 1983).

The quality of the water dating in the catchment Rietholzbach using $^{18}$O strongly depends on the parametrization of the local $^{18}$O input function. The developed parametrization approach, i.e. the extrapolation and weighting of the monthly $^{18}$O input function, essentially contributed to the quality of the simulation of the $^{18}$O output functions. The extrapolation of the local input function from the station Büel using the known $^{18}$O input functions from the stations Konstanz and Bern showed a good agreement for the reference year 1994. Nevertheless, the estimated elevation correction parameter is an approximative value only and cannot be directly applied in other regions. The weighting parameters used (lysimeter outflow and groundwater recharge rates modelled using the model BOWAM) also showed a very good applicability, although the physical significance of both parameters is not identical, i.e. the lysimeter outflow contains an additional flow component compared with the modelled groundwater recharge (Gurtz et al., 1997). In addition, all simulations performed could be carried out using one parametrized input function only. This can be explained by the relative homogeneity of the porous aquifers, in contrast e.g. to more complex porous-fissured aquifers containing more or less separated storage areas (e.g. Herrmann et al., 1986b). Nevertheless, the optimal weighting techniques of the $^{18}$O input functions may differ according to the investigated environment. The weighting approach should be, therefore, discussed for various types of catchments and groundwater recharge mechanisms. Since there is a very limited number of catchments equipped with a lysimeter, attention should be primarily oriented to parameters resulting from the ground-
water recharge modelling. In order to refine this methodological step in future studies, a higher time resolution of the measured input function (weeks) would be desirable.

Most of the measured $^{18}$O output functions at the outlet sites in the Rietholzbach catchment showed sufficiently large seasonal cyclic variations. These circumstances are favorable for dating using $^{18}$O because too slight output oscillations do not allow any suitable estimation of residence times, as discussed in case studies from other catchments (e.g. Pearce et al., 1986; Maloszewski et al., 1992). Among the output functions investigated, only those of the groundwater in the borehole B1 does not show any seasonal behaviour. The combined dating using $^{85}$Kr and $^{18}$O was, therefore, one possible solution to obtain the mean residence time of this groundwater. Although the result seems to be realistic, a confirmation using an independent dating method would be desirable. Besides the experimental approaches estimating the tracer delay in the unsaturated zone (e.g. using environmental gaseous tracers), the use of tritium might offer a suitable comparison. However, in both cases specific problems are expected. The first approach would require complicated water sampling within the unsaturated zone, and the latter may remain questionable because of the difficult interpretation of very low modern tritium input concentrations.

There is generally a good agreement between the measured and fitted $^{18}$O output functions. In addition, the correct interpretation of the estimated residence times and the additional fitting parameters was supported by application of two model variants for each output function, i.e. one variant of the exponential-piston flow concepts and one variant of the advection-dispersion concepts. Some weakness, especially when estimating shorter residence times, i.e. those of the percolated water within the lysimeter, should be improved using a higher resoluted input function.

In the second part, the components of storm runoff were determined using the tracer mass balance. A volume-proportional sampling of rainfall and the runoff at the catchment outlet was performed during five flood events in the summer 1995. The following tracers were used: the isotope $^{18}$O, and the ionic substances calcium, chloride, magnesium and silica, as well as the electrical conductivity. A new variant of the mixing calculation using electrical conductivity as tracer was applied. A contribution of the previously stored pre-event water ranging between 50-80 % of the total runoff was computed using $^{18}$O. The identification of flowpaths by ions resulted in three components: (1) stored groundwater mobilized during the event, (2) chemically enriched water passing through the soil matrix and (3) water flowing through the macropores and the drainage network or routed as overland flow. The contributions of these components to the total runoff vary during the flood event.

The results are in agreement with the concept of the water residence time distribution (Chapter 4) and contain several similarities to the runoff generation characteristics investigated to date in hilly catchments (e.g. Sklash and Farvolden, 1979; Hooper and Shoemaker, 1986; Fionke et al., 1993; Bazemore et al., 1994).

It was found that the most important runoff generation aspect in the investigated Rietholzbach catchment is the timing of the contributions of the previously stored water and of the chemically enriched current rainfall water which had passed the pathways in the soil matrix. The evidence of ionic substances showed that this enriched water substantially contributes to the total runoff after the runoff peak, i.e. after the expulsion of the stored water from previous events. This can be confirmed by two aspects: (1) by the subsequent increase of electrical conductivities in the stream over the pre-event values, and (2) by the negligible reactions of the lysimeter outflow during the whole event. It is obvious that the described mechanisms do not occur homogeneously within the whole
catchment. In addition, the described concept was identified for selected flood events in the summer season only, i.e. there is a variety of additional runoff mechanisms that could be identified during events under other boundary conditions (multiple runoff peak, longer duration of the event, different initial water contents within the soil etc). Larger datasets containing more tracing substances at more sites under different hydrological conditions would improve the evidence of controlling or determining processes.

The technique developed using the electrical conductivity as a conservative tracer of runoff components gave similar results to those obtained by \( ^{18}O \). Thus, it was possible to adopt the electrical conductivity as a possible substitute tracer for the isotope \( ^{18}O \). Nevertheless, the use of this method requires the knowledge of the stream chemistry of the most important substances during each event. In the present study, this condition was met for only one event; a testing of this conclusion on more flood events would therefore be necessary.

### 6.2 Contribution of the present work and outlook

Although this study was limited to the investigation of the Rietholzbach catchment, the developed concepts contribute to the understanding of the water turnover in small prealpine catchments. Due to the specific geographical conditions of each catchment, it is impossible to directly transfer the estimated mean residence times or proportions of runoff components to other catchments. Nevertheless, the spectrum of water residence times estimated here can be especially regarded as the first dating of natural waters in Swiss prealpine porous aquifers. In addition to the regional significance, two general aspects are pointed out. Firstly, new methodical approaches handling the parametrization of the \( ^{18}O \) input function and the coupling of results obtained by use of various environmental tracers were presented. Secondly, approaches for the coupling of concepts used in precipitation-runoff models with those used in the modelling of flow and mixing by assessment of environmental tracers were discussed.

The present work offers a large variety of possible improvements and refinements. Regardless of the character of the investigated area, the following basic steps are required for any future hydrological studies:

- The simulation of the \( ^{18}O \) output functions should be carried out at a higher time resolution (weeks). This could possibly improve the quality of the simulation, especially in the case of shorter water residence times such as that in the lysimeter.

- The realization of the previous step would require a refinement of the parametrization of the \( ^{18}O \) input functions. It would be therefore desirable to perform an area-distributed groundwater recharge modelling (e.g. using the model BOWAM) and to define area-related weighting parameters, i.e. to obtain different area-related input functions. This groundwater recharge modelling also would contribute to the better estimation of the delay of gaseous tracers (such as \( ^{85}Kr \)) in the unsaturated zone, although more detailed experiments are necessary here. In addition, this step would be of importance in catchments where no special investigations on the unsaturated zone (lysimeter) are carried out.

- The simulation of the \( ^{18}O \) output function of the percolated water flowing out of the lysimeter could be improved by investigating the changes of isotopic significance of the soil water towards the land surface. This would most likely lead to a refinement of the input function because the infiltrated water would be in part isotopically enriched. This experiment would require a very high temporal resolution of both input and output functions.
The inclusion of the tracer separation of runoff components could most likely improve the quality of the precipitation-runoff modelling. The runoff contributions obtained by use of environmental tracers could be used for optimization of storage parameters of several precipitation-runoff models (e.g. Gurtz et al., 1997, variants of the HBV model,). Unfortunately, this optimization would require a comprehensive collection of various flood events to be investigated using environmental tracers. Nevertheless, a successful application of such an approach would essentially enhance the methodological base of the catchment hydrology.
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