

GROUNDWATER RECHARGE FROM RUN-OFF, INFILTRATION  
AND PERCOLATION

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# GROUNDWATER RECHARGE FROM RUN-OFF, INFILTRATION AND PERCOLATION

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Cover Graph:

Discharge is generated by precipitation excess and transforms along interfaces into flow components with different turn-over-times and flow directions;. Overland- and inter-flow move both in lateral surface, respectively subsurface directions and have short turn-over-times. In contrast, groundwater recharge percolates vertical down and reappears very delayed in the surface water. The quantitative influence of the above mentioned interfaces on discharge depends from many factors changing with seasons, wet and dry cycles, rain intensities and even during individual rain events.

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## PREFACE

Life on continents depends on the availability of fresh-water. Hence, preferred sites for human settlements were situated close to springs, rivers, or shallow groundwater resources, and it was accepted at the dawn of mankind that the local social and economic development was limited by the natural available water resources in a quantity and quality sense; any shortage in the availability of water stimulated people to migrate.

With the growing earth population and during the industrial age, water availability reached a new dimension: By technical means, water became everywhere available by drilling and piping and in more recent times also by low cost desalination methods. This seemingly ubiquitous water availability led in many areas of the world to an overexploitation of water resources often with the consequence of a deterioration of fresh-water quality by salt water intrusions from deep aquifers and in coastal areas from the sea, or by subsidence, which changed hydraulic properties of aquifer systems. These adverse developments have always a transient character; this means the hydraulic system responds with a more or less long delay time till reaching new steady-state conditions and often create new situations that—when ever—can only be managed with high costs.

In humid areas of the world, the limiting factor for groundwater development became mostly water quality, in semi-arid and arid areas, it is both water quantity and quality. To overcome these problems, safe-yield concepts in terms of water quantity and water quality have been developed. Simplistically,

- The quantity safe-yield concept is based on the replenishment of surface/subsurface systems either by natural or artificial (groundwater) recharge; this concept has not only to consider average inputs and outputs, but also the year to year meteorological fluctuations, droughts, floods and socio-economic facts.
- The quality concept is based either on the natural, good water quality or on threshold concentrations to protect health and life of beings and ecosystems.

It is often overlooked that the amount of water extraction, according to the needs of the urban and industrial, agricultural and recreational development of a region, changes not only the local water cycle, but can also introduce new boundary conditions for recharge and discharge pathways. This is often also accompanied by a deterioration of water quality, which cannot be completely governed by respective water treatment measures. Finally, the local water demand has often been satisfied by water imports without considering seriously, if such measures exceed the water drainage and natural attenuation capacity of the respective region and aquifer system.

A new challenge raises with climate changes, in particular a change in the precipitation amount and pattern, which will modify the water cycle, specially the water availability on continents. The groundwater response to such climate changes will not be instantaneous, but transient; therefore, any prediction on respective changes in the fresh-water resources will not persuade at present water users, because negative effects do not appear instantaneously, but it will in a remote time, when deterioration of water resources already proceeded so far that it may have become irreversible.

This book focuses on the present global and local water cycle, especially how precipitation changes water fluxes at the interface atmosphere/lithosphere/biosphere, within the weathering zone of sediments/rocks and in the subsurface. The detailed understanding of these processes allow a better estimate and assessment of the components of the water cycle and a better prediction of the impact of men's activities on the water cycle. These facts are documented by some examples from the main climate zones of the globe. In contrast, this book does not consider the wide field of fresh-water quality.

Klaus-Peter Seiler  
Joel R. Gat

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## ABBREVIATIONS AND DIMENSIONS

$A$	Area	$m^2$ or $km^2$
BBM	Black-box models	–
b.g.s.	Below ground surface	–
$C$	Concentration	$mg/L$ or $g/m^3$
dpm	Decays per minute	–
$D'$	Dispersion coefficient	$m^2/s$
$D'_L$	Longitudinal dispersion coefficient ( $x$ -direction)	$m^2/s$
$D'_T$	Transverse dispersion coefficient ( $z$ - or $y$ -direction)	$m^2/s$
$D$	Specific run-off	$mm/year$ or $L/(s\ km^2)$ ; $1\ L/(s\ km^2) = 31,536\ mm/a$
$D_G$	Specific groundwater run-off	$mm/year$ or $L/(s\ km^2)$
$D_I$	Specific inter-flow run-off	$mm/year$ or $L/(s\ km^2)$
$D_M$	Molecular dispersion	$m^2/s$
$D_O$	Specific overland-run-off	$mm/year$ or $L/(s\ km^2)$
$D_T$	Specific discharge transfer	$mm/year$ or $L/(s\ km^2)$
$D_{SF}$	Specific surface run-off	$mm/year$ or $L/(s\ km^2)$
DM	Dispersion Model	–
$e$	Vapor pressure	mbar
eq.	Equation	–
EM	Exponential Model	–
EP	Evaporation	$mm/year$ or $L/(s\ km^2)$
ET	Evapo-transpiration	$mm/year$ or $L/(s\ km^2)$
$g$	Gravity acceleration	$m/s^2$
GMWL	Global Meteoric Water Line	–
$h$	Height	m
$h'$	Relative humidity	– or %
$H$	Hydraulic head at water saturation	
	<i>Volumetric related</i>	$Pa$
	<i>Weight related</i>	$m$

$H_c$	Capillary head	m
$H_g$	Gravity head	m
$H_o$	Osmotic head	m
$I$	Activity concentration	Bq/L
IN	Infiltration	mm/year or L/(s km <sup>2</sup> )
K	Hydraulic conductivity	m/s
LAI	Leave area index	–
LMWL	Local Meteoric Water Line	–
$m$	Empirical parameter	–
$M$	Mass	kg
MTT	Mean-turn-over-time, Mean-transit-time Mean residence time	day, year
MTT <sub>w</sub>	Mean-turn-over-time of the water	day, year
$n$	Empirical parameter	–
N		mol/m <sup>3</sup>
$p$	Pressure	mbar
$p'$	Porosity	– or %
pmc	Percent modern <sup>14</sup> C	%
$P$	Precipitation	mm/year or L/(s km <sup>2</sup> )
Pa	Pascal	kgm <sup>-1</sup> s <sup>-2</sup>
PFM	Piston Flow Model	–
$q$	Specific flow rate	m <sup>3</sup> /(s m <sup>2</sup> )
$Q$	Discharge/flux	m <sup>3</sup> /s
$r$	Capillary equivalent radius	cm
$R'$	Groundwater recharge	mm/year or L/(s km <sup>2</sup> )
R	Isotope ratio, e.g., <sup>2</sup> H/ <sup>1</sup> H	–
$S$	Storage	% or mm/year
$S'$	Water saturation	– or %
$S_c$	Storage coefficient	–
$S_e$	Effective saturation	%
$T$	Time	second, hour, day, year
$T'$	Thickness	m
$T_{0.5}$	Half live	year
$T$	Temperature	°C
TBT	Tracer break through curve	–
TP	Transpiration	mm/year or L/(s km <sup>2</sup> )
TU	Tritium unit	–
WMO	World Meteorological Organization	–
$v_f$	Filter velocity	m <sup>3</sup> /(m <sup>2</sup> year) or m/year
$v_a$	Apparent flow velocity	m/year
$V_T$	Total volume	m <sup>3</sup>
$V_V$	Void volume	m <sup>3</sup>

$V_w$	Water volume	$m^3$
$x, y, z$	Distances and Cartesian co-ordinates	m
$\alpha$	Separation factor	–
$\alpha^*$	Thermodynamic separation factor	–
$\alpha'$	Dispersivity	m
$\beta$	Water-solid contact angle	degrees
$\gamma$	Constant parameter	–
$\delta$	Deviation of stable isotope contents from a standard	%
$\varepsilon$	$(1 - \alpha)$	–
$\varepsilon^*$	$(1 - \alpha^*)$	–
$\lambda'$	Tortuosity	–
$\lambda$	Decay constant	$\text{time}^{-1}$
$\theta$	Water content	%
$\theta_s$	Water content at saturation	%
$\theta_{fc}$	Water content at field capacity	%
$\theta_r$	Residual water content	%
$\theta_w$	Water content at wilting point	%
$\sigma$	Surface tension	$\text{g/s}^2$
$\rho_w$	Density of water	$\text{g/cm}^3$
$\Psi$	Suction	
	<i>volumetric related</i>	<i>hPa</i>
	<i>weight related</i>	<i>mm</i>
$\Phi$	Hydraulic head as the Sum of $(\Psi + H)$	
	<i>volumetric related</i>	<i>Pa</i>
	<i>weight related</i>	<i>m</i>

## DEFINITIONS

**Active groundwater recharge zone:** Aquifer zone, which hosts groundwater recharge with mean turnover times of <100years. Groundwater in this zone is also named shallow groundwater (section 2.4, Fig. 2.10).

**Base-flow:** Surface discharge fed by groundwater (section 2.3, Fig. 4.3). Under dry weather conditions, groundwater is the only discharge component in rivers.

**Capillary fringe:** The capillary fringe is the transition zone from water unsaturated to water saturated conditions in the subsurface. In it, capillary forces still play a role, but gravity forces increasingly dominate, when approaching the groundwater table/surface (section 2.3).

**Connate water:** Water entrapped in sediments, which was not in contact with the biosphere since sedimentation time (section 2.4, Fig. 2.11).

**Deep groundwater:** Groundwater in the passive groundwater recharge zone with mean turnover times exceeding 100 years (section 2.4), but being by far younger than connate water (Fig. 2.11).

**Direct run-off:** Surface run-off, which immediately responds to rain events. Direct run-off consists of the components overland- and inter-flow (section 2.3).

**Discharge:** Discharge is made up of the residuals, produced by precipitation in excess to evapo-transpiration and to water retention in the unsaturated zone. It can take the form of base-flow, inter-flow or overland-flow (Fig. 4.3).

**DOC:** Organic carbon in water with particle sizes <0.45  $\mu\text{m}$  (**D**issolved **O**rganic **C**arbon). In contrast, the sum of all organic matter in water is called **T**otal **O**rganic **C**arbon (TOC).

**Epizone of consolidated rocks:** Zone of decompression and weathering upon consolidated rocks. The epizone collects infiltration, may create perched groundwater and distributes the infiltration flux between the flow paths of inter-flow and groundwater recharge (section 2.3, Fig. 2.7).

**Groundwater recharge:** Component of infiltration into the subsurface that joins groundwater through the unsaturated zone, the river bed or lake ground.

**Groundwater:** Underground water that completely fills the pores of an aquifer, following only gravity forces. Groundwater discharges to rivers, lakes or directly to the ocean.

**Indirect run-off:** Surface run-off, which responds delayed to rain events. Base-flow or groundwater discharge to rivers is synonymous with indirect discharge (section 2.3, Fig. 4.3).

**Infiltration:** Infiltration is the process of transition of precipitation or surface water into the lithosphere; strictly spoken, it describes the process of how the dimensions of unsaturated flux and storage are influenced by the entry of water into the lithosphere. Infiltration contributes to inter-flow and groundwater recharge (section 3.3, Fig. 4.2).

**Infiltration capacity:** Maximum amount of water that can infiltrate into the subsurface. Water in excess of the infiltration capacity produces either overland-flow or excessive ponding at the infiltration surface. Infiltration capacities depend on actual fabrics and water contents of the sediment.

**Inter-flow:** Run-off component that follows in the subsurface approximately the morphology of the landscape (Fig. 4.2) and was in exchange with stored water of the unsaturated zone, but not necessarily with groundwater (section 3.3). Inter-flow joins on its flow path surface run-off either directly or mixed with overland-flow.

**Overland-flow:** Run-off component that did not infiltrate (Fig. 4.2) or infiltration excess discharge. It follows flow paths along the land surface and joins surface run-off in rivers (section 3.3).

**Passive groundwater recharge zone:** Aquifer zone, which hosts groundwater recharge with mean turnover times of >100 years. Groundwater in this zone is also named deep groundwater (section 2.4, Fig. 2.11).

**Perched groundwater:** Local groundwater accumulation upon low hydraulic conductivity interfaces within the vadose zone; perched groundwater is over- and underlain by unsaturated zones (section 2.3, Fig. 2.7).

**Percolation:** Flow in the unsaturated zone. In contrast to groundwater flow, percolation can follow all directions, even against gravity, because it is driven by both gravity and capillary gradients (section 2.3).

**Regional groundwater:** Groundwater of large extent, forming a hydraulic continuum and discharging close to the water table to local and at depth to distant receiving rivers (section 2.3).

**Run-off:** Components of discharge like direct (overland- + inter-flow) and indirect run-off (base-flow or groundwater discharge), overland-flow, inter-flow, groundwater recharge (Fig. 4.3).

**Saturated zone:** Groundwater zone.

**Shallow groundwater:** Groundwater of the active groundwater recharge zone with mean turnover times of <100 years (section 2.4, Fig. 2.11).

**Surface discharge:** Discharge in a river, representing one or a mix of different run-off components (section 2.3, Fig. 4.3).

**Unsaturated zone:** The unsaturated zone contains water and air with sharp interfaces, in which flow is governed by both capillary and gravitation forces and in which most of the time capillary forces are dominant (section 2.3).

**Vadose zone:** The vadose zone stretches from the ground surface to the regional groundwater table/surface and consists of maximum three distinguishable elements: the unsaturated zone, perched groundwater and capillary fringes (section 2.3).

## CHAPTER 1

### INTRODUCTION

Fresh-water on continents is made up by two-third of ice and one-third of non-solid water. Groundwater accounts for 96.3% of all non-solid fresh-water resources (8,000,000 km<sup>3</sup>), followed by lake water (2.7%), soil water (0.8%), and river water (0.01%); the rest belongs to atmospheric water vapor. Most lakes are interrelated with groundwater; more than 45% of the surface discharge of rivers in humid and semi-arid climates originates from groundwater, whereas in arid (dry-land) and cold climates surface discharge contributes to groundwater. Hence, this subsurface resource is associated with altogether 8,300,000 km<sup>3</sup> of water. Less than 50% of this water was recharged within the last 100 years through the present water cycle, the rest was renewed in the historic and geological past under climate conditions, which are not precisely known; hence, groundwater hydrology is faced with various water storage forms and run-off systems, changing with time.

At present, groundwater is the major resource of water supply for about half of the nations. Approximately 40% of the world's population uses groundwater and about 50% of the world's food production depends on irrigated agriculture linked to groundwater. During the 20th century, the water demand of human beings increased 6 times while population tripled; it is expected that this trend will continue into the 21st century.

Apart from human needs, water plays an important role in distributing energy and matter over the globe, in the functioning of ecosystems and in natural attenuation processes. Fortunately and in contrast to other geological deposits of economic value, the water cycle results in the renewal of water resources and triggers together with local or regional, orographic, tectonic, and ocean level settings groundwater flow. In humid temperate and tropical climates, natural groundwater flow is mostly at steady-state, in permafrost and arid (dry-land) areas (Lloyd 1980) often transient. Groundwater management and land use, however, often add a man-made transient behavior to groundwater flow, which, however, is usually not immediately discernible.

It is evident from the data on water withdrawal and consumption (Table 1.1) and water availability (Table 2.2) that in some areas of the globe, water demand is close to or already exceeds the availability of the present rechargeable water. Thus, the social and economic welfare depends today and even more in the future

*Table 1.1.* Water withdrawal and consumption in the 20th century and the extrapolated development to the beginning of the 21st century

	Withdrawal (km <sup>3</sup> )	Consumption (km <sup>3</sup> )	Agriculture (%)	Industry (%)	Private sector (%)	Others (%)
1900	579	331	88.6	7.5	3.7	0.2
1950	1,382	768	78.1	14.8	6.3	0.8
1980	3,174	1,686	66.5	22.5	6.9	4.1
2000	3,975	2,182	65.6	19.5	9.7	5.2
2025	5,236	2,764	60.9	22.3	11.6	5.2

Water consumption is detailed according to the main sectors of water use (UNESCO, 1999).

on rechargeable, treated, and imported water. But all options of water import, if realized, may have various economic and environmental consequences, which have not yet been studied in sufficient detail.

In recent years, the possible diminution of water resources as a consequence of man-made global climate changes is drawing additional attention of the scientific community. Although the extent of such changes is still difficult to predict, new strategic approaches have to be developed to provide more flexible answers to both new and existing challenges.

Groundwater resource development is based on the concept of groundwater yield, which turns out to be difficult; it has to meet a set of hydrologic, social, and economic objectives and may be defined as the balance between the benefits of maximum allowed extraction rates and undesired changes by pumping and pollution. In this concept groundwater recharge is one important component, which is mostly determined under special steady-state initial and boundary conditions; however, groundwater development may change these conditions throughout the recharge–discharge regime with time. Therefore, the development of sustainable groundwater management strategies cannot refer to single numbers but needs an integrated concept within a specific timeframe.

The management of groundwater resources involves, among others, the following subjects:

- Determination of the range of groundwater recharge with appropriate methods,
- Manipulation of groundwater recharge according to local needs and possibilities,
- Protection of the recharge pathways to safeguard natural attenuation,
- Monitoring aquifer exploitation,
- The development of special control (early warning) systems to recognize, assess, and prevent groundwater degradation in time.

The paramount importance of the recharge process in this scheme is clear. Therefore, this book is devoted to groundwater recharge.

Groundwater recharge in humid temperate and tropical climates typically accounts for more than 10% and in arid (dry-land) areas for less than 5% of the precipitation; in semi-arid and cold climates the values lie in between these numbers.



There are six general approaches to determine groundwater recharge:

- Bulk mass balance methods,
- Methods based on outflow characteristics,
- Mixing approaches,
- Numerical/hydraulic,
- Tracer flux, and
- Mean-transit-time methods.

The precision in determining groundwater recharge depends significantly on

- The conceptual model, based on which percolation has been evaluated,
- The precision in determining the source (precipitation, snowmelt, dew formation, and infiltration) and loss functions (evapo-transpiration, overland-flow, inter-flow),
- The time span, to which groundwater recharge refers to.

According to the precision and the time increment for which groundwater recharge has to be determined, lots of modifications of these six basic approaches have been established.

The results of these various methods to determine groundwater recharge have different scale relations. Flux methods, are based on artificial tracing, refer to the smallest, bulk mass balance methods to the largest scale and inverse calculations as well as many discharge analysis often deal with an intermediate scale of groundwater recharge.

In contrast to infiltration, percolation is a rather slow process and both change with boundary conditions mostly in a non-linear way: therefore, only average values of groundwater recharge result from most studies. Nowadays, however, there is also a strong interest to obtain short-term information on infiltration, discharge, and the storage of subsurface water for agriculture and irrigation planning as well as for early-warning systems to improve flood control.

Long-term information on the water balance refers mostly to precipitation and discharge measurements on a catchment scale; this needs a minimum of 10 years to more than 25 years of observation in humid temperate, respectively tropical and arid (dry-land) climates. Such long-term observations

- smoothen the short-term variability of precipitation and evapo-transpiration, which govern the input function of discharge and
- reduce errors related to delayed responses of the subsurface system in connection with water storage and release and slow percolation velocities.

In developed countries, such long-term observations on discharge and groundwater level fluctuation exist continuously since the end of the 19th and beginning of the 20th century and are still operating. In many developing countries and areas with a small population, such measurements mostly started in the second half of the 20th century by the initiative of the WMO; however, these observations often stopped after some years or decades, because of logistic problems. Because of these circumstances it is important to apply complementary methods, which also act in support of the long-term observations, that deliver time- and space-integrated information on groundwater recharge. For the last 60 years, this was step by step realized

with artificial and environmental tracer techniques that have been developed since the 1940s using chlorides (Schoeller, 1941) and environmental isotopes (Münnich, 1968) or analyzing in rivers the hydraulic (Natermann, 1951) or environmental tracer response (Sklash et al., 1976) to storm events.

Groundwater recharge on continents has an uneven horizontal and vertical distribution;

- Horizontally, it depends
  - on climate and weather trajectories (section 2.2.2),
  - transformations of precipitation and air humidity at the interface atmosphere/biosphere/lithosphere (section 3.2),
  - topographic factors and lithology (section 3.3),
  - hydraulic interfaces in the effective root zone (section 3.5);
- Vertically, it depends on the depth-related sequence of hydraulic parameters and the thickness of aquifer systems (section 2.4).

In all climate zones, old (>100 years) and fossil groundwater (>10,000 years) are more abundant than the presently recharged groundwater (<100 years old); these old (historic) and fossil groundwater should not be wasted, in order to keep operational a buffer system for variable natural, man-made recharge, the many ecological functions of water and emergency situations (Vrba & Verhagen, 2006).

Groundwater recharge can be manipulated by selecting an appropriate vegetation cover, by forced gradient river-infiltration (section 3.6) and by artificial recharge through basins, ponds, artificial lakes, and wells (section 3.7).

Both the quality and the quantity of the recharged waters are significantly influenced by the plant cover and land use, especially by irrigation practice, urbanization, industrialization, traffic, and in more recent times also by the import of blue water from distant areas.

Considering the above-mentioned general facts, this book intends to

- describe the factors that influence groundwater recharge,
- describe methods to measure groundwater recharge,
- draw attention to possibilities and limitations of manipulation of groundwater recharge.

## CHAPTER 2

### THE WATER CYCLE

The lithosphere, oceans and the atmosphere form the largest reservoirs on earth. The main link between these reservoirs is the hydrological cycle, which provides fresh-water for humans, continental ecosystem functions, weathering, and sediment transport and is co-responsible for the temperature equilibration on earth. The driving force of the water cycle is solar radiation, contributing with an average of  $10^{24}$  J/year to water evaporation; for comparison, the European Community consumes about  $7 \times 10^{19}$  J/year of energy.

Annually, about  $1 \text{ km}^3$  of water enters the water cycle from both the earth's interior and the space. The escape of water into the space and the return of water either to the earth's interior through plate-tectonics or by binding water through the weathering of feldspars and others (about  $0.7 \text{ km}^3/\text{year}$ ) are estimated to be of the same order of magnitude. As compared to the yearly turn over of  $577,000 \text{ km}^3$  of water through the water cycle on continents and oceans (Fig. 2.1), uncertainties in determining this  $1 \text{ km}^3$  are negligible on a long and short run of time.

#### 2.1. DISTRIBUTION OF WATER ON EARTH

Water on earth accounts for about  $1.386 \times 10^9 \text{ km}^3$ : most of it is liquid, some occurs as ice and very little is in the form of vapor (about  $13,000 \text{ km}^3$ ). Ocean water constitutes about 97.5 vol.% and fresh-water the remaining 2.5 vol.%. The distribution pattern of solid, liquid and vapor water is temperature dependent and accounts for the difference between conditions on earth as compared with other known planets within the solar system.

Except for sea-ice at the North Pole, all fresh-water is found on the continents:

- 68.9 vol.% is fixed in ice shields, glaciers ( $27,000,000 \text{ km}^3$ ) and permafrost (about  $300,000 \text{ km}^3$ , Shiklomanov, 1990); glaciers and perennial snow cover an area of about  $680,000 \text{ km}^2$ );
- 29.9 vol.% belongs to groundwater,
- 0.9 vol.% to soil moisture and atmospheric water vapor and
- 0.3 vol.% appears as surface water.

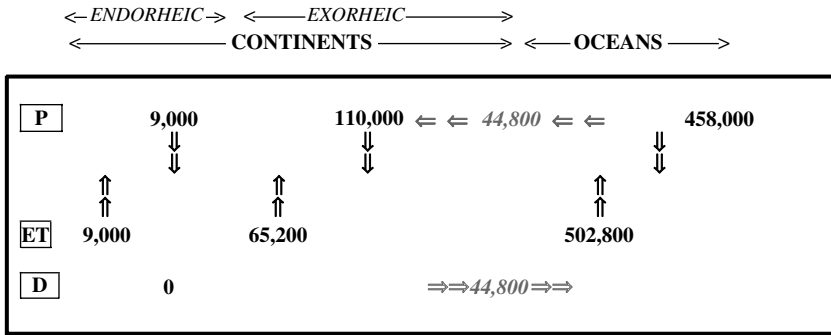


Figure 2.1. The global water cycle. All numbers in km<sup>3</sup> (UNESCO, 1999)

Groundwater represents the most important resource for continental ecosystems. This is especially not only true for semi-arid and arid areas but also for all rock formations in other climates with unlimited infiltration capacities (karst, gravels).

On the time scale of a century, the hydrologic water cycle is to a first approximation balanced; however, on different time scales it appears imbalanced according to the reservoirs through-flown by the different run-off components. To better understand the importance of such reservoirs for the fresh-water balance, mean-turn-over-times (MTT) are considered (Table 2.1). From these it becomes evident that connate water represents a non-renewable resource within geologic time scales (section 2.4); in contrast, atmospheric water vapor, shallow groundwater, lakes and rivers are significantly recharged by the present water cycle. In between renewable and non-renewable groundwater occurs an intermediate zone, named deep groundwater by Seiler and Lindner (1995), which received its groundwater recharge in geologic or historical times and is little fed by the present groundwater recharge.

All glaciers and perennial snow represent these days a long-term water reserve, contributing to water supply; ice shields do not in the same extent, because they are too remote from consumers. With global warming they are expected to reduce in

Table 2.1. Average mean-turn-over-times for waters in different reservoirs

Ocean	~2,500 years
Cold glaciers	>100,000 years
Temperate glaciers	<500 years
Connate water	>1,000,000 years
Deep groundwater	>>100 years
Shallow groundwater	<100 years
Lakes	~15 years
Rivers	~16 days
Atmospheric water vapor	~10 days

volume, which may hide for a long period the real consequences of climate changes on fresh-water availability in the respective areas (section 6.3).

Continental water resources have an unequal latitude distribution. This is due to the uneven distribution of solar radiation on earth, the global atmospheric circulation pattern and its modifications by heat capacities and albedo, the size and topography of continental masses and interactions between the atmosphere and warm or cold ocean currents (section 2.2.1).

According to the most recent world water balance (UNESCO, 1999), the yearly discharge from all continents amounts to 44,800 km<sup>3</sup> (Fig. 2.1), and the distribution of average discharge from the different continents to the oceans is summarized in Table 2.2. In the time span 1921–1985, discharges did not show a marked tendency of increase or decrease (UNESCO, 1999); this may either be interpreted in terms of

- Steady-state conditions in the water cycle over this run of time or
- Changes in temperatures, precipitation and evapo-transpiration do not show up instantaneously, because of long mean residence times in the respective reservoirs, hence, of a transient character of discharge.

Based on world population census in 1985, discharges are related in Table 2.2 to the capita of the respective area. These numbers should be assessed relative to the demand per capita, which approaches

- an average of 1,000–1,500 m<sup>3</sup>/year (maximum 2,500 m<sup>3</sup>/year in the USA); this quantity includes
- about 50 m<sup>3</sup>/year for the private sector and
- about 5–10 m<sup>3</sup>/year for survival.

The numbers in Table 2.2, however, do not consider that any use of blue water produces gray water; empirically, 1 m<sup>3</sup> of untreated gray water needs for the restoration of natural attenuation before reaching the ocean in exorheic or terminal areas in endorheic systems (Fig. 2.2)

- About 9 m<sup>3</sup> of blue water if rejected untreated and
- About 3 m<sup>3</sup> of blue water if rejected after physical, chemical and biological treatment.

The numbers in Table 2.2 show on the average that

*Table 2.2.* Relative distribution of renewable water resources in world regions (1921–1985) as related to a discharge of 44,800 km<sup>3</sup> and the availability of rechargeable water in m<sup>3</sup> per capita and year (UNESCO, 1999)

Continent	Percentage of discharge	Rechargeable water in m <sup>3</sup> /(capita and year)
Asia	31.5	3,920
Europe	6.7	4,200
Africa	9.8	5,720
North America	18.4	17,400
South America	28.0	38,200
Australia and Oceania	5.6	83,700

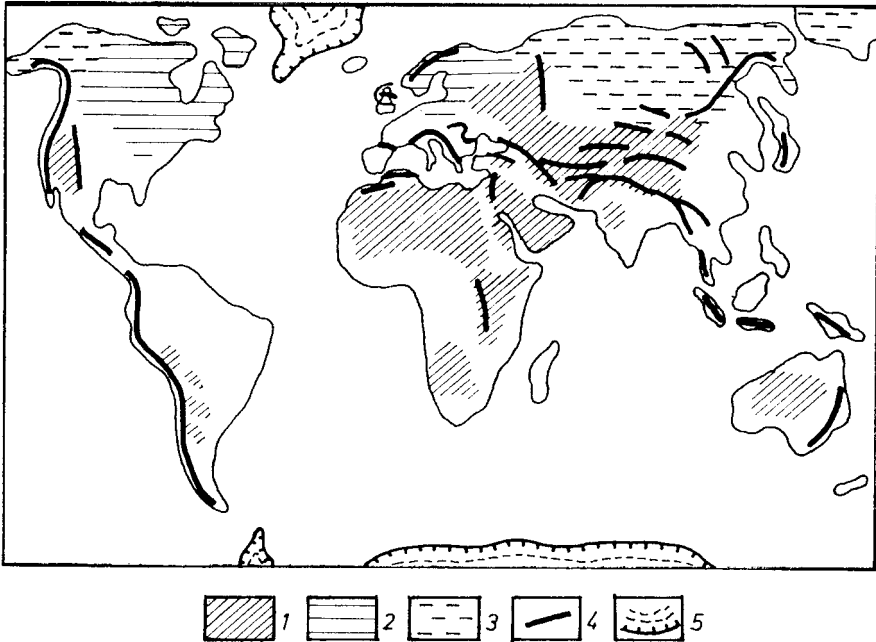


Figure 2.2. The influence of morphologic and geologic factors on discharge. 1 = endorheic areas, 2 = ice melt areas, 3 = permafrost, 4 = mountains, 5 = ice sheets (Starkel, 1995)

- Australia, Oceania and the American continent have a significant excess of fresh-water,
- Europe, parts of Asia and Africa might soon or already do reach limits in using rechargeable water of the present water cycle.
- The Near East and North Africa are so short in water recharge that most of the nations in this area are already over-exploiting their water resources; as an example Kuwait has only  $0.2 \text{ m}^3/(\text{capita and year})$ .

Shortening of available water by means of a non-adapted management or an excessive demand becomes evident in many parts of the world; the Aral Lake and the Dead Sea are shrinking in size; since 1972, the Yellow River (China) runs dry over increasing periods of time a year (Fig. 2.3); water follies are known in North America (Glennon, 2002) and in many areas of India groundwater levels decline continuously. Under these circumstances, renewable fresh-water resources can no longer be considered as a free-of-charge-gift of nature.

## 2.2. THE CONTINENTAL WATER CYCLE

By means of water quantities, the main present source and sink area of the water cycle are oceans. No doubt, on a long time scale, the naturally waxing and waning ice shields and permafrost areas, which exist on earth since the Miocene period, also act as a significant source and sink term of the water cycle, producing ocean

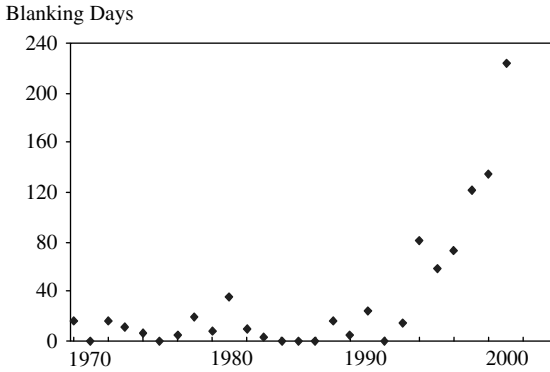


Figure 2.3. Days without surface discharge (blanking days) in the Yellow river in the period 1972–2000

level fluctuation of 150–200 m compared with the present ocean level; however, on a short time scale, this sources or sinks are not too appreciable.

One can distinguish between a continental and an oceanic branch of the water cycle (Table 2.3, Fig. 2.1), which are interconnected. Most of the water evaporates over oceans and falls back as precipitation to the ocean; however, 9% (44,800 of 502,800 km<sup>3</sup>) of the water vapor of the oceanic evaporation joins air humidity of continental evaporation, precipitates on continents and returns as surface or subsurface run-off to the oceans (exorheic areas). There is also an endorheic water cycle branch on continents, which has no outflow to the oceans (endorheic areas, Fig. 2.2), but operates an intra-continental run-off evaporation mechanisms (such as the catchments of the Aral Lake, Baikal Lake and Dead Sea).

Strictly speaking, any safe water use in quasi-equilibrium with the present water cycle is limited to the present run-off, discharging from the continents to the ocean either as river water or as groundwater. Any potential use of ancient water, stored in deep aquifers, beneath permafrost or in glaciers as well as of waters, which are

Table 2.3. World water balance (UNESCO, 1999) and the distribution of exorheic discharge to the oceans

		Oceans	Exor. areas	Endor. areas	Σ
Evapo-transpiration	mm/a	1,393	548	300	
	km <sup>3</sup>	502,800	65,200	9,000	577,000
Precipitation	mm/a	1,269	924	300	
	km <sup>3</sup>	458,000	110, 000	9,000	577,000
Discharge	mm/a		124	0	
	km <sup>3</sup>	–	44,800	0	
					44,800
Discharge in % of 44,800 km <sup>3</sup> into the					
			46.9		
			29.9		
			11.4		
			11.2		

unproductively consumed by evaporation in endorheic areas, must be approached with caution to ensure that no negative feedback is produced, affecting delicately balanced ecosystem functions and, hence, may lead to severe supply and ecological problems on a long run of time.

### 2.2.1 The Components of the Water Cycle

The motors of the water cycle are *evaporation* and gravity; evaporation occurs along ocean and continental surfaces (Fig. 2.4) and is enhanced by the transpiration of continental plants.

This EP-/ET-flux amounts to:

- Oceans (502,800 km<sup>3</sup>/year or 1,393 mm/year),
- Exorheic areas of the continents (65,200 km<sup>3</sup>/year or 548 mm/year),
- Endorheic areas of the continents (9,000 km<sup>3</sup>/year or 300 mm/year).

Ocean areas with an excess of evaporation are the central and south Atlantic, the south Indic and the central and south Pacific oceans, all at low latitudes (Fig. 2.4). Depending on the distribution of land and ocean surfaces, these regions of preferential evaporation reach up to 40° in the south-hemisphere and to 30–35° in the north-hemisphere (Fig. 2.4).

The limited availability of water at continental surfaces is the one reason that the evaporation rate on continents is less than 40% of that on oceans. The other factor is the low net solar radiation received by the land surface compared with the ocean surface; this is mainly caused by the albedo—the reflection of solar radiation – which is only 3–10% for oceans and ranges on continents from 7%

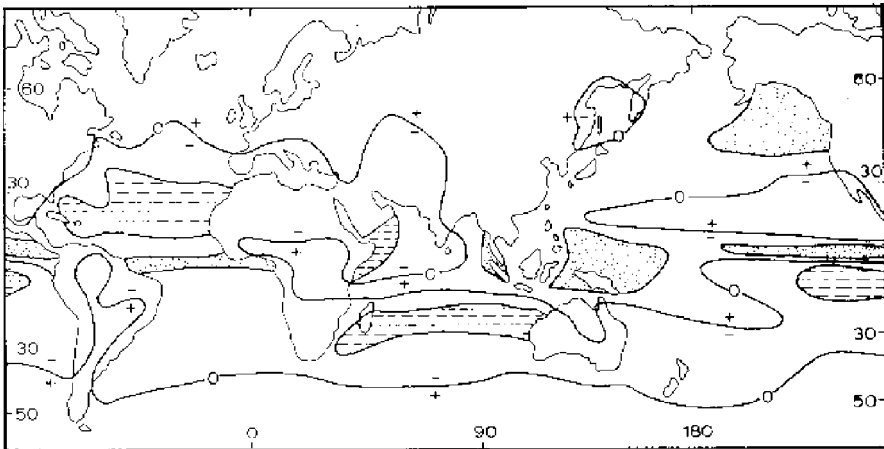


Figure 2.4. Precipitation/evaporation ratios exceeding (+) or remaining below (-) mean global ratio. Stippled areas: precipitation excess >100 mm/year; dashed areas: evaporation excess >100 mm/year (Lisitzin, 1971)



*Table 2.4.* Albedo of different surfaces without and with vegetation covers (List, 1951)

Surface	Albedo in %	Surface	Albedo in %
Fresh-water lake	6–10	Humic soil, dry	14
Forest, green	3–10	Humic soil, wet	8
Forest, snow covered	10–25	Wheat field	7
Sand, dry	18	Grassland, dry	15–25
Sand, wet	8	Grassland, wet	11–33
Death Valley desert	25	Snow, fresh	80–90
Bare soil	10–20	Snow, old	70
		Glacier with few snow	46

The albedo is the ratio of reflected/incoming short wave radiation.

(tropical rain forests) to about 25% (dry, white sands). Some albedo values are indicated in Table 2.4.

The evaporation (EP) from an open water surface under given environmental conditions is termed ‘the potential evaporation’ and is a measure of the to-be-expected EP-flux. The magnitude depends inter-alia on the surface temperature, which determines together with the saturated vapor pressure at the water surface the energy supply that balances the cooling of the surface because of a loss of the latent heat, the humidity gradient across the atmospheric boundary layer and the turbulent air exchange, related to the wind speed (section 4.1.1).

Evaporation from a land surface is enhanced by transpiration of plants that pump water from beneath the evaporating front in the subsurface (Fig. 4.30) to be evaporated at the plant surface. As a result, the ET depends on a combination of

- the energy and moisture balance at a specific surface,
- the aerodynamic conditions, which involve considerations of the effect of the surface roughness and
- physiological parameters related to the plants.

The best-known energy balance/aerodynamic method to calculate EP (section 4.1.1) was developed by Penman (1948). Haude (1954) simplified and Monteith (1965) modified Penman’s formula so as to make it applicable to vegetation surfaces, by introducing monthly constants for different types of vegetations (Haude, 1955) (Table 4.5) or by introducing biological and plant aerodynamic resistance factors, expressing development and respective physiology characteristics of the vegetation cover (Monteith, 1965). With the Haude (1955) method an ET close to the present one originates, but reliable data can only be achieved for periods of months or longer although calculated on the base of daily data. On the contrary, Monteith (1965) refers predominantly to a potential ET and with some restrictions can be applied on a daily, better on a weekly base.

On green areas of continents, TP amounts in the vegetation period to more than 65% and evaporation to less than 35% of the total ET; during the cold seasons of mid- and high latitudes, evaporation accounts more or less only for water losses; in this cold season also some sublimation from the snow covers can play a role (Moser & Stichler, 1975; Stichler et al., 2001), albeit very little.

**Precipitation:** The average annual vapor content in the atmosphere reaches about 50 mm of water equivalent in low latitude regions and decreases to less than 5 mm over high-latitude areas; air humidity generally travels from the warm, low latitudes to the cold, high latitudes, and precipitates out along this trajectory.

Precipitation is caused by condensation of water vapor when air is cooled below its dew point. This cooling is caused by the interaction of air masses, by adiabatic expansion of uplifted air, because of the decrease in atmospheric pressure with elevation. This process releases heat, which can provide additional energy for a further rise of air masses, resulting occasionally in convective thunderstorms (section 3.1).

The rising air along the equatorial convergence zone produces the high rainfall of the tropical areas, whereas the high pressure belt in mid latitudes with its heating of the descending air by compression lacks relative humidity and is responsible for the desert areas of North Africa. In contrast, the low relative humidity of the inner Asian deserts results from continental and topographic effects (Fig. 2.2) on rain-out of air moisture.

On the continents, annual rainfall exceeds continental ET in exorheic areas, because ocean evaporation contributes 44,800 km<sup>3</sup> to continental precipitation; this contribution is in equilibrium with the present run-off of fresh-waters to the ocean.

According to the main source areas of excessive marine evaporation (Fig. 2.4) as well as the mechanisms and influencing factors on rain-out of air humidity (section 3.1), precipitation is very unevenly distributed on the continents (Fig. 2.5); this results together with the uneven heat distribution on earth in cold, temperate, tropical, subtropical and arid (dry-land) climate zones (section 2.2.2); these climate zones are further subdivided according to the local conditions.

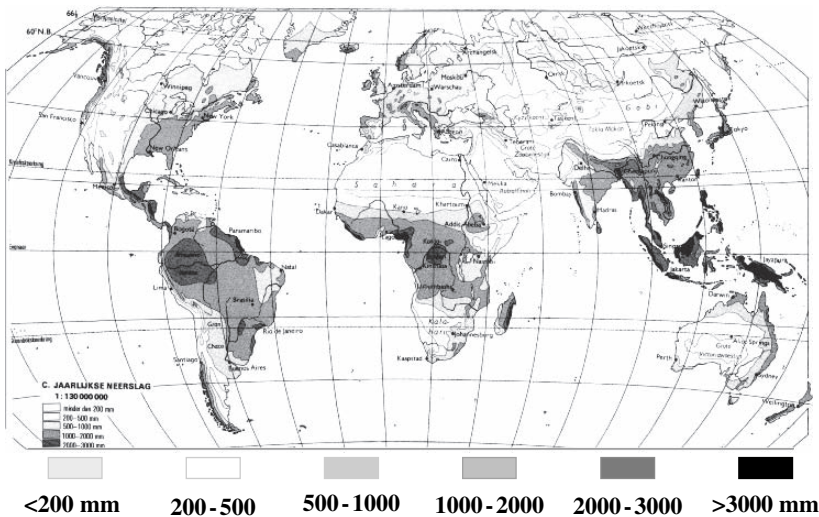


Figure 2.5. The global pattern of annual precipitation

An average of 5% of all precipitation falls as snow and covers over 60–70% of the surface of the North American and Eurasian landmasses during the winter season; it melts from end of winter till the early summer, depending on temperatures, the latitude and the altitude (section 3.1).

Discharge appears in rivers (Fig. 2.6) either as overland-flow, inter-flow or base-flow or a mix of these components. Continental discharge into the oceans happens in exorheic areas to more than 90% through rivers and less than 10% by direct groundwater discharge to the ocean; in endorheic areas discharge is entrapped in the catchment, vaporizes to the atmosphere and re-precipitates.

Global discharge in exorheic areas amounts to 44.800 km<sup>3</sup>; in most climate zones an average of >45% of the annual discharge belongs to the indirect run-off (groundwater or base-flow), <55% to the direct run-off (section 4.1.2, Table 4.6). In areas with low infiltration capacities (e.g. crystalline areas) as well as in permafrost and arid (dry-land) areas, direct run-off recharges groundwater only in special infiltration sectors.

In many areas of the world run-off exhibits some seasonality. This is caused by

- precipitation variations and intensities,
- changing interception capacities and water contents at the interface atmosphere/lithosphere/biosphere,
- changing consumption of water by ET,
- temperature-driven melting of snow and ice,
- The duration of wet and dry seasons in low latitudes.

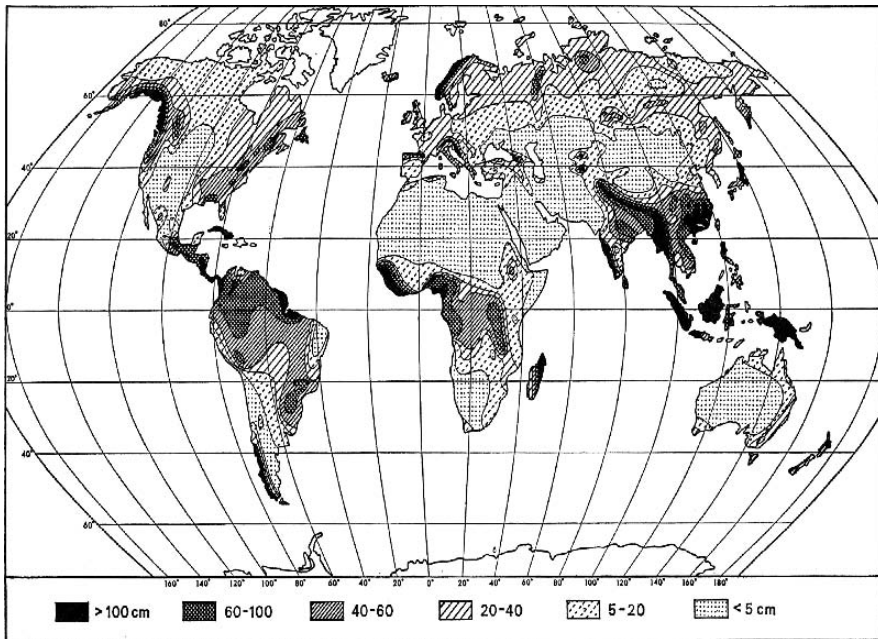


Figure 2.6. The global pattern of annual discharge in cm (Barry, 1969)

These factors may produce perennial (humid tropical and temperate climates), seasonal (subtropical, boreal and nival climates) or episodic run-off (arid climates).

It becomes clear from Fig. 2.6 that Australia, Africa, central North America, the south of South America and large areas of Eurasia belong to low discharge areas (<20 cm) with an episodic surface run-off.

In some areas of the world, however, there exist poly-zonal rivers with a source area in wet or cold climates and a downstream sink area in dry-lands. Examples of such rivers are the Nile, the Yenissey, the Punjab rivers, the Yellow River and others.

### 2.2.2 Characteristics of Different Climate Zones

There is no unanimous definition of climate, because it comprises different meteorological (climate elements) and land surface characteristics (climate factors); therefore, climatology has also been named regional meteorology, describing the annual weather conditions of a macro-area of the globe.

Climate elements are solar radiation, temperature, air pressure, air humidity, precipitation, wind and evapo-transpiration, which all undergo daily and seasonal variations. Climate factor enhances or diminishes the expression of climate elements according to latitudes, altitudes, land-ocean distribution, ocean currents and any vegetation influence. Both climate elements and factors, however, are only semi-quantitatively correlated, which makes systematic in climatology crucial.

Climate has a scale relation; one distinguishes between micro- ( $m^2$ ; e.g. room climate), meso- (small regions; urban climate, canopy climate) and macro-climate (large region; e.g. equatorial climate). Because hydrology is much more a macro- and meso-scale science, both meso- and macro-climates are of special interest.

Climatology is a field of geography and meteorology as well. Therefore, many attempts have been made from both sides to propose a systematic approach. Penck (1910) based it on water balances, Köppen (1931) on climatologic elements and geographic factors and Thornthwaite (1943) on the precipitation–evaporation ratio. Till today, the Köppen (1931) scheme on climate zones seems to be a good approach although it does not satisfy everywhere.

If the earth was a flat, uniform ball with no differences in albedo, heat storage or heat conductivity, a very regular distribution of climate belts would have resulted, which can be characterized by temperatures:

1. Wet tropics with mean annual temperatures exceeding 20°C in the equatorial zone (0–10°N),
2. Dry-lands with mean annual temperatures exceeding 20°C (11–35°N),
3. Temperate zone with temperatures of 10–20°C over a run of 4 months (36–70°N),
4. Cold climates with mean annual temperatures lower than 10°C (71–80°N) and
5. Polar climates with mean annual temperatures below the freezing point (81–90°N).

However, because of the different albedo (Table 2.3), as well as heat storage/conductivity properties of oceans, vegetation covers and land masses, one further has to distinguish between continental and maritime sub-zones of

the above-mentioned climate zones. Seasonal temperature amplitudes are low in maritime and high in continental climates and precipitation is high at coastal areas and diminishes along weather trajectories with the distance from the coast.

Topography further differentiates these zones into mountain and flat-land sub-zones, depending on the temperature drop with altitudes (on an average  $-0.5^{\circ}\text{C}/+100\text{ m}$ ) and the exposition of the area of concern to the incoming solar radiation and to weather trajectories as well.

In other schemes, only precipitation and rain fall variability is taken as a base of classification, which results in eight climate zones

1. Equatorial zones with rain all the year round ( $P/ET \gg 1$ )
2. Tropical zones with dry winters and significant rains in summer ( $P/ET > 1$ )
3. Semi-arid zones with dry winter and some rain in summer ( $P = 250\text{--}500\text{ mm/a}$ ,  $P/ET < 0.5$ , Table 2.5)
4. Arid zones with sporadic rains in some years ( $P < 250\text{ mm/a}$ ,  $P/ET < 0.5$ , Table 2.5),
5. Dry Mediterranean zones with little precipitation in winter and dry summer ( $P/ET < 1$ ),
6. Mediterranean zones with precipitation in winter and dry summers ( $P/ET \approx 1$ ).
7. Temperate zones with precipitation all the year round but lower than in equatorial zones ( $P/ET > 1$ )
8. Polar zones with little precipitation, mostly snow all the year long.

In this scheme, zones 1–6 have high rain fall variabilities and with respect to existing temperatures, the isohyet of 250 mm/a (dry line) is supposed to separate the semi-arid from the arid climate zone.

As temperature and precipitation characterize directions and kinetics of rock weathering, and hence, soil formation, climate also expresses in a respective vegetation cover; therefore, there exists also a climate ecological subdivision, which seems to be the most comprehensive definition, because it qualitatively includes temperature, precipitation/humidity and plant cover. From this classification, there result five climate zones:

1. Tropical climate with rain forests and savannas,
2. Dry climates, in which an extended closed vegetation cover is missing,
3. Warm-temperate climates with leaf and needle forests,
4. Cold climate with a moss and lichen vegetation and
5. Polar climate without vegetation.

*Table 2.5.* Classification of different forms of aridity according to a proposal of UNEP (1992)

	P/ET ratio	Rainfall variability in % of the average
Hyper-arid	<0.05	100
Arid	0.05–0.02	50–100
Semi-arid	0.02–0.5	25–50
Sub-humid	0.5–0.65	<25

As compared to humid temperate or tropical zones, groundwater recharge in arid (dry-land) and cold climate zones is sporadic in time and space; in tropical climates, groundwater recharge is low because of old and very thick weathering crusts ( $>>10$  m, Fig. 5.1), which reduce infiltration of rain; in contrast, in warm- or cold-temperate climates, groundwater recharge is significant in unconsolidated sediments, because of the existence of young and thin soil layers ( $<1$  m); finally, in polar climates, groundwater recharge is missing or only sporadic, because of deep-reaching permafrost conditions.

### 2.3. THE VADOSE ZONE AND ITS WATER BALANCE FOR DIFFERENT CLIMATE ZONES

The vadose zone stretches from the ground surface to the regional groundwater table/surface and has up to three different elements (Fig. 2.7):

- The *unsaturated zone*, in which flow is governed by both capillary and gravitation forces (section 4.3) and in which most of the time capillary forces are dominant;
- *Perched groundwater*, which accumulates on very low hydraulic conductivity interfaces within the vadose zone; it is over- and underlain by an unsaturated zone;
- The *capillary fringe* on top of groundwater tables.

The flow motor for perched and regional groundwater is gravity; however, perched groundwater

- follows flow directions of the inclined low permeable interface;
- occurs only locally;
- is thin and feeds in outcrop areas only small springs or wetlands.

In many small catchment areas ( $<5$  km<sup>2</sup>), surface and subsurface run-off areas often differ in size and extent and perched groundwater admits groundwater exchange with neighboring orographic catchments. This makes the establishment

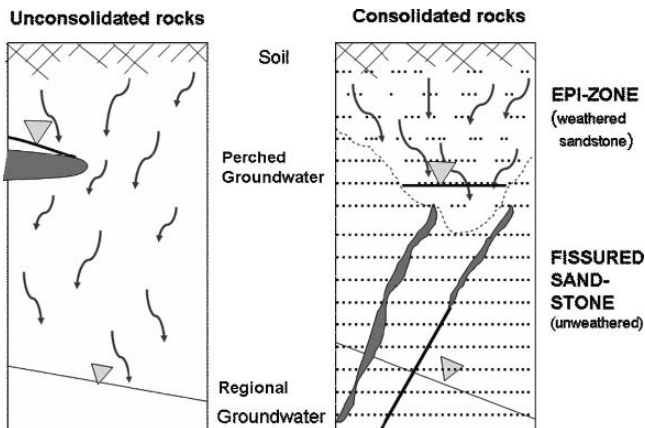


Figure 2.7. Schematic presentation of the structure of the percolation zone in unconsolidated and consolidated rocks

of water balances for small catchments crucial, although discharge levels of rivers in both catchments were at the same altitude (Fig. 4.1, left side).

Above both the perched and the regional groundwater table ( $H_c = 0$  and  $H_g =$  atmospheric, eq. 4.27) a capillary fringe occurs, forming a transition from the unsaturated to the saturated zone. The capillary fringe is thick in fine and thin in coarse-grained sediments (Fig. 4.6, section 4.3). After drying out, perched groundwater does not immediately lose the water content of the capillary fringe; therefore, it is often observed that water contents in the unsaturated zone do not only differ according to soil/sediment fabrics but may also express a memory of recently dried out, perched groundwater.

Drying out of perched groundwater occurs frequently in the epi-zones of consolidated rocks; this epi-zone parallels more or less the ground surface and coincides with the physical and chemical weathering zone on top of consolidated rocks; it facilitates and accumulates infiltration and drains perched groundwater laterally according to the inclination and morphology of its base and vertically if fissures reach into it (Fig. 2.7).

The word seepage is sometimes used for all kinds of subsurface flow, sometimes for the infiltration process at the atmosphere/lithosphere interface and sometimes for flow in the unsaturated zone. To avoid any confusion, in this book, flow in the unsaturated zone is called percolation; it links infiltration with the perched/regional groundwater table and, hence, generates groundwater recharge and directs inter-flow to overland-flow or directly to surface discharge. In contrast to groundwater flow, percolation can follow all directions, even against gravity, because it is driven much more by capillary gradients than by gravity. This makes percolation different from groundwater flow; however, both can be quantified applying the same hydraulic laws of filter flow (section 4.3).

Percolation is initiated by infiltration (section 3.3) and directed by intrinsic parameters of the unsaturated soils/sediments; such intrinsic parameters are the hydraulic functions, but also discontinuities of hydraulic conductivities in the vadose zone, which may both result from geologic, biotic and anthropogenic processes (section 3.5). As gravity, capillarity and intrinsic parameters modify the speed and direction of percolation, infiltration often exceeds groundwater recharge, because it is partially lost by ET or inter-flow.

In the pores of the unsaturated zone, there is a sharp interface between

- Pore-water and air and
- Pore water and solid surfaces.

The ratio surface area of pore water and water volume is in the unsaturated zone always greater than in the saturated zone; this high ratio favors at the water-air-side gas exchanges (e.g., with  $O_2$  and  $CO_2$ ) and thus enhances chemical reactions or must be considered in determining water ages through gas tracers ( $He$ ,  $^{39}Ar$ ,  $^{85}Kr$ ). Only the water/solid contact area of an aquifer is the same in the percolation and groundwater zones.

On the one hand, the slow-down of infiltration to percolation speeds favors the quantitative development of physical or chemical processes with slow kinetics much more in the percolation zone than in groundwater. On the other hand, dilution

of solute matter is less important in the unsaturated than in the saturated zone. Finally, microbial activities are supposed to be low in the unsaturated zone beneath soils, because water films provide only thin habitats and organic matter in percolation water is rare, because of mechanical filtering within the percolation zone (section 5.1.1); in contrast, high  $C_{\text{org}}$  contents in rocks stimulate microbial activities in the vadose zone: thus, geometries of the percolation zone are considered to be mostly unfavorable for dilution processes and an efficient microbial incubation, but favorable for any oxidation and slow kinetic sorption processes of solute matters.

From a flux point of view soils, the epi- and unsaturated zone

- determine quantitatively and qualitatively the discharge processes,
- produce different forms and reaches of subsurface run-off (section 3.5),
- influence together with the prevailing climate and morphologic conditions the physical, chemical and microbial weathering of sediments and the design of landscapes,
- have a high physical and chemical reaction potential, but very often low microbial reactivity,
- are responsible for the long-term stability of land surfaces and of constructions.

Hence, the vadose zone beneath soils has a specific regulation function for run-off generation and water quality, but often limited functions for natural attenuation processes.

In contrast to groundwater flow, percolation is generally directed perpendicular to bedding planes, along which significant changes in the hydraulic properties may occur. As a consequence, flow vectors undergo in the unsaturated zone much more reflections and refractions along beddings than in the groundwater zone. If significant changes in hydraulic conductivities also occurred along these interfaces, percolation may turn from vertical to lateral flow (section 3.5) or in a more advanced stage produces transient or permanent perched groundwater and thus contributes to the generation of different subsurface run-off components. Such interfaces may be of sedimentary origin and then mostly occur without any relation to present morphologies of a landscape. Others have been produced in the recent geologic past by weathering, rock dilatation, permafrost, aeolian sedimentation or originate from anthropogenic activities (section 3.5); all these interfaces parallel morphology.

The generation of run-off components throughout the unsaturated zone depends on

- the hydraulic functions, which change with seasons and even during infiltration events, and
- the geometry of the above-mentioned interfaces.

Hydraulic functions vary in space and time, because of seasonality of plant activity, soil cultivation and soil animal activities, and hence, produce together with changing capillarities and temperature/water interactions unstable sediment fabrics.

In the past, the unsaturated zone was mostly of individual interest for different disciplines (soil sciences, agriculture, soil mechanics and hydro-geology). Therefore, processes in it have predominantly been studied from singular scales, rather than in scale steps. This has improved in recent research efforts. Essential tools to achieve this change to a more integrated evaluation have been interdisciplinary



and combined investigations relating to different scales in one studied area; in this attempt, outstanding tools have been tracer methods and the transfer of tracer results to hydraulic parameters and mathematical models on flow and transport in the vadose zone. This combination of hydraulic, tracer and mathematical techniques enabled to

- cross-check results on water balances, flow and transport in the vadose zone through independent methods and thus to better adjust conceptual models,
- receive better quantitative results on homogeneity and heterogeneity of the studied unsaturated zone,
- better approach groundwater recharge and
- highlight the origin, genesis and the transport potential of run-off components for solute and particulate matter in the subsurface.

In general, surface run-off triggered by rain events is composed of an immediate, short-lasting (direct run-off; O-F and I-F in Fig. 4.3) and a delayed, long-lasting response (indirect run-off; B-F in Fig. 4.3); the latter prevents surface discharge from drying out over long periods of time.

Both direct and indirect run-off relate to reservoirs with small respectively significant storage capacities: slow discharge relates to flow velocities of less than meters per day or year, whereas quick discharge refers to flow velocities of meters per second or hour. These slow/rapid run-off components are commonly separated with hydrograph (Naterman, 1951) (section 4.1.2) or tracer techniques (Sklash & Farvolden, 1979) (section 4.4.2.3). A comparison of the results of both methods, however, makes evident that both are not equivalent, because

- the hydrograph method analyzes slow and quick run-off responses on rain events or direct (inter-flow and overland-flow) and indirect run-off (base-flow), and
- tracer methods refer to event and prevent tracer signals.

As inter-flow equals a chemical and isotopic mix of prevent and event water, tracer methods mostly overestimate the indirect run-off. The combination of both methodologies, however, allowed approaching a differentiation of the direct run-off into inter-flow and overland-flow (sections 4.1.2 and 5.1.2).

Both these methods of discharge analysis refer to intermediate scales of catchments and allow elaborating strategies to

- manipulate flow processes in the unsaturated zone,
- improve and protect natural attenuation functions of ecosystems and
- thus contribute to groundwater protection.

In humid temperate and tropical climates, groundwater recharge mostly happens through areal infiltration (section 3.3). In dry-lands, recharge occurs preferentially as line infiltration through river beds and as local infiltration through ponds. In all climates, most efficient recharge takes place through snow and ice melt of temperate glaciers (section 3.1).

The water balance in the unsaturated zone is triggered by infiltration and becomes modified by water storage and consumption and the role of hydraulic interfaces paralleling morphology. In this interaction, water storage close to the surface, e.g.

within the effective root zone (0.5–1.5 m b.g.s.), plays an important broker role. It refers (eq. 2.1) to (Fig. 3.2).

$$IN = (D_G + D_I) + \Delta S + (TP + EP) \quad (2.1)$$

As an average of the year,

- In humid temperate and tropical climates

$$D_G + D_I > TP + EP \quad (2.2)$$

$$\Delta S < IN$$

$$\theta_w \ll \theta \leq \theta_{fc}$$

- In semi-arid and arid climates

$$D_G + D_I < TP + EP \quad (2.3)$$

$$\Delta S \geq IN$$

$$\theta_w = \theta \ll \theta_{fc}$$

This classification is based on annual means and becomes modified by randomly high-intensity rains or by wet seasons of short duration in arid (dry-land) areas as well as by the way of land use.

- As compared with arable land, forests reduce groundwater recharge and inter-flow,
- Deforestation in semi-arid areas increases effective precipitation, thus enhancing infiltration, erosion and groundwater salinization,
- Constructed drainage pattern of urban areas can enhance or completely impede groundwater recharge,
- Any change of evergreen areas into arable land transforms the effective root zone from a reducing into an oxidizing chemical environment and enhances the mobility of nutrients (S, N, P, DOC) and heavy metals, which were both prior fixed on solid surfaces,
- Reduction of the water content may lead to shrinking of soils and sediments, with local (compaction) or regional (subsidence) consequences.

In cold climates (section 5.4), water in the unsaturated zone is frozen all or most of the years, thus forming permafrost conditions at mean annual temperatures of less than 0°C. Present permafrost covers an area of about 22,000,000 km<sup>2</sup> and occurs predominantly in the north-hemisphere between 60 and 90°, and all of this permafrost is a relict of ice ages.

During summer, permafrost may partly thaw (wet permafrost) or not (dry permafrost). Freezing of water in the unsaturated zone generates either a closed subsurface ice cover or results in the formation of ground-ice (ice pillows) with a respective drying out of soils around the ground-ice; under favorable conditions, the

formation of ground-ice becomes visible through structured soil surfaces and ice wedges.

In the subsurface, seasonal air temperature variations are smoothed progressively with depth (Fig. 3.16) and reach a mean annual subsurface temperature, which equals the mean annual air temperatures in 1 m above the ground plus 1 or 2°C; at the so-called neutral zone or depth, which is about 15–20 m b.g.s., this subsurface temperature has zero annual temperature variation. If minus temperatures reach beneath this depth, all percolation water will freeze on the way down and thus keep the permafrost ice cover closed all the year round. This mechanism in mind, it becomes difficult to generalize a water balance under permafrost conditions. Independent from any percolation, however, all permafrost areas produce most of or even all the year round a significant direct discharge, hence,

$$D_{\text{DIRECT}} \gg \text{IN}. \quad (2.4)$$

## 2.4. RECHARGEABLE AND FOSSIL GROUNDWATER AND WATER EXPLOITATION

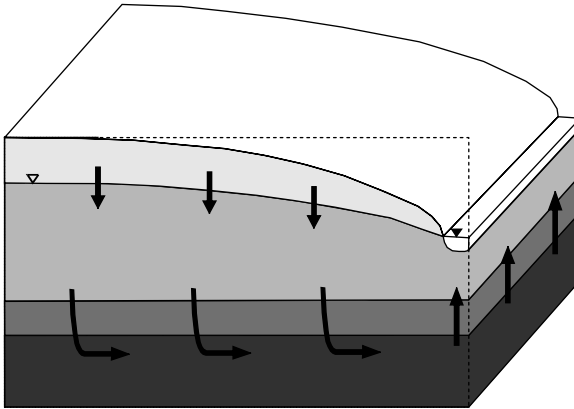
Groundwater recharge occurs in all climate zones, albeit at different rates;

- In desert regions there is little groundwater recharge (<5 mm/a), which occurs very irregularly (Verhagen et al., 1979),
- In semi-arid regions it is <50 mm/a and undergoes large annual fluctuations,
- In humid tropical regions <100 mm and again varies considerable by years,
- In humid temperate regions groundwater recharge is up to 300 mm/a.
- Recent investigations have shown that groundwater recharge occurs also through permafrost (Michel & Fritz, 1978), but at very low amounts.

Supposing that the measured continental discharge of 44,800 km<sup>3</sup> recharged groundwater resources homogeneously throughout the profile, then a minimum of mean residence time of 178 years would ensue (8,000,000 km<sup>3</sup>:44,800 km<sup>3</sup>); the smaller the recharge the longer was the mean residence time. This bulk calculation and assumption is in disagreement with all field observations on hydrochemistry, isotopes and the occurrence of pollution, in groundwater and thus indicate that flow in the subsurface cannot be homogeneous throughout the vertical profile.

Groundwater flows in aquifer systems, having particular hydraulic properties. In unconsolidated aquifers, the hydraulic conductivity and porosity generally decrease with depth; statistically, hydraulic conductivities of fissured rocks also decrease with depth. Therefore, groundwater recharge cannot be distributed equally among all aquifers; to investigate this assumption numerical modeling was performed (Fig. 2.8):

- With aquifer sequences of different hydraulic conductivities,
- A groundwater movement between an underground water divide (left in Fig. 2.8) and a stream, which collects all subsurface discharge (right in Fig. 2.8),
- Model dimensions of  $z = 400\text{m}$ ,  $x = 15,000\text{ m}$  and  $y = \infty\text{ m}$ , and
- A groundwater recharge over the entire catchment of 150 mm/year.



*Figure 2.8.* The modeling plane for representing the influence of hydraulic conductivity distributions in rocks upon the distribution of groundwater recharge with depth. A groundwater recharge of 150 mm/a and no underflow of the receiving stream was assumed. Depth of the model 400 m, length in flow direction 14,000 m, length perpendicular to flow direction infinite

Results of some hundreds of such numerical scenario simulations, representing well-known and typical geologic sequences, refer to

- Specific hydraulic conductivity/depth distributions (Figs. 2.9, 2.10 left column), and
- Lead to turnover quantities of groundwater in the individual layers in percent of groundwater recharge (Figs. 2.9, 2.10 right columns).

It turns out from this modeling exercise that generally more than 85% of the recharged groundwater discharges through near-surface layers (active groundwater recharge zone) and less than 15% of the groundwater recharge reaches deep-lying aquifers (passive groundwater recharge zone) (Seiler & Lindner, 1995). Related to this, groundwater in near-surface aquifers is young (<100 years) and in deep aquifers always old (>>100 years) (Fig. 2.10). Both of these zones have been found to occur worldwide in humid tropical, humid temperate and semi-arid climate zones. In dry and hyper-dry areas with extended catchments, groundwater recharge is often of a patchy type and, therefore, it becomes difficult to differentiate between the active and passive groundwater recharge zone (Fig. 2.11).

In semi-arid regions, the active groundwater recharge zone has a thickness of a few meters, in humid tropical climates the thickness is typically decameters, and in humid temperate climates up to 100 m; the thickness depends upon effective groundwater recharge and the storage and drainage properties of the aquifer system.

The groundwater within the active and passive groundwater recharge zones is always of meteoric origin. In the active groundwater recharge zone, hydraulic transient conditions do not play a significant role but in the passive groundwater recharge zone they often do, when this system is stressed by human, tectonic, or climate impacts.

The low flow velocities in the passive groundwater recharge zone (<10 m/year) result in slower leaching speeds than in the active groundwater recharge zone.

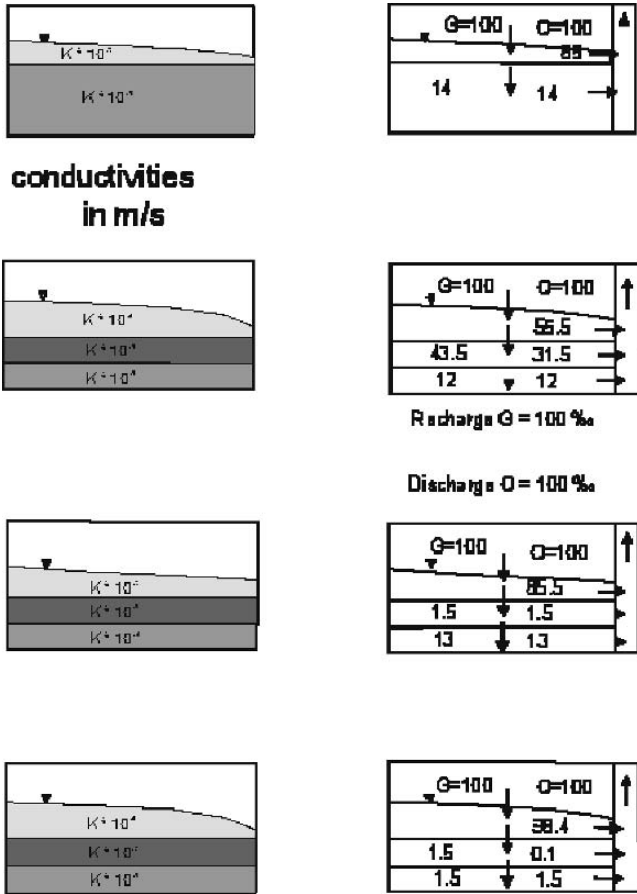


Figure 2.9. Selected examples of hydraulic conductivity series, as frequently occurring in nature (left columns) and the distribution of the groundwater recharge (in percent of infiltration) upon the individual layers. G = infiltration, Q = discharge to rivers

Therefore, the chemical composition and concentration of deep groundwater often differs from shallow groundwater (Richter & Lillich, 1975).

The interface between the active and passive groundwater recharge zone can be identified by very sudden changes:

- In water ages, hence, in the concentrations of  $^3\text{H}$ ,  $^{39}\text{Ar}$ ,  $^{14}\text{C}$  (Fig. 2.12), as well as
- The chemical composition of groundwater (Fig. 2.12).

Bearing these facts in mind, one can define the boundary between shallow and deep groundwater with the radioactive, environmental tracer  $^3\text{H}$  (section 4.4.2.2), which reaches subsurface water only through infiltration. A tritium naught line (TNL) can be defined below which the  $^3\text{H}$  concentrations have fallen to values under the usual, analytic detection limit (Seiler & Lindner, 1995) of  $\pm 0.7$  TU. Because

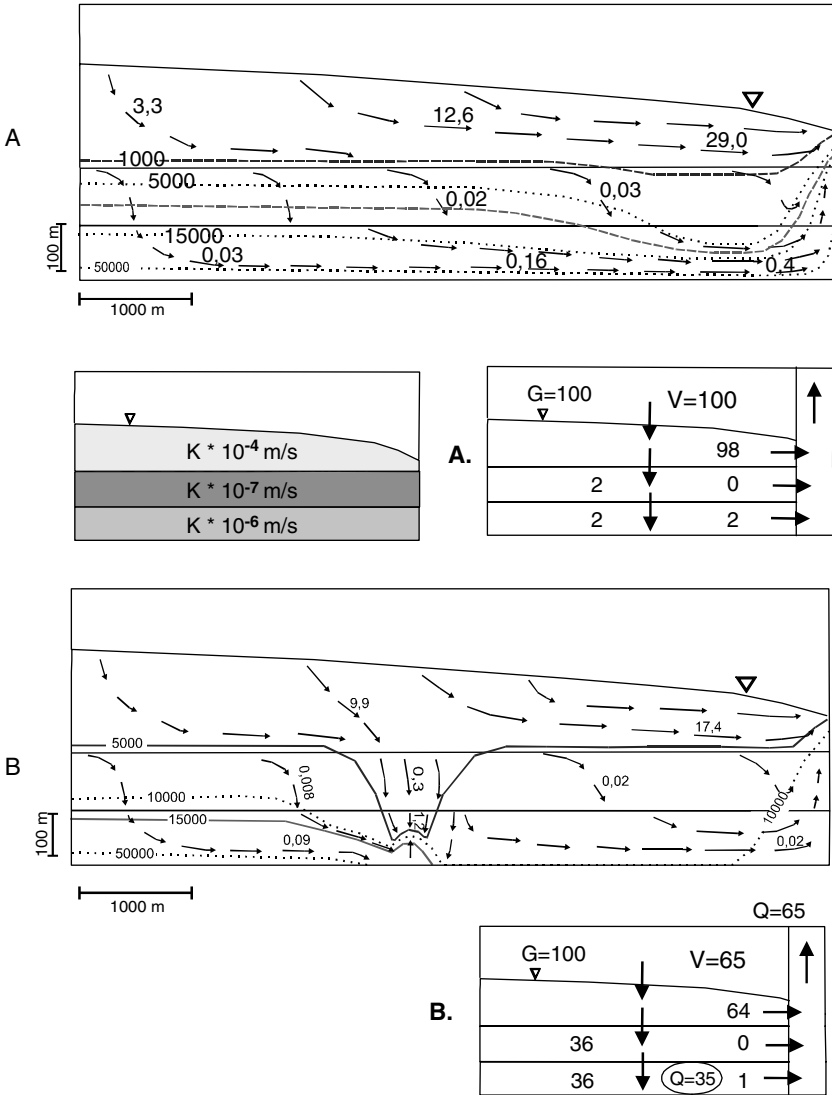


Figure 2.10. Flow lines (arrows), apparent flow velocities of the groundwater (m/day) and age distribution (years) in the groundwater (dotted lines) at a certain hydraulic conductivity distribution (m/s) in the aquifer systems. A. Without, B. with 35% of groundwater exploitation from the passive groundwater recharge zone

$^3\text{H}$  occurs worldwide in precipitation (Fig. 4.17), the TNL stands for about 50–100 years of water age, is based on a half-life of  $^3\text{H}$  of 12.34 years and the natural  $^3\text{H}$ -input. With this approach, groundwater of the active groundwater recharge zone stands for water younger than 100 years and deep groundwater for groundwater much older than this.

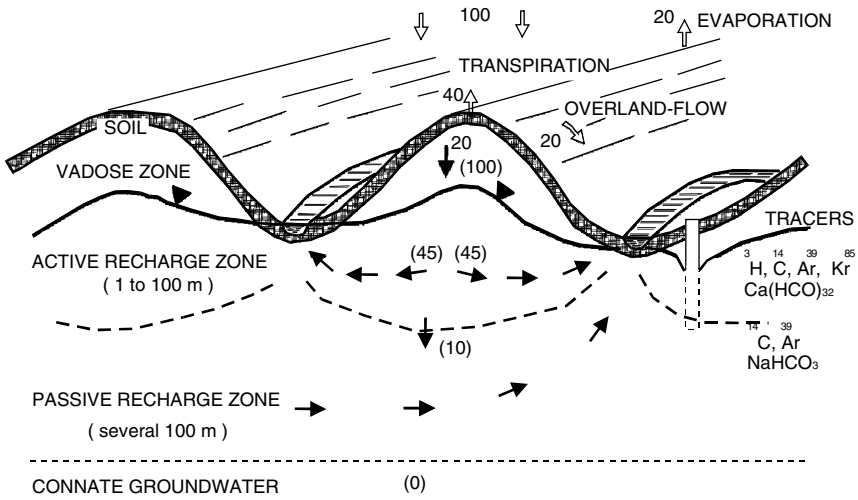


Figure 2.11. Subdivision of the aquifer systems in an active and passive groundwater recharge zone and connate groundwater; not to scale. 100 = 100% of precipitation, (100) = 100% of groundwater recharge

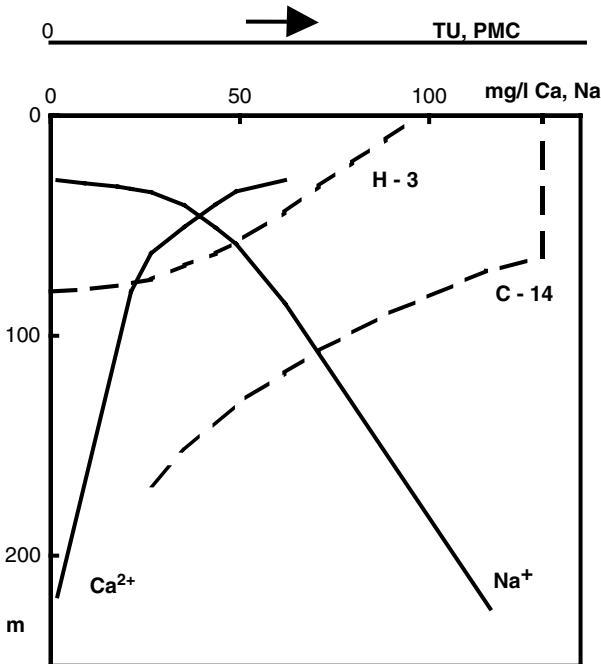


Figure 2.12. Changes in  $^3\text{H}$ -,  $^{14}\text{C}$ -,  $\text{Ca}^{2+}$ - and  $\text{Na}^+$ -concentrations with groundwater depth;  $^3\text{H}$ -concentrations in TU,  $^{14}\text{C}$  concentrations in PMC (modified after Egger, 1978)

As only a shallow portion of the continental groundwater is actively affected by the present recharge process, the majority of the groundwater belongs to a long-term reserve (Toth, 1963; Freeze & Witherspoon, 1967; Seiler & Lindner, 1995; Toth, 1995; Alvarado et al., 1996).

The passive groundwater recharge zone is usually several 100 m thick; below it, occurs the connate or formation water (Engelhardt, 1960) (Fig. 2.11), which is mostly of non-meteoric origin, generated with the origin of sediments and was since that time no more in contact with the biosphere. Connate groundwater can be found at shallow depth below desert areas and several hundred meters below ground in tropical and humid temperate areas. Hydrocarbon resources entrapped in special sediment structures are always associated with connate waters.

In contrast to shallow and deep groundwater, which are driven by gravity forces, flow of connate water is driven by sediment compaction, pressure changes because of tectonic deformations, thermal and geochemical convection, molecular diffusion, and osmotic processes. The interaction of connate waters with the rechargeable part of the hydrological cycle occurs by slow upward flow and mostly as an admixture to thermal and mineral springs in areas with tectonically deep-reaching dilatation elements like in the bordering zones of tectonic blocks, horsts and grabens; it manifests itself in salinization and temperature increase in fresh-water.

This recharge-related stratification of the subsurface water into an active, passive, and connate water zone dictates the susceptibility of subsurface water for contaminants, entering the system with the groundwater recharge. Pollution has

- easy access to the active groundwater recharge zone,
- little access to the passive groundwater recharge zone within sustainable intervals of time, and
- no access to connate water except by molecular diffusion.

As a consequence of the above considerations, which have been confirmed by field investigations (Andres & Egger, 1985; Seiler & Lindner, 1995; Alvarado et al., 1996; Ghergut et al., 2001; H. Raanan, Ben Gurion University – personal communication), effective groundwater recharge diminishes with depth. If this depth-related distribution of groundwater recharge is not considered in deep groundwater exploitation, then significant and on a long run transient changes in the groundwater flow field appear (Seiler & Lindner, 1995; Vrba & Verhagen, 2006).

The development of water supply in the last 150 years went from springs over shallow wells to deep wells (>100 m), penetrating into the passive groundwater recharge zone. Deepening of wells provides large dilution volumes but does not solve water pollution problems on a long run of time. On the contrary, missing groundwater protection measures will end after years or centuries in a discernible pollution situation of the passive groundwater recharge zone, according to the depths and quantities of exploitation (Ghergut et al., 2001).

As a consequence of these findings, drilling of wells should not only consider the hydraulic conductivities of aquifers but also recognize differences in the immediate groundwater availability within the active and passive groundwater recharge zone. Very often groundwater abstraction from the passive groundwater recharge zone



is not based on the low, depth-related groundwater recharge (<15%), but on the calculated all-over groundwater recharge for the entire catchment. The consequence of such groundwater exploitation from deep layers was also calculated in scenarios (Fig. 2.10). Thereby, it was shown that such exploitation would lead to hydraulic short cuts between the different aquifers, if the groundwater abstraction is higher than the aquifer or depth-related groundwater recharge; hence, the resulting groundwater deficit must be compensated (Einsele et al., 1987) by flux contributions from adjacent aquifers. This compensation process reaches equilibrium only after years to decades or centuries, thus keeping the hydrodynamic system for a long run of time under transient conditions.

In most desert areas of the world, former exorheic discharge systems from pluvial times changed to endorheic systems under present climate conditions. This transformation diminished the thickness of the active groundwater recharge zone and leads to a change from small to large catchment areas. Today, in many semiarid and arid zones, an overexploitation of groundwater resources overshadows the natural transformations of catchment sizes and extent.

## 2.5. THE PLACE OF RECHARGE IN THE WATER CYCLE

The earth crust is composed of 95 vol.% of crystalline and 5 vol.% of sedimentary rocks; in contrast, at the continental surface 75% sedimentary and 25% crystalline rocks crop out. As sediments favor groundwater recharge and storage much more than crystalline rocks, there is a pretty high average potential of infiltration on the continents.

As a golden rule in water management, the availability of water resources for human beings and ecosystems should not exceed the excess water (P-ET) in the continental water cycle, draining to oceans; in the special case of groundwater exploitation for water supply, it should not exceed the average groundwater recharge or unproductive water losses in dry-lands by evaporation. All continuous water use in excess of groundwater recharge or unproductive groundwater losses are called water mining or overexploitation and leads on a long run of time to

- a regional water table decline,
- ecological,
- soil fertility,
- hygienic and
- soil/rock mechanic problems.

To avoid groundwater mining, which is often met in dry-lands and urbanized areas, the following options exist:

- Store surface run-off,
- Enhance groundwater recharge by forced infiltration,
- Transfer water over long distances to water scarce areas,
- Desalinate ocean or brackish water, or
- Recycle treated gray water.

The latter two methods produce soluble wastes and are energy consuming. All these methods may locally contribute to changes of the

- Natural water storage in the subsurface and
- Water availability for ecosystem functions;

although many facets of the consequences of such actions are well known from special areas of the world (e.g., Punjab, Lake Maracaybo, China, India, and Mexico City), they have not yet been studied in an integrative way.

Both groundwater recharge and orographic, tectonic, and sea-level settings are driving forces of groundwater flow. However, there exists an outstanding difference between groundwater run-off in humid temperate/tropical and semi-arid/arid, permafrost climates:

- Areas with high groundwater recharge ( $>50$  mm/a) are essentially split into small-sized sub-catchments; natural discharge is mostly of the exorheic type and at steady-state;
- On the contrary, cold, semi-arid, and arid areas with low groundwater recharge ( $<50$  mm/a) have catchment areas of  $>1,000$  km<sup>2</sup>, which are not subdivided into sub-catchments and discharge often ends in terminal areas (endorheic discharge) and may have a high percentage of transient components.

Small recharge rates in dry and cold areas, however, sum up to high groundwater discharges at the outlet of extended catchment areas; to assess such discharges reliably, it is very important for dry-lands to elaborate a good estimate of groundwater recharge.

River discharge on continents does not always reflect the amount of present, average groundwater recharge; in most arid and some semi-arid areas, it often includes a transient component, dating back to groundwater recharge from historic ( $100 < t < 10,000$  years) or geologic times ( $>10,000$  years). Because only renewable water resources contribute on a long run of time to sustainability of health and life in ecosystems, it is important to determine the present and past recharge with high precision (section 4.1.2, 4.1.3, 4.2, 4.4.2, and 4.4.3) as well as on different scales and to assess these results with observed discharges of catchments.

Flow in the active recharge zone is slow in porous and to a specific percentage (60–70%) also in fissured and karst media. Apparent flow velocities are in the range of

- few centimeters to meters per year in the unsaturated zone (section 4.4.3),
- less than decameters per day in near surface groundwater (Fig. 2.10), and
- less than few meters per year in deep groundwater (Fig. 2.10).

Hence, they always produce in the subsurface a delay time before re-appearing at the surface. This delay time smoothens yearly variations of the intensity of groundwater recharge because of variations in precipitation and, to a minor extent, also to evapo-transpiration; this makes groundwater more continuously available for exploitation than the collection and surface storage of rain-fall, provided wells are appropriate positioned, constructed, and managed.

The delayed run-off of groundwater recharge enhances natural attenuation processes in the subsurface and thus contributes significantly to subsurface water quality.

- Surface run-off offers easy access to contaminants; it has an abundant biomass and bioactivity of all animal and plant sizes; here, phototropic processes dominate and oxygen is abundantly available for oxidation processes, because  $O_2$  can easily be replaced by gas exchanges between water surfaces and the air or becomes enhanced when surface flow turns from laminar into turbulent. However, in rivers, mean residence times (Table 2.1) are short and dilution is not strong because of a weak transverse dispersion.
- In contrast, ground- and percolation water have low biomasses and bioactivities by habitat reasons (small pore and fissure sizes), low water contents and flow velocities and hence, low potential nutrient exchange between water and biofilms. As the physical solubility of  $O_2$  in water is limited (about 10 mg/L at 10°C and decreasing with increasing temperature), chemotropic processes dominate in the subsurface. Furthermore, strong transverse dilution, high residence times, and the ratio of sediment surface/water volume favor in the subsurface metabolisation processes. Such attenuation processes are supposed to be quite efficient in the subsurface, but still are not yet well understood.

In between rivers and groundwater, lakes play an intermediate ecologic role. They are mostly interrelated with groundwater, are often simultaneously through-flown by rivers, and have a significant biomass and bioactivity coupled with long turnover times (Table 2.1).



## CHAPTER 3

### MECHANISMS AND PROCESSES OF RECHARGE

The groundwater recharge flux is the residuum of the infiltration flux after accounting for water storage, losses by evapo-transpiration and of inter-flow in the percolation zone; it enters groundwater through the capillary fringe and the groundwater table.

Precipitation, run-off, and evaporation are the main characteristics of the water cycle all over the world; on continents transpiration, surface and subsurface run-off as well as storage appear as additional elements. The transformation from the input (precipitation) to the output quantities (evapo-transpiration, overland-flow, inter-flow, and groundwater recharge) on continents is schematically shown in Fig. 3.1 and is detailed in the following paragraphs of this chapter. This scheme is a simplification of reality, because it represents only main processes and neglects all interferences, which modify real fluxes.

The transformation scheme in Fig. 3.1 has a special climate association shown by the broken, horizontal line. In arid and cold climates the run-off is characterized by quick discharge (direct run-off) and in semi-arid, humid tropical and temperate climates mostly by slow discharge (indirect run-off).

As precipitation falls to the ground and produces run-off, discharge passage through the terrestrial environment depends on

- Characteristics of the precipitation event, like specific rain amounts and durations,
- Properties of the atmosphere/biosphere/lithosphere interface,
- Size and antecedent moisture contents of the reservoirs, reached by precipitation.

All these factors affect the widely different residence time of the run-off components in the respective reservoirs.

Quality changes of water occur from the formation of precipitation in clouds to the outflow of a terrestrial reservoir. Main factors of these quality changes are

- rain-out, wash-out, and re-evaporation in the atmosphere,
- transformations at the interface atmosphere/lithosphere/biosphere by interception, evaporation, and biological processes and
- Water/rock interactions.

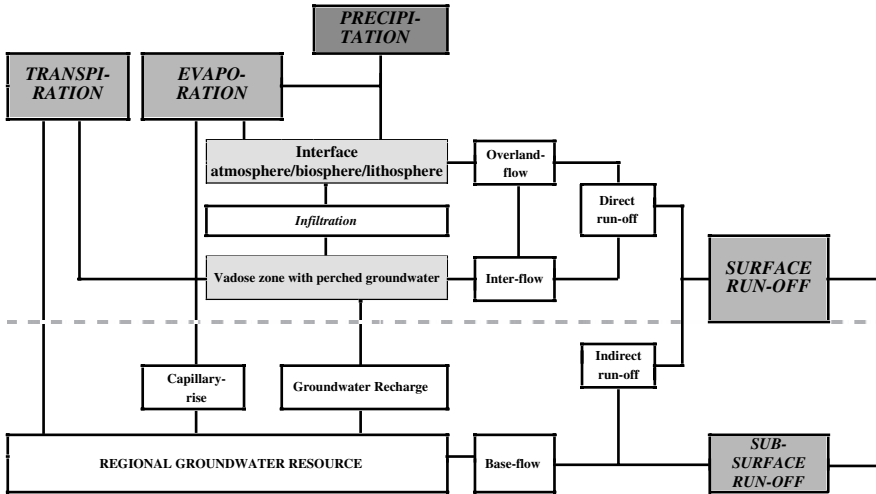


Figure 3.1. Transformations of the input (dark grey) to the output (medium grey) in the continental water cycle. Transformation paths above the broken line are dominant in arid and cold climates. Light grey: main transformation compartments

### 3.1. THE INPUT: PRECIPITATION AND SNOWMELT

The main input to the continental water cycle comes from rain (about 95%), followed by snow (about 4%) and the melting of glaciers. Compared to these components, the contribution of dew to the input is small, except perhaps during the transition periods in areas above the regional condensation altitude (section 3.2) or in desert regions under clear winter sky.

Precipitation is generated when warm and humid air masses

- slide up onto cold air masses as frontal or depressional precipitation,
- up-drift vertically, cooling adiabatically and condensing rapidly, forming heavy rain or hail (convective precipitation),
- ascend along high-altitude landscapes, thus cooling and forming the so-called advective or orographic precipitation.

During the fall of raindrops from the cloud base to the ground precipitation undergoes some evaporation, which under low air humidity conditions can result in the loss of all or most rain by evaporation. Such a process explains the occurrence of steppe vegetation of low-altitude valley floors in the midst of the Himalaya or the evaporative signature in the stable isotope composition of groundwater in North African deserts (Gonfiantini et al., 1974; Fontes et al., 1986; Guendouz et al., 2003).

Depressional or frontal rainfall occurs widespread and generally is of weak or medium intensity; orographic rainfalls are often medium in low altitudes and less intensive in high altitudes. In contrast, convective rainfall tends to be local, strong, and of short duration; it occurs frequently in tropical and arid (dry-land) zones, less frequent in other climates.

Rain events are classified according to their intensities as

- weak with  $<2.5$  mm/h,
- medium with 2.6–7.5 mm/h, and
- strong with  $>7.6$  mm/h.

Strong rain showers contribute often more to overland-flow than to infiltration; in contrast, medium and in particular weak but continuous rainfalls favor infiltration. During many rain events, rain intensities often change from weak at the beginning of the shower to medium in the middle, petering out to weak ones toward the end of the rain event. This is reflected in stable isotope (Fig. 4.25) and solute concentrations in rains.

Rain intensities, frequencies, and spatial distributions are rather variable in arid, semi-arid areas, and to some extent also in the tropics. They are less variable under polar, cold, and temperate climates; therefore, in tropical, arid, and semi-arid areas, it is more difficult than in other climates to quantify the yearly average hydrological input to determining mean regional groundwater recharge. One finds that in temperate and polar regions averaging of inputs can be made over a period of 10 years, whereas as much as 20 years may be necessary in arid, semi-arid, and tropical climates; hence, it is evident that the transformation of local precipitation data to the catchment scale is easier to perform in polar and temperate than in all other climates.

Precipitation has an uneven global distribution, depending on wind systems, transporting water vapor up and down through the atmosphere, and regional factors such as mountains, heating and cooling areas, influencing condensation of water vapor. High precipitation rates on continents occur only in humid temperate and tropical zones; in all other warm and cold climates precipitation is scarce.

Local enhanced fluxes or local changes in the roughness parameters of the land surface can increase the updraft of even relatively stable air masses, resulting in cloud formation and precipitation. The so-called urban heat-island effect is one such manifestation. Cloud seeding by industrial emissions is another way to change precipitation locally.

Usually, precipitation is measured at a given point by rain samplers and in special cases in an integrated form over large areas by means of calibrated weather radar. The precision of such radar measurements for rain and snow is at best 15%.

In arid, semi-arid, and tropical climates as well as in areas characterized by high relief energy, lots of measurement points are needed to evaluate the temporal and areal variability of the precipitation cluster and thus to get a representative catchment input from local measurements.

To transfer point precipitation measurements into the catchment scale, a net of precipitation samplers of the same recipient surface (mostly 200 cm<sup>2</sup>) and installation mode (1 m above floor in a homogeneous open aerodynamic field) are imperative. From an orographic point of view, it can be stated that

- if a sufficient number of precipitation samplers exists in hilly catchments, the arithmetic mean of all measurements can be considered as representative,
- if the number of samplers is limited, the polygon method is practiced (Thiessen, 1911; Horton, 1923), and

- if the catchment is mountainous, the isohyet integration method applies (UNESCO-WMO, 1977).

Rains of less than 4 mm/day are mostly completely absorbed by dry biologic and soil/sediment receptors. Rains exceeding 4 mm/day generally contribute to a discharge response in rivers and creeks, but no overall proportionality exists between inputs and outputs. For example, it has been reported from temperate climates that summer rains produce higher discharge peaks with short discharge duration than winter rains do (section 4.12).

All observations on non-linearity and low correlation coefficients in rain/discharge approaches can be related to the preconditioned hydraulic properties of the receptor surfaces and intrinsic sediment fabrics:

- Dry surfaces oppose matrix infiltration and favor overland and preferential flow, because of high surface tensions, which, however disappear after a sufficient wetting of the solid surfaces.
- Soil/sediment surfaces are often reduced in infiltration capacities by capillary compaction or shrinking, fine dust, chemical and microbial crusts, which must first be widened, respectively removed, to enhance infiltration.

Thus, infiltration varies often in space and time during one single rain event.

All these transient influences make the detailed input/output analysis difficult; the averaged long-term behavior of discharge systems can be well approached with bulk assumptions and the short behavior with stochastic tools.

In humid areas the top soil is wet most of the year, in arid (dry-land) areas it is bone dry, because of intensive evaporation over a long run of time. The depth to which the evaporation reaches down depends on the pore size distribution and the time span lapsed since last wetting; the evaporating front or wet/dry interface (Fig. 4.30) descends at rates of  $<0.2$  m/day under dry and less under humid climates. In sand dunes of hyper-arid areas desiccation depth can reach down some meters, in clays without shrinking cracks some decimeters and with shrinking cracks some meters down too. Drying of soils/sediments by evaporation is significantly enhanced by the transpiration activity of plants (Table 3.1). One percent of water taken up by plant roots are incorporated by plant cells, 99% pass through the plant and evade to the atmosphere. One hectare of growing vegetation can transpire as much as 90,000 L/day or 9 mm/day

On continents, snow and glaciers constitute extended reservoirs (Kotlyakov, 1997), which undergo only little sublimation losses at temperatures below the melting point. Snowmelt depends ultimately on the radiation balance of the cover itself or on heat gains and losses. The snow cover acts as an isolation during both the cold and snowmelt season and also acts as a mixing reservoir, because the out-melt follows a process of repeated melting and freezing within the same snow cover. Thus, any snow cover keeps infiltration capacities high and slows down infiltration velocities.

According to low or high altitudes and the increasing horizontal and vertical warming of the atmosphere from the cold to the warm season snowmelt discharge appears with a short or long delay time a year. As mountain areas with snow



Table 3.1. Transpiration of plants in liters to produce 1kg of dry mass

Plant	L/kg dry mass
Oak	340
Birch	320
Spruce	300
Larch	260
Pine	230
Beech	170
Douglas fir	170
Soja	>700
Pumpkien	>700
Pea, beans	700
Rice	680
Potatoes	640
Rye	630
Sunflower	600
Wheat	540
Barley	520
Millet	250

and glaciers are presently the most important water towers of continents, they are important components for the groundwater recharge in the non-rainy or high-evaporation period of the year. A compilation of altitudes on earth is shown in Fig. 3.2.

Diminished by water retention on receptors and storage in the subsurface, rain events generate much direct run-off; in contrast, melting snow covers contribute preferentially to indirect run-off. Furthermore, snow covers act as a filter for air pollution, thus creating a contamination source for groundwater (section 3.2), which can lead to acid spills in spring times, when rain and snowmelt occur simultaneously.

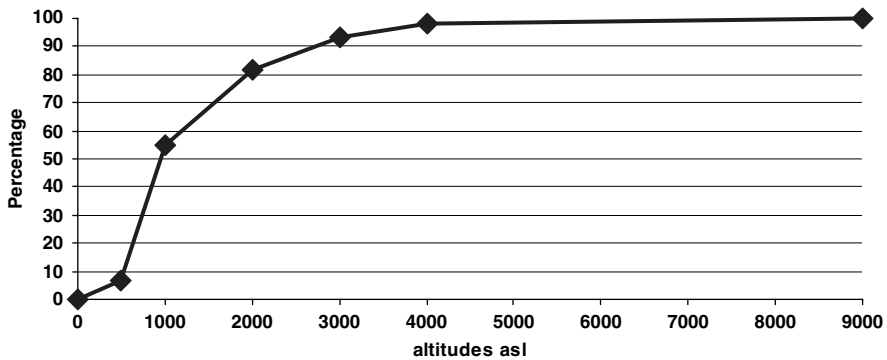


Figure 3.2. Summed up altitudes on continents

Melting of glaciers and snow produces a temperature-driven discharge, delaying winter discharge according to the altitude of the snow and ice cover; therefore, mountain areas often act as natural water reservoirs, favoring the availability of water in the dry or ET-excess season. Mountain discharges play an important role for groundwater recharge in about 80% of all semi-arid and arid areas (e.g., Punjab, North Africa, west coast of the Americas, and many Inner Asian deserts) and in about 45% of all humid areas of the world; all the big rivers of the world receive more or less significant amounts of this temperature governed run-off. The delay and time span of mountain water run-off, contributing to the foreland, depends on the amount of snow, extent of glaciers, the altitude range of the mountains, and the potential of river bed infiltration within the mountain area and its immediate foreland; discharge delay of winter precipitation may last from beginning of spring till the early summer (Fig. 3.3).

During low groundwater recharge seasons, temperature-driven discharges enhance river fan and river-infiltration respectively point and linear groundwater recharge. The river discharge during the dry season can also be used favorably to increase groundwater recharge by forced river-infiltration or artificial water ponding.

In continuous discharge registrations, snowmelt produces close to the melting source

- a regular daily up and down of discharge with a time shift related to the mean flow velocity of water and the distance of the gauge station from the melting snow plot, and
- daily amplitudes according to the duration and intensity of solar insolation to the snow cover.

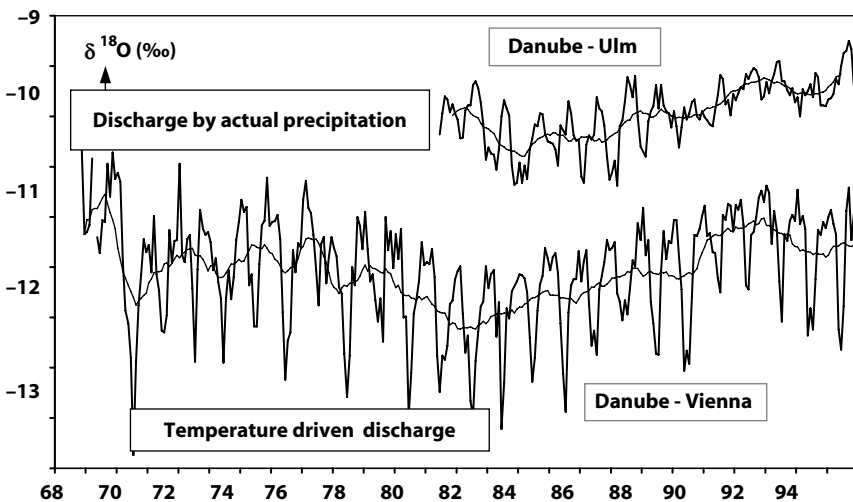


Figure 3.3. Time series of  $\delta^{18}\text{O}$  for the Danube at Ulm (upper reach without the influence of Alpine discharges) and Vienna (central reach with an Alpine discharge influence) and trend curves for  $\delta^{18}\text{O}$ , calculated using 12-month moving average (Rank et al., 1998)

Because the input function of natural tracers into discharge is less variable from melting snow covers than from rain events and because discharge is proportional to the melt intensity, the tracer input signal of snowmelt has often been used for tracer-based discharge and recharge analysis (section 4.4.2.3).

During the second half of the 20th century, many dams have been constructed world wide to govern the discharge characteristic of individual catchment areas according to the local water demand in the low reach of the dam; today about one-third of continental discharge (about 15,000 km<sup>3</sup>) is regulated by dams. Water stored by dams suffers 3–4 times more evaporation than water stored in snow and glaciers; therefore, melting snow and glaciers are from efficiency, not from a management point of view, so valuable for water availability in water-scarce areas. However, the more glacier melt intervenes, the less the present discharge process reflects the present precipitation-discharge balance, because ice masses of temperate glaciers are several hundred and ice masses of cold glaciers even many thousand years old; as compared to these ages, traditional water balances refer only to input–output relations of at least 10–30 years.

### **3.2. WET AND DRY DEPOSITION AT THE INTERFACE ATMOSPHERE/LITHOSPHERE/BIOSPHERE**

The role of plants for groundwater recharge is important from a quantity (Table 3.1) and quality point of view (this chapter).

- Plants influence the albedo, hence, ET through the heat balance. Forests have a lower reflectivity of solar radiation (albedo) than grass lands; it has been reported that grass lands reflect 26%, oak woods 15%, and pine forests 10–15% of incident radiation. The lower the albedo the higher is the energy available for evaporation.
- Both the roughness of the canopy surface and the leaf area index (LAI) influence
  - the stored amount of precipitation by interception, which re-evaporates, hence, reduces effective precipitation for infiltration,
  - the deposition of air moisture on plant surfaces, which can precondition canopy discharge, and
  - favors the deposition of chemicals, which remain as residuals of evaporation or which sediment from fall-out on receptors and later become leached by rains.
- Plant metabolism makes plant surfaces, especially leaves, to sink and source areas of chemicals. Plants take transpiration water in humid and semi-arid areas from the effective root zone (0.5–1.5 m b.g.s.), in desert areas typically from 4 to 6 m b.g.s. and most trees are deeper rooted than other forms of vegetation, hence, transpire much more percolation water than shallow rooting plants do.
- Forests decrease much more than crops stream peak flow, the discharge volume as well as the amount of infiltration, because of the higher specific receptor surface than crops.

Thus, plant covers trigger the heat balance, increase or decrease discharge (Table 3.2), retard run-off, and diminish the energy impact of rain drops on

Table 3.2. Annual means of discharge and evapo-transpiration from a forested and deforested area in mid-latitudes (Baumgartner & Reichel, 1975)

	Forested	Deforested
Precipitation	100	100
Evapotranspiration	52	42
Discharge	48	58
Evapotranspiration	100	100
Surface evaporation	29	62
Interception evaporation	26	15
Transpiration	45	23

All data in percent of precipitation (upper three lines), respectively of evapo-transpiration (lower four lines).

soils/sediments, so reducing the erosion potential of direct run-off, especially overland flow. From these facts, it becomes very clear that land use impacts significantly run-off processes.

There was a debate as to how much forests increase the amount of precipitation. Although forest may affect precipitation distribution, there is no clear evidence that they alter the total amount of precipitation in a region. There exists, however, a substantial increase of precipitation in forests by fog drip in areas above the regional condensation level. In Central Europe, this condensation level rises from the coast to the continental interior from about 500 m a.s.l. to more than 700 m a.s.l. and areas with a regional condensation level above 700 m a.s.l. may receive at an altitude of 900 m a.s.l. in summer 8% and in fall even 30% of dew as compared with the open area precipitation (Grunow, 1965).

In some areas of the world the replacement of the native tree vegetation by pasture, crop land (e.g., Australia, South Africa, and North America) or bare land (Mediterranean areas) increased groundwater recharge by one to two orders of magnitude and simultaneously enhanced both water (e.g., Mediterranean) and wind erosion (e.g., Middle West of North America). Because of the low percolation velocities (section 3.4), such changes have often been noticed late, hence, initiation of appropriate protection and remediation measures started too late.

The interface atmosphere/lithosphere/biosphere plays an important role on water, particulate as well as solute matter fluxes; here, the atmospheric input becomes

- selectively distributed on separated surface and subsurface pathways (Fig. 3.1),
- retarded and stored,
- The signals of isotopes of the water molecule get sometimes lost by total evaporation of intercepted water,
- Chemical enrichment of solute matter by evaporation is typical, and
- Chemical reactions occur along this interface.

Thus, after the atmospheric pathway of precipitation (section 3.1), discharge is labeled at this interface with specific chemical, isotope, and microbial fingerprints.

With day/night, seasonal cycles, and plant growth, the intensity of the interaction between plants and the atmosphere has a pronounced seasonal character. The larger the specific surface of the plant cover, the stronger is this transformation process and seasonality.

The transformation process at the atmosphere/lithosphere interface on water and matter fluxes is significant, but not as pronounced as on plant surfaces; however, more important are water/rock interactions in the subsurface, the intensity of which is depending on

- the reactivity of the water,
- pedologic, mineral, and physical properties of soils and sediments,
- the seasonality of climates,
- land use,
- the activities of plants, soil animals and micro-organism, and
- the thickness of the root zone.

The total wet and dry, air-borne input to the atmosphere/biosphere/lithosphere interface is called total deposition, which subdivides into the liquid/solid/solute matter deposition by precipitation and interception (Fig. 3.4).

Emissions from

- combustion of hydrocarbons and coal,
- the intensification of land use (native or crop vegetation, fallow and vegetation periods, urbanization, resource exploitation and traffic), and
- industry

underlie seasonality, and as emissions increased during the past 50 years significantly, qualities of precipitation and interception changed with seasons and increased during all industrial time. Therefore, today's water qualities and quantities of discharge differ from geogenic. This is expected to change further, if the existing prognoses on climate and land-use changes are taken into account.

Plants make the atmospheric input to the lithosphere acceptor-dependent. These acceptors may act constantly throughout the year (e.g., evergreen plants) or are seasonally different according to the biorhythm and the plant development during

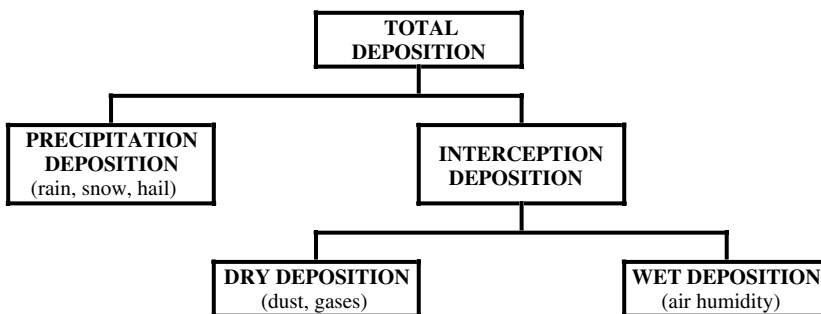


Figure 3.4. Different forms of atmospheric depositions at the interface atmosphere/lithosphere/biosphere

the vegetation period (e.g., leaf, needle trees, or crops). Through these influencing factors different interception efficiencies result, depending on

- the specific physical and geometric properties of the acceptors,
- the orientation of the vegetation acceptors to weather trajectories (wind-side, lee-side), and
- the altitude, in which they interact with the atmosphere.

Among all plant covers, evergreen pine forests develop the highest specific surface and therefore, the year around dry and wet depositions from the atmosphere are stronger in here than in fallow or agricultural crop areas. This led to the statement that forests act as the lungs of nature.

The air contains aerosols, particles, gases, and solute matter, which deposit on interceptors by fall-out and rain/washout. As a rule, rain/wash-out concentrations reach 10–1% of the respective concentrations in the air. The true chemical air composition precipitates with the interception of dew and accumulates in snow and rime covers on plants as well as on wet and rough barks by sorption and evaporation to a level, which may even exceed concentrations in the air.

Interception in forests of temperate climates reduces precipitation to about 70 and 80% of open air precipitation (Fig. 3.5), for crop areas no reliable data are known; it is greatest at the beginning of rain events and slows down according to a decreasing interception capacity of the vegetation cover.

Plant-stand precipitation consists of

- through-falling precipitation,
- canopy discharge, and
- stem flow.

In forests

- through-fall rain amounts to less than 50–60% of the open area precipitation,
- interception of precipitation may reduce the open area precipitation by about 25% in tropical rain forests, by 14–20% in deciduous and coniferous forests, respectively, in the Appalachians (Kendall, 1993), by 25% in spruce forests of Central Europe.

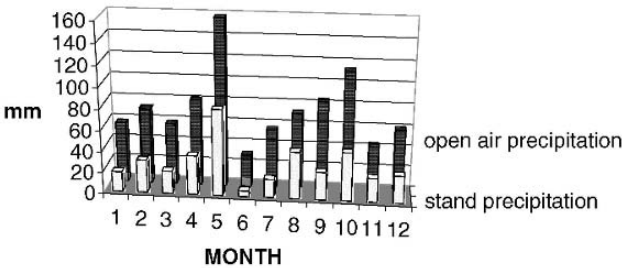


Figure 3.5. Monthly open area (prairie, black columns) and stand precipitation (pine forest, white columns) in the Bavarian forest. Months beginning with November and ending with October

- Stem flow from leaf trees is smaller in the summer than in the winter season and achieves an average of 15–25% of open area precipitation; for pines it amounts all the year around to only 5% of open area precipitation.

In some areas of the world, re-evaporation through forests allows air humidity to migrate deep into the continent. Villa Nova et al. (1976) showed for the Amazon area that about one-half of the precipitation originates there from ET of the jungle; hence, the Atlantic weather fronts reach also the north of Argentina; this has been confirmed by isotope studies from Salati et al. (1979). Deforestation of the Amazon area would significantly change this present rain-fall cluster

- by a decrease of TP and
- a moisture reduction down-wind the present weather trajectory, which would not satisfy any more the water demand of the jungle in remote areas from the ocean.

The wet interception deposition is favored by the exposition and by the transition from laminar to turbulent airflow, which occurs mostly along the canopy. As an example, the wet deposition at the wind-side of a forest yields about 3 times more dew than within the tree-stand or at the lee-side.

Wiedey & Gehrmann (1985) report that in north Germany the acid and heavy metal deposition ( $H^+$ ,  $NH_4^+$ ,  $Al^{3+}$ ,  $Fe^{3+}$ ,  $Mn^{2+}$ ) on the wind-side of a tree stand was 3.23 kmol/(ha year), on the lee-side 1.88 kmol/(ha year), and in the open area only 0.65 kmol/(ha year). As shown by Georgii et al. (1984) the pH in fog, dew, and rime may carry 10 times more protons than precipitation does. Furthermore, wet and rough biologic and geologic surfaces and the snow cover favor the retention of protons, thus increasing the chemical reactivity of water before infiltrating into the lithosphere.

The acceptors also contribute by dry/wet interception in eliminating from air masses the acids of carbon, sulfur and nitrogen, and of heavy metals, all from the combustion of organics, and in forwarding it with the canopy and stem discharge to soils and sediments. In Central Europe, in 1982, the acid deposition had increased 100 times and the heavy metal deposition 10 times the normal value (Ulrich & Matzner, 1982/1983). As a consequence, the pH in precipitation declined to 4.1 [0.8 kg protons/(ha year)] as compared with pH of 5.6–6.5 in pre-industrial precipitation (Schnoor et al. 1983). With the longitudinal and transverse distance from Central Europe, a main emission center of acids, the pH in precipitation increases presently to 5 in north Scandinavia.

Soil moisture measurement from MPI in Hannover (Prof. C. Blumenberg) in the Negev (Table 3.3) showed that daily wetting and drying in a bare loess, resulting from water condensation respectively evaporation, reached a depth of about 20 mm; beneath this depth the water content kept constant at 2.3 vol.%. Moisture variations at the soil surface went from 2 vol.% in the evening (18 00 h) to 4.4 vol.% in the early morning (06 00 h).

In general, the intensity of dew formation per year depends on the

- orographic elevation,
- exposition of plant receptors to air mass trajectories,
- density, roughness, and size of the receptors,

Table 3.3. Soil moisture, generated by dew during 1800 h and 600 h in bare loess of the Negev in 0 to 20 mm below the surface (measured by Prof. Dr. C. Blumberg, MPI, Hannover)

September 1978	11./12.	12./13.	13./14.	14./15.	15./16.	16./17.	17./18.
mm/night of condensation	0.077	0.048	0.068	–	0.079	0.1	0.085

- the extent of day/night temperature variations and
- the throughput of air masses at the interceptors, as well as
- the distance from the wet source.

Dew in arid to semi-arid areas is important for the survival of ecosystems; its supply is mostly regular although small and more pronounced in spring and autumn (the transient seasons) than in summer and winter. It acts as a water source for soil animals, plants, and biological crusts (Waisel, 1958; Broza 1979). In humid temperate and tropical climates, it may be a precondition for or even increase groundwater recharge.

It was also found that desert-seeding distribution was greatest close to stones, and it is supposed that stones act both as a dew collector and funnel for dew formation. In the Gobi desert, it can be seen that on the lee-side of lakes there is less sporadic vegetation on the hills than on the wind-side.

Arid and semi-arid sediment surfaces are often covered by biotic crusts composed of cyan bacteria, mosses, lichens, and algae (Lange et al., 1992). This crust formation and conservation depends on rain and dew; it stabilizes sand dunes (Danin et al., 1989), forms a nutrient base for soil animals (e.g., snails), inhibits evaporation, but also reduces the initial infiltration capacity. It seems that river sediments in arid (dry-land) areas have less-permeable crusts than aeolian sediments; hence, rain infiltration in dunes was more efficient than in river sediments. These differences in the crust formation may be attributed to the pore size distribution and the natural water contents of both types of sediments; river sediments achieve higher natural water contents than sand dunes and thus favor the crust formation. Therefore, one observes after rain events in arid (dry-land) zones much more water ponding in areas with river sediments than in dune areas.

In low altitudes (see below) of the humid temperate zones, dew contributes to the plant and lithosphere surface by about 0.05–0.3 mm/day during cold summer and more during cold winter nights, when rime forms; in mid-Europe dew formation accounts to about 30 mm/year and in tropical West Africa dew formation of 3 mm/night is known. Dew formation in hyper-arid areas accounts to 10–30 mm/year (Evenari et al., 1971; Shiklomanov et al., 2004). However, most of this dew is re-evaporated next day, only little reaches the root zone of plants, which are specially adapted to this mode of water supply.

The plant surface acts not only as a receptor but also as a sink and source for matter fluxes.

- Source elements are  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Fe^{3+}$ ,  $NO_3^-$ , and  $SO_4^{2-}$  from altering leaves, the metabolism of micro-organisms on the plant surface, and the residuals from



evaporation, which all influence the chemical concentration of stem and canopy discharge and may increase the solute matter fluxes to the lithosphere by about 3–5% as compared with regular precipitation.

- The plant surface also acts as a sink for nitrogen and protons by exchange of  $H^+$  against  $Ca^{2+}$  or  $Mg^{2+}$  and the uptake of nitrogen by leaves; this proton buffering may reduce the acid input during the vegetation period by about 70 and 50% in pine and oak/beech forests, respectively (Horntvedt et al., 1980; Greenfelt & Hultberg, 1985; Ulrich & Büttner, 1985) and varies with the biorhythm of plants. Wiedey and Gehrman (1985) found that during summer in beech forests the pH of the effective precipitation beneath the plant cover was 5.2 as compared with 4.3 above it, and in pine forests it was 6.0 beneath the plant cover as compared with 5 above the canopy.

The interface atmosphere/lithosphere contributes only little to water qualities by interception, however significantly to the generation of run-off components, because of infiltration capacities, which divert water fluxes into a quickly moving branch (overland-flow) with random liquid/solid and liquid/liquid interactions and a slowly moving branch (groundwater recharge) with long reaction times respectively a close contact of the water with the soil/sediment surface. An intermediate behavior has the inter-flow, moving quickly and having some liquid/liquid but usually little liquid/solid contacts.

A very pronounced effect on groundwater recharge is executed by plant roots. Phreatophytes as well as deep-rooting plants consume a lot of water from the unsaturated zone through transpiration, which may reach from normal to abundant and is then also called luxury consumption. A very good example of the role of water consumption by plants is known from Tunisia. According to the decreasing amounts of precipitation from North to South Tunisia, the distance of the olive trees increases. This is known since ancient times and respects the fact that increasing aridity reduces infiltration, hence, subsurface water storage per unit area is available for olive trees. Similar in Australia, native forests have been cut down to increase the area of crop-lands; as these forest trees were deep-rooting and have been replaced by shallow rooting plants, water consumption from the percolation zone decreased and groundwater recharge increased respectively, resulting in groundwater logging. As forests keep evaporation from soil/sediment surfaces lower than crops, also salinization in the unsaturated zone increased, thus enhanced groundwater salinization. It is also known that trees may harm constructions by root growth or by extracting too much water from the unsaturated zone, which causes shrinking of fine grained clay/silt sediments and thus damages to constructions.

### 3.3. OVERLAND-FLOW AND INFILTRATION

There exists a relation between precipitation and run-off; however, the explicit focus of run-off generation to precipitation was an oversimplification. Many factors redistribute precipitation before hitting run-off; among these

- kind, duration and intensity of precipitation,
  - pre-event climate,
  - land use (Fig. 3.6),
  - types of sediments and soils, and
  - topography
- play important roles.

The surface discharge in a river (Fig. 4.3) comprises the sum-total of various discharge components; under natural conditions the river run-off consists of one or all of the following

- Groundwater run-off discharging into the river, also called base-flow,
- Inter-flow,
- Overland-flow.

Inter-flow and overland-flow are often named direct run-off, because they appear as an immediate response to precipitation events, hence, reach the river with a minimum delay. In contrast, groundwater run-off is often named indirect run-off, because it appears with a considerable delay time, thus smoothing out the episodic nature of precipitation inputs and constitutes the base-flow in river discharge; it prevents most rivers in humid and some rivers in semi-arid areas from drying out during extended rainless periods.

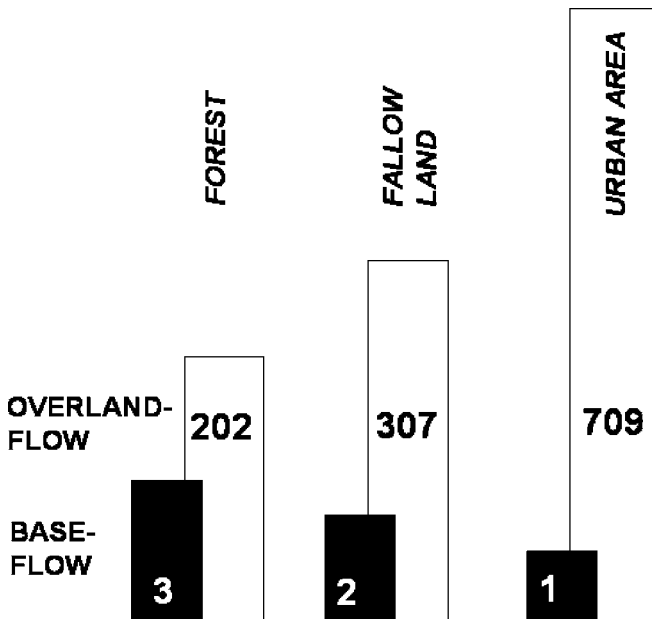


Figure 3.6. The role of land use for flood and base-flow (Geiger, 2004). Generalized for the Ruhr area in Germany

Surface discharge as a direct or indirect response to present rain events plays a very different role in arid and humid areas;

- In arid (dry-land) areas overland-flow is a dominant run-off component, recharging groundwater along the river course and through ponds; long ago it has been pointed out by Schoeller (1959) that floods are the preferential mechanism of groundwater recharge in the arid North Africa, which has since been evidenced by the evaporation signature of stable water isotopes of groundwater (section 3.1) for many arid areas.
- Under humid climates, rain preferentially infiltrates areal, hence, reducing overland-flow and increasing subsurface flow.

Overland-flow is generated by precipitation, ice, or snowmelt in excess of infiltration capacities of sediments/soils; it does not enter the subsurface and discharges immediately along hill slopes to a river. According to this definition, overland-flow is missing in flatlands; hence, water in excess of infiltration capacity contributes in flat lands to ponding and enhances both infiltration, transpiration, and evaporation.

Forests diminish overland-flow more than crop- and bare-lands or different forms of constructed surfaces (Table 3.4). Supposing the same type of sediments/soils, it turns out that corn crops favor overland flow more than wheat or potatoes crops and overland-flow in hilly crop-lands increases with field sizes and land cultivation. Large-sized fields favor the formation of overland-flow more than small fields and straight row-ploughed fields more than contour-ploughed fields.

Both overland-flow and inter-flow contribute to areal soil/sediment erosion and, therefore, may also be named erosive discharge in hilly terrains.

Overland flow is mostly calculated using the CN method (US Soil Conservation Service, 1975; Kleeberg & Overland, 1989). This empirical method has been gained by the statistical analysis of discharge events in bare- and agro-lands in the USA, refers to precipitation and present/potential infiltration, and became a standard method.

Infiltration is the process of transition of precipitation or surface water into the subsurface; hence, it describes the process of how infiltration influences the dimensions of fluxes and storage in the percolation zone.

*Table 3.4.* Overland-flow ratios as compared to total discharge in urban areas

Substrate	Overland-Flow ratio
Roofs, cement, bitumen and pavement	0.90
Boulder pavement, asphalt and macadam pavement	0.60
Graded macadam pavement	0.45
Dry-brick and macadam pavement	0.40
Non-lining pavement	0.30
Parks or greenbelts	0.15

Infiltration may happen locally through ponds, lineal along river courses, or areally distributed in landscapes. In all topographies, local and lineal infiltration triggers a two- or three-dimensional percolation flow; in contrast, areal infiltration produces in flat areas always and in hilly areas often a one-dimensional, vertical percolation.

Infiltration interfaces with very high or very low water contents favor the generation of overland-flow much more than soil water contents in between. Whereas the overland-flow in wet climates results from an excess of moisture along the infiltration interface, in arid (dry-land) areas it becomes a skin effect, because the extreme dry surfaces with high surface tensions and biotic and non-biotic crusts force rain drops at the beginning of discharge events into lateral instead of vertical directions.

The process of infiltration can be quantified by a short term or a cumulative infiltration rate and is limited by the infiltration capacity of the subsurface, increasing often with the rain duration. According to soil/sediment fabrics and the topographic conditions, infiltration capacity is higher

- in coarse-grained than in fine-grained soils/sediments,
- in dune than in river sediments,
- in karst than in fissured rocks, and
- in flat lands than in hilly areas.

In riverbeds and ponds and especially under arid climates this ranking is often modified by biotic and abiotic crusts, which both reduce the initial infiltration capacity. The absence of a vegetation cover favors crust formation; in contrast, any vegetation cover maintains hydraulic properties favorable for infiltration into the subsurface, however also reduces the amount of effective rain reaching the ground.

Similar to percolation, infiltration is governed by the physical interaction between capillarity, gravity, and the geometry of the water source; additionally, a series of processes and boundary conditions intervene in infiltration related to precipitation, specific properties of the interface atmosphere/lithosphere/biosphere, as well as to fabrics and mineralogy of soils/sediments and hydraulic functions, respectively, to the water content before infiltration (Gardner, 1967).

Following a specific wetness of the infiltration interface in humid areas, any excess water can infiltrate in much larger amounts than previous, hence, fills up the pores in the unsaturated matrix and moves vertical down; however, infiltration and infiltration capacity (Horton, 1933) are not constant with the change of the seasons and not even during a single rain event.

- During the seasons they depend on
  - soil cultivation and silting,
  - the activity of soil organisms and plants in the active root zone,
- During single rain events they depend on
  - topography,
  - plant cover and plant development,
  - swelling of clay minerals,
  - the detention of capillary forces,

- the dissolution of crusts,
- air, entrapped in pores,
- the stability of soil aggregates, and
- the speed of all these changes as compared with rain intensities.

With all these influences

- A catchment area exhibits in time and space quite different responses to infiltration the year around; therefore, reported numbers on discharge and evapo-transpiration always refer to an average behavior of a landscape.
- The mode of generation of overland-flow and infiltration has a climate association:
  - In arid (dry-land) and cold regions, direct discharge prevails and groundwater recharge discharges mostly through local springs;
  - In humid and semi-arid regions, groundwater recharge dominates and groundwater contributes significantly to stream flow or directly to the ocean.

Through a common dependence on the hydraulic conditions of the soil/sediment surface, infiltration determines overland- and subsurface-flow and the unsaturated zone subdivides subsurface-flow into inter-flow and groundwater recharge (section 3.5). Hence, the interfaces atmosphere/lithosphere and the unsaturated zone determine the nature and quantity of run-off on the one, and of stored water, which is later available for transpiration, on the other hand. Infiltration very often exceeds groundwater recharge by a factor of 100 to 1.7, because some infiltrate contributes to water storage in the unsaturated zone, hence, contributes to evapo-transpiration, and some is transformed into inter-flow (section 3.5).

According to the complexity of the infiltration process, differences in the mathematically predicted as compared with any observed infiltration are inevitable. Therefore, modes of infiltration have been classified and mostly refer to a one-dimensional, vertical flow. On this base, percolation has been studied in considerable detail using tensiometers, TDRs, neutron moisture results in combination with mathematical models, and tracers experiments (section 4.4.3); all these efforts have advanced the understanding of an average infiltration process.

At constant infiltration rates as generated from ponds, by repeated flood irrigation or river-infiltration into the subsurface with a homogeneous pore size distribution, the infiltration process involves four sub-zones (Fig. 3.7):

- The saturation zone, becoming few millimeters thick on top of the profile with positive, as well as
- The transition,
- The transport and
- The wetting zone, all with negative soil water potential.

In the case of small and time-limited infiltration rates, the saturation and transition zones do not develop, and in the case of an inhomogeneous pore size distribution both matrix- and preferential-flow (section 3.4) issue from infiltration.

Frozen soils and snow cover influence the infiltration process in different ways. On the one hand, soils with low water contents become more permeable under frozen conditions, because ground-ice forms, which is simultaneous linked to a

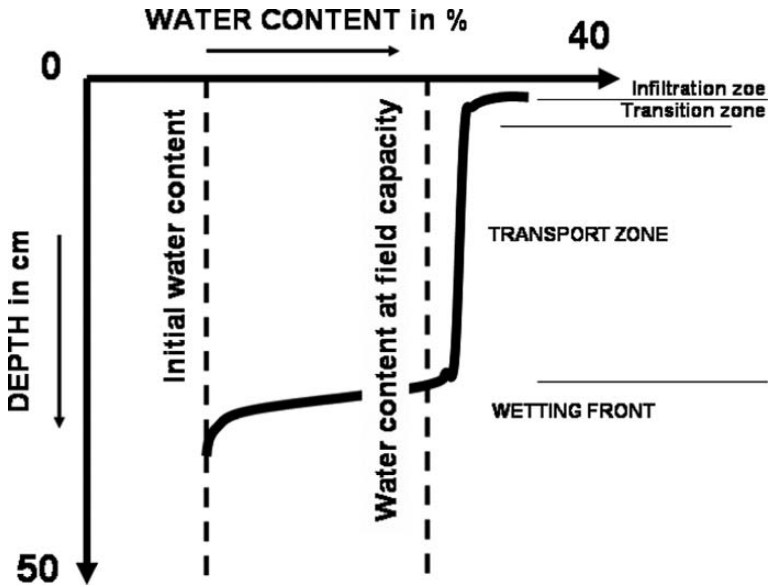


Figure 3.7. Infiltration beneath soils/sediments with constant head at the surface

soil/sediment drying and shrinking in the vicinity of the ground-ice (section 5.4); in contrast, soils with high water contents freeze completely, hence, become quasi impermeable. On the other hand, temperate snow covers act as a heat shield, protecting soils mostly from freezing and thus conserving soil fabrics and allowing the establishment of a saturated zone at the interface snow/soil/sediment during snowmelt, which favors infiltration (Fig. 3.7). Cold snow covers have a continuous transition to frozen soils and impede infiltration.

Water flow in the unsaturated zone follows Darcy’s law on filter flow; however, hydraulic conductivities  $[K(\theta)]$  and the capillary potential  $[\psi(\theta)]$  are functions of the volumetric water content. The one-dimensional, vertical water flux in the unsaturated zone is expressed by

$$\frac{\partial v}{\partial z} = \frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z} \left( K(\theta) \left[ \frac{\partial \psi(\theta)}{\partial z} + 1 \right] \right) \tag{3.1}$$

$$\frac{\partial \theta}{\partial t} = K(\psi) \text{grad}(\psi + z)$$

and using the diffusivity term

$$DIF = K(\theta) \frac{\partial \psi(\theta)}{\partial \theta} \tag{3.2}$$

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z} \left( DIF \frac{\partial \theta}{\partial z} + 1 \right)$$

This partial differential equation must be solved for appropriate initial and boundary conditions using numerical or analytic techniques. However, data acquisition and scale problems make the numerical description of infiltration and percolation often difficult, and therefore, approximation solutions have been developed.

Gardner & Widtsoe (1921) describe the infiltration process by an exponential function

$$Q_{t=0} = Q_{end} + (Q_{t=0} - Q_{end}) e^{-Et} \quad (3.3)$$

with the infiltration rate  $Q$  at the beginning ( $t=0$ ) and end of the infiltration process and  $E$  as an empirical constant of the percolation process or  $E^{-1}$  as the MTT; this MTT relates to the hydraulic functions of the unsaturated zone and varies as much as they do. As the solution of this equation underlies narrow soil hydraulic constraints, Philip (1957) developed a solution for a cumulative infiltration

$$IN = S\sqrt{t} + K(\theta)t. \quad (3.4)$$

$S$  expresses the sorptivity or storage of the unsaturated zone, which mostly dominates at the beginning of the infiltration process and  $K(\theta)$  is the water content-related hydraulic conductivity, becoming increasingly dominant with the duration of infiltration or if the water content is at field capacity, then the first term in eq. 3.4 becomes zero; such conditions occur during winter, snowmelt, river-, pond-infiltration, and repeated flood-irrigation.

The measurement of infiltration under field conditions is important, because the transfer of laboratory-determined hydraulic properties to field conditions has doubtful relevance, because of the role of inhomogeneities in the unsaturated zone on percolation. The results of infiltration measurements support in validating models on infiltration processes, as far as they do not relate to daily rain means but on rains with a short-term resolution; if time discretization of rain is not high, correction factors must be introduced to mathematically describe the infiltration process.

Four methods are frequently applied to gather field-related infiltration information:

- Sprinkler methods,
- Ring infiltrometer measurements,
- Monitoring the changes of water contents in the unsaturated zone during infiltration events, and
- River-discharge analysis (section 4.1.2).

The sprinkler method provides indirect information about infiltration; it measures infiltration as the difference between applied rain and run-off from an experimental plot. Difficulties exist in getting reliable results from drop size distribution and the kinetic energy of falling rain drops as compared with natural rain fall (Mutchler & Hermsmeier, 1969).

The measurement with ring infiltrometers is undertaken by ponding water in a ring infiltrometer driven a few centimeters ( $<10$  cm) into the infiltration interface, to simulate conditions as shown in Fig. 3.7. The water level is kept constant

by compensating for water losses, which are recorded. The evaluation of these experiments is based on eq. 3.4. At the beginning of such experiments data refer to storability and at the end to hydraulic conductivity under field conditions. As soils and sediments are very heterogeneous in the small scale, the transfer of local infiltration results to agriculture plots or the catchment size needs appropriate experience and respective datasets.

Measurements that are based on profile responses on infiltration refer to results from neutron moisture probes or TDRs often combined with tensiometer registrations. As homogeneity of soils and sediments in small scales differ widely from reference elementary volume (REV), fixed installations are preferable to record true relative changes instead of true and fabric related changes. Evaluations of these data refer to eq. 3.2 in considering moisture increments over a given vertical depth interval.

As compared with the before-mentioned, small scale methods (REV), the value of tracer-based discharge analysis (section 4.4.3) in combination with hydrograph analysis (section 4.1.2) result in catchment-related data on infiltration, as the sum of groundwater recharge and inter-flow. In combination with other data acquisitions, these integrative methods show how the catchment aggregates the local behavior of infiltration and run-off generation.

Field measurements, however, are also imposed by constraints on initial and boundary conditions, the heterogeneity of sections smaller than REV, and on the aggregate stability in the studied medium. Further variations may occur where hysteresis has to be taken into account (Fig. 4.9). In arid regions salt in the profile induce fabric modifications, which change hydraulic properties (Slatyr & Mabbut, 1964) during the infiltration process.

### 3.4. MATRIX-FLOW AND PREFERENTIAL-FLOW

Percolation occurs in the vadose zone and is mostly inhomogeneous. Field observations show that

- infiltration causes simultaneously rather quick and slow groundwater level responses,
- solute matter and bacteria (0.2–5  $\mu\text{m}$  in size) may reach rather quickly following a rain event the groundwater table in unconsolidated coarse grained and in consolidated fissured rocks, and
- measured and reported flow velocities in the unsaturated zone are always very slow.

These seemingly contradictory observations can be explained by the following:

- According to the magnitude of binding, capillary water can favor pressure equilibration from the ground to the groundwater surface, becoming damped if perched groundwater occurs in between; this pressure equilibration differs from usual mass transfer.
- There exists a rather quick mass transfer through large pores or fissures from the ground to depth, named preferential-, bypass-, or channel flow (Hillel, 1971;



Feddes et al., 1988; van Genuchten, 1994); this preferential-flow was already recognized at the end of the 19th century but has never been systematically quantified;

- In contrast, tracer experiments document that slow flow in the range of less than meters per year dominates percolation velocities; it is named matrix-flow.

From systematic tracer experiments in the unsaturated zone (section 4.4.3), it came out that an instantaneous tracer signal (Dirac signal), starting at the ground surface, produces (Fig. 3.8)

- always an extended tracer-break-through (TBT) response,
- sometimes a short-term high TBT concentration peak at the beginning of the tracer exercise, followed by the already mentioned extended TBT, or
- followed repeatedly by short-term low concentration peaks in the extended TBT; these low concentration peaks always parallel infiltration events.

The single short-term high and the many short-term low concentration peaks in the extended TBT indicate preferential-flow, increasing or diluting as a flux-pulse the prevailing tracer concentration in the unsaturated zone.

The observation of TBTs from one tracer exercise in replicate, fixed-sampling points (Fig. 3.8) shows that short-term high or low concentration peaks appear only if very high tracer input concentrations have been applied; as compared with the tracer Deuterium ( $^2\text{H}$ ), concentrations should exceed the background concentration by about 10–20 times; preferential-fluxes are always smaller in amount than matrix-fluxes (Fig. 3.8), hence, matrix-flow always dominates the mix of matrix- and preferential-flow.

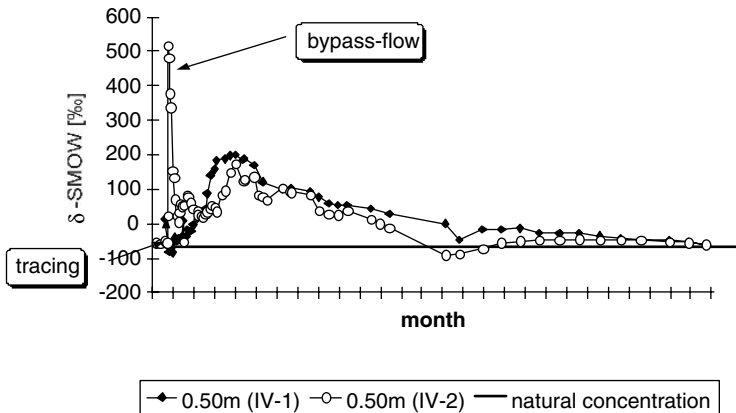


Figure 3.8. Quick and slow tracer-break-through (TBT) from a tracer experiment in Quaternary loess of the Scheyern test site in south Germany. Deuterium ( $^2\text{H}$ ) was used as a tracer and sampling was performed continuously at two points in 0.5 m b.g.s., which have been 50 cm distant from one another. Preferential-flow is indicated by a positive pulse at the beginning and many negative pulses during the break through of the tracer test

Analyzing repeated tracer experiments in one site shows that preferential-flow may or may not be a reproducible phenomenon, indicating that the flow-path-way of preferential-flow may or may not be constant in extent, position, and functioning (see below).

From such tracer experiments in the unsaturated zone also came out that the quick preferential-flow not only bypasses the slow matrix-flow but also exchanges with and incorporates into matrix-flow.

Matrix-flow accounts under humid temperate climates to vertical down flow velocities of 0.5 m/year in loess and 3 m/year in Quaternary gravels (Eichinger & Schulz, 1984; Eichinger et al., 1984; Seiler et al., 2002); they are lower under semi-arid to arid climate conditions (Dincer et al. 1974) and may reach zero with depth in hyper-arid areas. Generally spoken, matrix-flow velocities depend on

- the pre-event water contents in the subsurface,
- the amount of infiltration,
- fabrics of the subsurface soils/sediments, and
- E'T following the infiltration event.

In contrast, preferential-flow depends on special steady-state or transient texture conditions of soils/sediments (see below), hence, is often not constant, but always amounts to more than 0.5 m/day (Table 3.5).

Many tracer experiments have been performed using the sorbing tracer brilliant blue FCF to color percolation flow paths and to visualize any fingering of flow by excavating the propagation front of this tracer: This fingering has also been named preferential-flow (Fank & Berg, 2001) but could also be attributed to an inhomogeneous matrix-flow. Thus, it becomes clear that a reliable distinction of matrix- and preferential-flow is needed, which is not an easy task.

*Table 3.5.* Calculated preferential-flow velocities in Tertiary sediments and Quaternary loess after rain events from the Scheyern test site in south Germany

Station	Geology	Preferential-flow m/day	
		1997	1998
2-17	Loess, Quaternary	0.5	0.2
2-18	Loess, Quaternary	0.7	<0.5
6-18	Colluvium, Quaternary	1.0	n.d.
9-3	Sand/gravel, Tertiary	1.0	n.d.
9-B	Sand/gravel, Tertiary	<2	n.d.
12-9	Sand, Tertiary	1.0	0.7
12-R	Sand, Tertiary	0.8	0.6
13-16	Sand, Tertiary	0.7	0.5

Flow velocities have been deduced from the response of tensiometer cups on infiltration events.

n.d. = not determined.

On the one hand, the hydraulic evaluation of some 50 TBTs from different experimental sites in south Germany (Behrens et al., 1980; Seiler & Baker, 1985; Seiler et al., 2002) showed that an extended TBT can often only be interpreted in terms of percolation velocities and dispersion parameters if more than one flow velocity differing up to 1.5 orders of magnitude are assumed. Such a multi-flow-component interpretation of extended TBTs is still attributed to matrix-flow.

On the other hand, any analysis of event-related river discharges in humid climates by hydrograph methods (section 4.1.2) results in direct- and indirect run-off components feeding surface discharge. As inter-flow belongs to direct run-off, issues from the percolation zone and shows up rather simultaneously with overland flow, it must be concluded that

- either both flow components move in the same order of flow velocities along the same extent of flow paths or
- inter-flow moves somewhat slower on short subsurface-flow paths and emerges to the surface to join overland-flow.

Field observations confirm that the latter interpretation corresponds better to the real world than the first. It is preferential-flow approaching flow velocities in the range of meters per day, joining after short flow distances overland-flow with flow velocities of  $>100$  m/day. Hence, preferential-flow is two to three orders of magnitude quicker than matrix-flow and fingering of flow in the unsaturated zone should not automatically be interpreted as preferential-flow. Also, with respect to the run-off generation (sections 3.3 and 3.5), it seems to be more appropriate to interpret the usual fingering as inhomogeneous matrix-flow, which is also known from groundwater tracer experiments. From this view of interpretation, matrix- and preferential-flow in the unsaturated zone have some similarity with flow in bi-porous, consolidated rocks (Maloszewski & Zuber, 1990).

Preferential-flow needs special flow paths, in which gravity dominates over capillary forces. Referring to preferential-flow exceeding apparent flow velocities of 1 m/day and considering an hydraulic gradient of one and a water content of 0.2, the  $K(\theta)$  in eq. 3.1 was  $>2.3 \cdot 10^{-6}$  m/s. Comparing this order of unsaturated hydraulic conductivity with the respective values close to field capacity (Table 4.11), it becomes evident from the point of view of granulometry that preferential-flow must be expected from all uniform medium sands and coarse-grained gravels. However, uniform materials are only characteristic for marine and marine delta-sediments (Seiler, 2000); in contrast, terrestrial, fluvial sediments have always an uneven pore size distribution.

Figure 3.9 shows some pore size distributions for fluvial gravel and sand sediments; a slope of zero of these summed up pore-size-distribution-curves indicates a very homogeneous pore size range; if this is interrupted by steep slopes, a bi- or poly-modal pore size distribution exists. In such bi- or poly-modal media of coarse-grained sediments preferential-flow is common. Although a single-sized equivalent capillary tube model is not as representative as a bundle of capillary tubes model of a wide range of capillary diameters or a rigid sponge model, pore size distributions as shown in Fig. 3.9 can be considered as a good first approximation.

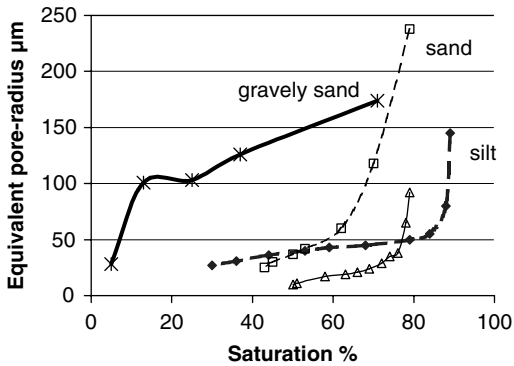


Figure 3.9. Pore size distribution of typical terrestrial sediments of Tertiary (sand, silt) and Quaternary age (gravely sand)

Natural pore size distributions can generate preferential-flow, which may change in velocity and quantity according to the infiltration intensity and the hydraulic conditions of the sediment before infiltration, but always operate stable in time and place. It is, however, also known that preferential-flow may change with time/season and may move from one place to another. This indicates that it depends also on parameters others than granulometry. In between these

- plant root channels,
  - subsurface activities of animals (e.g., worms),
  - ploughing activities of farmers, and
  - shrinking cracks, because of summer drying or winter freezing of sediments
- are outstanding. It seems that fabric destroying human, animal, and plant activities often exceed the influence of the natural pore size distributions on the generation of preferential-flow; this becomes very evident shortly before, during, and shortly after the growing season.

TBTs from tracer experiments prove that preferential-flow is not only bypassing but also interacting with matrix-flow by an exchange of solute matter and by an incorporation of preferential into matrix-flow. As a consequence, preferential-flow in unconsolidated sediments has often a limited depth reach depending on sediment fabrics, and anthropogenic and biotic activities close to the ground surface. Evaluated tracer exercises in the unsaturated zone beneath agro-lands in humid temperate climates suggest that preferential-flow reaches about

- 1 m down in loess,
- 2 m in medium to coarse grained sediments, and
- >3 m in Quaternary fluvial gravels

before becoming incorporated into matrix-flow or being transformed into inter-flow (section 3.5); in consolidated rocks, depth limitation depends on rock expansion and weathering and may reach 50–100 m deep (Seiler, 1968). In semi-arid and arid climates with native vegetation as well as beneath forests, this depth is greater than

in agro-lands, because most of the plants are deep rooting; in wet permafrost areas it is shallow again.

Preferential-flow can be approximated in the field by

- a combination of hydrograph and isotope discharge analysis (section 4.1.2, Fig 4.5),
- isotope analysis in creeks without groundwater contact (see below), and
- studies of stable isotope profiles in the unsaturated zone (see below),

All these methods refer to a quick lateral subsurface run-off (inter-flow), issued by preferential-flow following morphology; it occurs only during or just after rain events and mostly extends the discharge event (Fig. 4.3 c); none of these methods allow determining the whole magnitude of preferential-flow in the infiltration zone. The last of these three methods is not yet completely validated but was developed theoretically by the authors. The two other approaches may be considered standard methods.

The determination of preferential-flow through studying stable isotope profiles in the unsaturated zone close to the ground surface starts from the observation that in medium to fine grained sediments the subsurface acts in humid climates during the summer season mostly as a rain store, and during the winter season as a through-flow reservoir; in contrast, in permafrost and arid (dry-land) areas, overland-flow dominates all over the year and the subsurface acts seldom as a through-flow reservoir.

If no preferential-flow occurred in the unsaturated zone, and when percolation behaved as piston flow, the isotope profile in the unsaturated zone should reflect all recharge events during the recharge season, hence, causing a vertical stable isotope or chloride strip pattern according to the quality of the tracer signal of effective precipitation and the frequency and intensity of infiltration events. This can be simulated using a compartment (Belmans et al., 1983) or a discretizing numerical model. However, if preferential-flow bypassed and exchanged with the matrix-flow, the isotope profile became smeared according to the isotope exchange between preferential- and matrix-flow, and therefore, the calculated isotope profile differs from the measured one. Using, however, an algorithm for flow in bi-porous media with diffusive tracer exchange, the alteration of the isotope strip pattern from the exclusively matrix-flow to the interaction of matrix with preferential-flow can be simulated inversely, starting from

1. the calculation of infiltration during the recharge season,
2. recording the mean isotope concentration in precipitation during the recharge season,
3. measuring a medium flow velocity for both matrix- and preferential-flow,
4. inserting a diffusion parameter lower than effective molecular diffusion in water, and
5. applying different mean numbers of quantities of preferential-flow as fit parameters.

In practice, an isotope profile at the beginning and end of the recharge season, the calculation of infiltration and a registration of the isotope composition of precipitation during this time are necessary.

Such a modeling procedure will issue either higher or the same values of preferential-flow than the combined hydrograph/isotope separation method does. This profile method delivers a time-integrated average number of preferential-flow for the studied profile and also for the area, if sufficient profiles have been analyzed, respectively, transfer functions have been developed.

The evaluation of isotope analysis of discharge in creeks without groundwater contact (Fig. 4.5) is based on the assumption that overland-flow was not in contact with pre-event subsurface water and, therefore, reflects only the isotope signature of precipitation, whereas inter-flow represents a mix of precipitation and pre-event water in the unsaturated zone. Sampling this mix and precipitation allows calculating the subsurface/inter-flow contribution to creek discharge. This method integrates not over time but over scales, hence, refers to single events.

### 3.5. INTER-FLOW

Inter-flow occurs as saturated and close to saturated flow. It represents a quick subsurface run-off, which parallels morphology and originates from preferential-flow; the change from preferential vertical down to lateral flow (inter-flow) produces along hydraulic discontinuities, paralleling morphology. Such hydraulic discontinuities occur natural and man made.

- Natural discontinuities are related to
  - the remnants of permafrost, which changed sediment fabrics and produced fossil hill slides,
  - the decompression of rocks according to a change from a tri-axial state of stress in depth to a one-axial stress at the land surface, which favors rock/sediment disintegration, followed by weathering,
  - the deposition of eolian sediments, and
  - bioactivities in the effective root zone.
- Men add such discontinuities by
  - ploughing,
  - digging,
  - earth movements, and
  - the deposition of all kind of materials.

Such interfaces behave under special boundary conditions like capillary barriers and turn flow from vertical down into lateral. Tracer experiments have documented this lateral flow (Behrens et al., 1980) and Seiler & Baker (1985) simulated it numerically.

Figure 3.10 presents the  $K(\psi)$  function for a gravel and a sand, measured in laboratory experiments, and demonstrates that hydraulic conductivities within a certain range of suctions reach lower values in gravels than in sands; in the special case shown in Fig. 3.10, at suctions  $<100$  mm and  $>600$  mm, respectively, there is

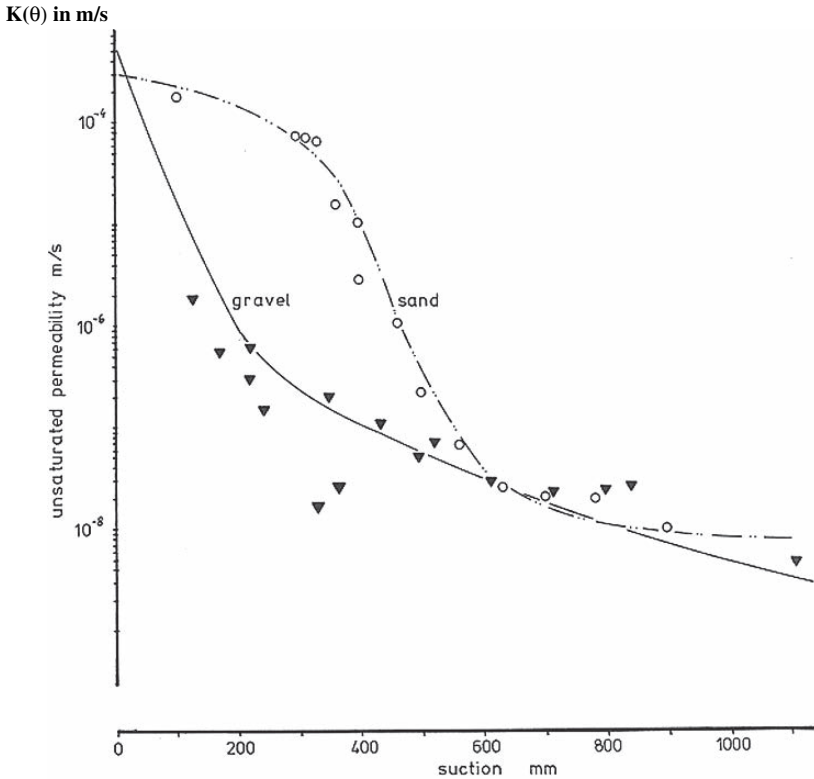


Figure 3.10. Hydraulic functions of an unsaturated gravel and sand, measured under laboratory conditions

no significant difference in hydraulic conductivities between the unsaturated sand and gravel; here, the inclined interface between sand and gravel (Fig. 3.11) does not act as a hydraulic barrier for percolation water, but within the mentioned suction range significant differences in hydraulic conductivities occur from the investigated sand and gravel (Fig. 3.10); hence, the functioning of the inclined sand/gravel interface as a total or partial barrier depends on the intensity of infiltration. This explains, why

- preferential-flow in hilly terrains produces inter-flow only according to special geologic and hydraulic initial and boundary conditions of infiltration (Fig. 3.12), and
- correlating inter-flow with preferential-flow may underestimate the real amount of preferential-flow in the unsaturated zone (section 3.4).

From Fig. 3.10 it is concluded that lateral flow is missing, when rain infiltrates after the unsaturated zone has dried, e.g., after a vegetation or rainless summer period. It reaches at the beginning of the infiltration period a maximum and at the end again a minimum. The same appears within the season if rain or snowmelt

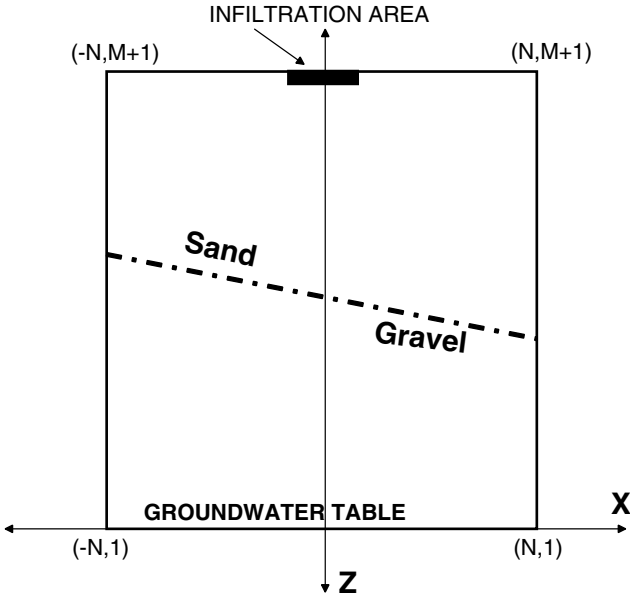


Figure 3.11. The model plan with an inclined interface between sands and gravels

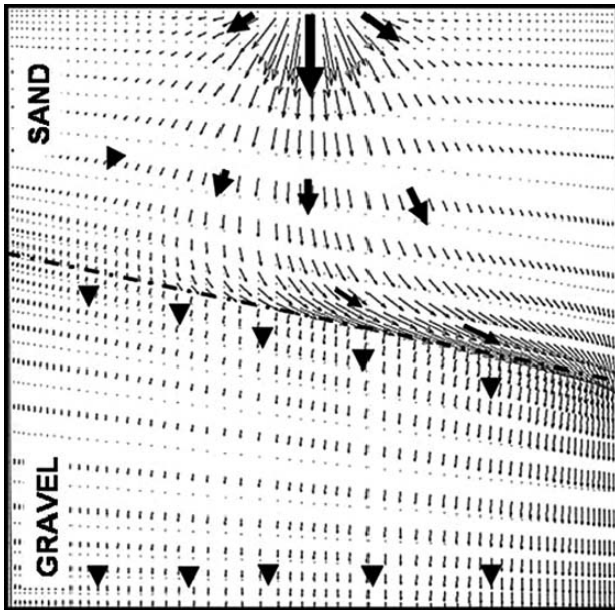


Figure 3.12. Flow vectors showing the role of the interface between sands and gravels at an infiltration of 50 mm/day. Infiltration is of line type as in the case of river-infiltration



reaches significant amounts or lasts for a long period of times. So the functioning of any capillary barrier, producing inter-flow (Seiler & Baker, 1985), cannot be considered as constant; it varies according to changes in hydraulic functions in the season, with time and with input conditions.

The discharge analysis to quantify inter-flow in rivers without and with groundwater contact is best performed using environmental tracers (section 4.4.2.3) in combination with hydrograph methods (section 4.1.2). By definition, environmental tracer-based discharge analysis results in the determination of one component without and one in contact with subsurface water. Among the run-off components, only overland-flow had – in a first approximation – no contact with subsurface water; whereas, inter-flow and base-flow had. Therefore, environmental tracers allow as a good approximation to separate the sum of inter-flow ( $Q_I$ ) and base-flow ( $Q_G$ ) from overland-flow ( $Q_O$ ).

$$Q = (Q_G + Q_I) + Q_O \quad (3.5)$$

In contrast, hydrograph methods differentiate between slow ( $Q_G$ ) and quick run-off components ( $Q_I + Q_O$ )

$$Q = Q_G + (Q_I + Q_O) \quad (3.6)$$

Hence, combining both equations allows approximating inter-flow.

### 3.6. RIVER-INFILTRATION

Rivers discharge surface water and according to existing differences in water level elevations between the river and groundwater table, surface water either infiltrates into the subsurface or groundwater exfiltrates to the surface water (Fig. 3.13).

Unidirectional infiltration from rivers into the subsurface occurs

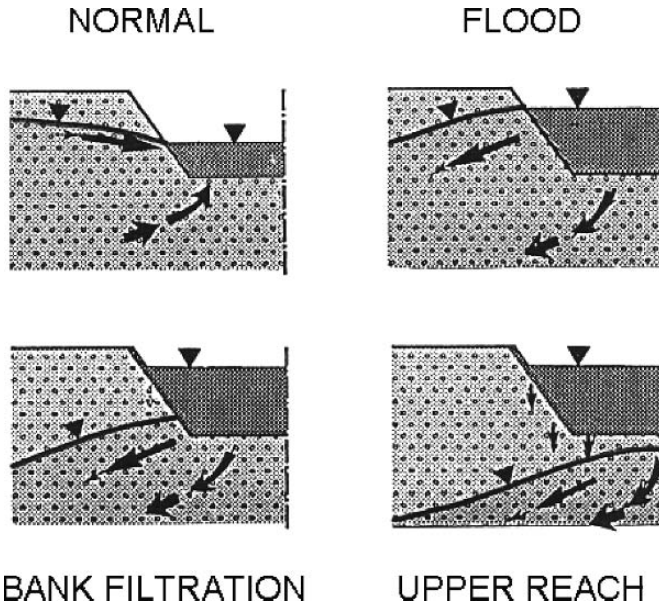
- in the upper reach of mountain-rivers,
- in wadis/oueds,
- in areas with a steep slope of the river course,
- from artificial lakes, and
- unlined canals.

Such infiltration recharges groundwater either permanently or for a limited period of time through the unsaturated zone.

In contrast, surface water stands in direct groundwater contact in areas with

- low relief energy and
- in the low reach of rivers.

When surface and groundwater are in direct contact, more than 45% of surface discharge originates from indirect (groundwater) and less than 55% from direct run-off (Table 4.6); under these boundary conditions, river-infiltration and river-exfiltration is linearly related to water level differences between both media. This allows increasing groundwater recharge through forced river-infiltration by creating



*Figure 3.13.* Schematic presentation of the interaction between river water and groundwater. Upper row left: Dry weather (normal); right: flood discharge, both in humid climates, Lower row left: River-infiltration in humid areas; right: Wadis/Oueds, mountain river, etc., infiltration

a hydraulic gradient from the river to an unconfined groundwater level. This manipulation is linear as long as hydraulic gradients do not disconnect the surface water from the groundwater body, e.g., by an unsaturated zone between the river bed and the groundwater table (Fig. 3.13 right down).

A reasonable investment to profit from forced river-infiltration and, hence, enhanced groundwater recharge for water-supply by technical means requires that the thickness of the aquifer close to the river should not be lower than 5 m in gravels and much more in sands to achieve an economic yield with a reasonable draw down. Therefore, most of the forced river-infiltration installations are located along main rivers with a thick quaternary valley fill.

In areas with

- low groundwater recharge, like in many semi-arid and almost all arid areas,
  - high relief energy, like in mountains, and
  - side-rivers entering grabens or glacial over-deepened valleys,
- river water is disconnected from the groundwater table (Fig. 3.13 right low); here, forced groundwater recharge is no more linearly related to any differences in surface/groundwater levels, because it is now influenced by
- the saturation stage of the vadose zone and its respective hydraulic functions,
  - infiltration capacities of the river bed, which depend on
    - chemical and biological crusts and
    - external as well as internal sediment clogging.

Under these conditions, manipulation of groundwater recharge through forced river-infiltration may become difficult or even inefficient. In the case of external sediment clogging, fine-grained particles accumulate at the surface of the river bed, and in the case of internal sediment clogging, fine-grained particles penetrate into the sediment and reduce the through-flow through pores; external clogging is reversible, internal clogging not as much.

Riverbeds clogged by sediments or crusts may significantly reduce natural and forced river-infiltration and sometimes also water quality, if the infiltration process lasts uninterrupted for too long. Clogging is generally negligible when exfiltration dominates infiltration or the flow velocities in the river cause permanent or frequent erosion. Under all other conditions clogging of the river bed by fine-grained sediments, once occurred, does not disappear any more by natural means. In contrast, biological clogging is always time-dependent.

In South Germany, systematic field studies on external clogging of river beds in Quaternary, fluvial gravels have been conducted with respect to the efficiency of mechanical filtering and the consequences of a reduction of forced river-infiltration; in these investigations, the mechanical filtering was studied with *Escherichia coli* (body sizes 0.5–5  $\mu\text{m}$ , which stands for clay particles) and compared with existing pore size distributions (Fig. 3.9) and the efficiency of forced river-infiltration was quantified, using stable environmental isotopes (section 4.4.2.3). For six study sites came out that pore size distributions of these gravels, allocated beneath the band in Fig. 3.14 retain completely particles <5  $\mu\text{m}$  and had a little river-infiltration

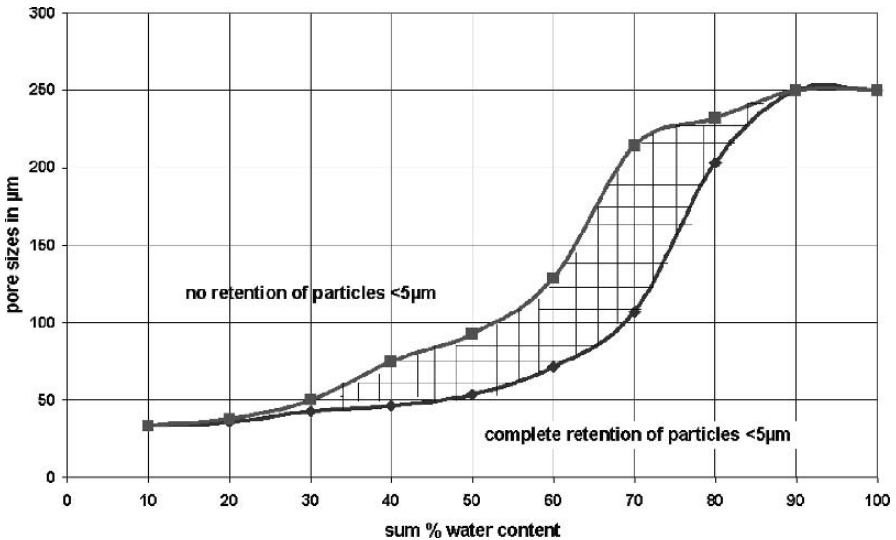


Figure 3.14. Pore size distribution range in Quaternary gravels of south Germany (95% carbonates), beneath which particles >1  $\mu\text{m}$  are completely mechanically filtered, hence, producing clogging (colmatation) of the river bed and reducing the efficiency of river-infiltration into aquifers

efficiency (Seiler, 1997); in contrast, areas above the band in Fig. 3.14 did not show up measurable external clogging after a run of several decades of forced river-infiltration.

Erosion or exfiltration counteracts against river bed clogging; erosion intervenes, when river flow is undersaturated in sediment load, which occurs, if river flow was accelerated by canalization for flood protection, by water import from neighboring catchment areas or if along the river-course dams have been constructed for hydro-power production, collection of irrigation water, or also for flood protection; under these circumstances of enhanced erosion, main river water level will decline and thus aquifers become drained with the consequence of groundwater level decline; such groundwater level declines and aquifer depletions are known from many areas of the world.

River-infiltration into the subsurface occurs according to the width of the river water surface, the water depth in the channel centre, and the hydraulic gradient from the river to the aquifer. If both the depth and hydraulic gradients are taken as constant, infiltrations into the subsurface increases from a triangular over a trapezoid to a rectangular river cross-section. The magnitude of this increase depends on fabrics of sediments and the clogging or crusting status at the infiltration interface.

Tracer experiments at point and line river-infiltration sites with an unsaturated zone between the river bed and unconfined groundwater table (Behrens et al., 1980) showed that percolation is not only vertical down but follows much more than under saturated conditions a pronounced transverse flow direction according to the orientation of beddings that percolation has to cross; bedding in the unsaturated zone generally produces hydraulic discontinuities with reflections and refractions along this interface. A result of such a tracer experiment in Quaternary gravels is shown in Fig. 3.15 and has been numerically modeled (Fig. 3.12; Seiler & Baker, 1985).

River-infiltration with and without an unsaturated zone between the river bed and the groundwater surface domes up the groundwater table of perched and regional groundwater beneath and in the close vicinity of the river course (Fig. 3.13). This doming is caused by mass transport and pressure equilibration and represents a hindrance to natural groundwater flow toward the river. According to hydraulic and water-quality observations, this doming creates groundwater level fluctuations, which may reach 400 m distant to both sides of the river; however, in the case of an infiltration/exfiltration system, only the immediate vicinity of the river bed really stores infiltrated surface water, which is commonly called bank storage and which is short after infiltration time again released to the river; further distant to the river water is only banked up. Hydraulically, low conductive aquifers do not store significant water volumes in the river-bank, high conductive aquifers do so. Bank-storage is commonly not considered in both hydrograph analysis or isotope and chemical techniques to separate flow components and thus introduces an error bare in overestimating inter-flow and underestimating overland-flow.

River-infiltration with direct contact between river and groundwater has a transient hydraulic character, when occurring during rain events. This transient

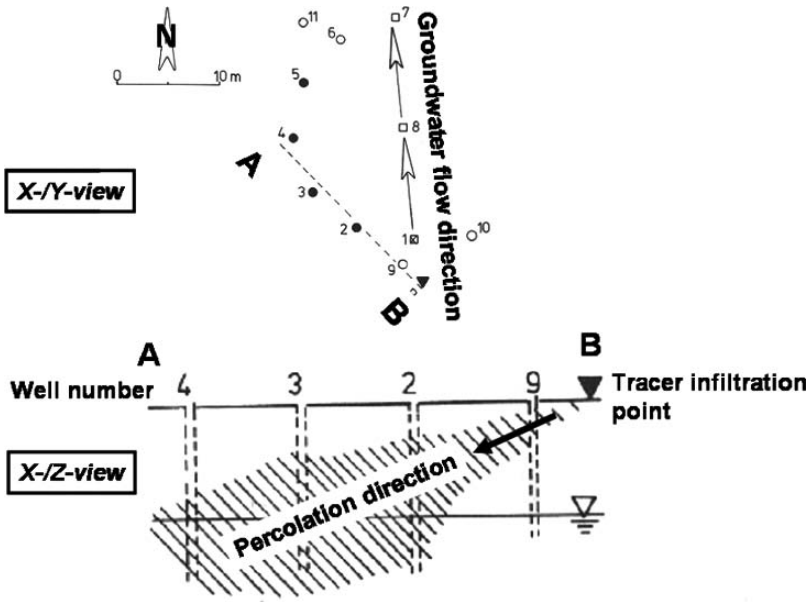


Figure 3.15. Result of tracer experiments on groundwater flow (upper part, bird view) and percolation between ground surface and an unconfined groundwater table at 2 m depth (vertical cross section). The percolation experiment has been performed with an infiltration of 50 mm/day. The hatched area in the lower part of the figure represents the propagation field and the line AB the flow direction of percolation water

character becomes enhanced when crusts and clogging intervene at the beginning of infiltration and disappear thereafter. In contrast, exfiltration has generally a steady-state character. Under saturated conditions (Fig. 3.13 right up and left down) and without bedding in the aquifer, the transition of surface water into groundwater is radial close to the river and turns in some distance away from the river into a quasi horizontal groundwater flow; these two consecutive geometries of the flow field have to be considered in applying mathematical models (Dachler, 1933) to quantify river-infiltration.

Contrary, in horizontally bedded aquifers flow starts quasi horizontal through the sidewalls and only a little flux leaves the bottom of the riverbed perpendicular to bedding. The latter case corresponds best to the flow of a partly penetrating well into an aquifer with great filter length and the before-mentioned homogeneous case to a partly penetrating well with short filter length. There, the mathematical treatment of the river-infiltration into the saturated zone relates to the same assumptions as for abstraction or injection wells, however, with the difference that river-infiltration must be treated as a two dimensional and well hydraulics as a three dimensional exercise, which expresses in respective integration methods. Consequently, in the pioneer time of river-infiltration research (1930–1940), the Dupuit-Forchheimer and the Theis assumptions opened this manipulation to mathematical description. With

the introduction of electric analogy and later computers, an almost endless array of aquifer and boundary conditions now applies (Dillon, 1989).

River infiltration with an unsaturated zone between the river and the aquifer makes mathematical formulation somewhat more complicated, because a leakage factor has to be introduced, which corresponds in a first approximation to the ratio of hydraulic conductivity and the thickness of the infiltration layer; Furthermore, hydraulic functions of unsaturated sediments intervene and must be coupled with flow in the saturated zone; here

- the determination of a leakage factor and
- of representative hydraulic functions (section 4.3), as well as
- the assessment of heterogeneities, which percolation water has to cross (Behrens et al., 1980, section 3.5),

often do not allow an appropriate prediction of the consequences of river infiltration for groundwater resources with a fitted model.

In general, river-infiltration can be quantified using either

- mathematical groundwater models,
- discharge measurements along the river course, or
- environmental tracers (section 4.4.2.3).

The mathematical groundwater model follows a hydro-geologic conceptual model, approaching and abstracting the real geologic and hydraulic conditions. Commonly, an inverse procedure is chosen by taking measurements of river and groundwater levels as the fitting parameters, assuming different amounts of river-infiltration.

### 3.7. ARTIFICIAL RECHARGE

Many human activities result in artificial groundwater recharge; from the very beginning of agriculture terracing of hills, later irrigation contributes to enhanced recharge; all kind of water storage on dam sites and the construction of unlined canals leak water to the subsurface and in many urban areas groundwater recharge intensifies by forced infiltration or by leakages from urban water distribution and collector systems. From urban areas, losses of 5% to more than 50% from water supply and waste water collector systems and of 10–20% from septic tanks are known. In irrigation areas, losses of up to 15–20% of applied irrigation (return water) or about 10 mm/day have been reported. All these recharges are classified as incidental artificial recharge. In contrast, forced recharge happens through

- injection wells,
- infiltration basins, charged by floods or harvested rains,
- water ponding, and
- abstraction of river water through groundwater wells (section 3.6);

These measures aim

- to extend natural groundwater recharge and
- to meliorate groundwater quality.

Taking the depth/extent ratio of aquifers in a catchment, which is in the range of 1:1,000 to more than 1:10,000 and in arid areas much more, it becomes clear that all kind of artificial groundwater recharge have on a short run of time only local impacts.

Three important aspects in artificial groundwater recharge are quantities, the quality of water sources, and the hydraulic properties of the sink area.

- Quantities are responsible for a continuous recharge supply and need an optimal reservoir design;
- Qualities are of interest if dealing with the chemical compatibility of surface and groundwater or with the long-term efficiency of basin or well installations. Especially, suspended matter has often a disastrous influence on well clogging, which is difficult to clean up, and can be minimized in infiltration basins by selecting graded sand/gravel packs to keep clogging close to the surface of the infiltration interface and, hence, to be easily removable.
- Best subsurface reservoirs for artificial groundwater recharge are unconsolidated sediments with hydraulic conductivities in the range  $10^{-2}$ m/s to  $10^{-5}$ m/s and a high storage coefficient. These bulk hydraulic data also stand for efficient groundwater exploitation.

If the nutrient content of water (C, N, P) in infiltration basins or ditches is high, incoming light develop and favor algal growth, hence,

- clogging of the filter bed or
- increases of the pH of water, which involves precipitation of calcium carbonate, aggravating clogging problems at the infiltration interface.

In unconfined aquifers, artificial recharge relates mostly to infiltration basins or ditches, which have large surfaces and are easily accessible for filter cleaning; usual infiltration rates are in the order of 100–500 mm/day.

Injection wells apply in confined aquifers; however, they are very sensitive to mechanical filtering, chemical reactions, and air entrapment along the interface screen/borehole wall. To avoid these skin effects in wells, water needs pre-treatment to eliminate pathogen bacteria, suspended matter, and toxic substances; the still-missing attenuation process then happens on the subsurface flow path and becomes more complete the higher the residence time and the specific surface of the sediment is. In the special case of injection wells, water should not be aerated and should not expand when released and before reaching the groundwater in order to avoid air entrapment in pores and any disturbance of the carbonate/ $\text{CO}_2$ -equilibrium, which both reduced hydraulic conductivities.

Fissured rocks are often too problematic for artificial groundwater recharge, because flow velocities in wide fissures exceed mostly a range of deca-meters per day, and storage capacity is mostly below 2 vol.%. Consequently, the attenuation potential is not well developed along fissure flow paths, and the percentage of reuse of infiltrated or injected water is small, except artificial recharge happened within an extended pumping depression. Opposite to this, bi-porous fissured rocks, which are typically represented by sandstones, reef lime-stones, and chalk, may develop

storage capacities in excess of 6 vol.%, and mean residence times are high enough to approach a significant natural attenuation.

Artificial groundwater recharge is intensively used

- in semi-arid and arid areas (e.g., Arab peninsula, California, Israel),
- in areas with significant mineral resources (e.g., Australia, Germany),
- in crystalline rocks (e.g., Sweden), or
- in areas with a high population density (e.g., Berlin, Netherlands).

A special form of artificial recharge is water ponding or rain harvesting. This method applies often in arid (dry-land) areas, guarantees a vegetation cover in restricted areas, and even provides some groundwater recharge. A sporadic rain in an arid area produces primarily direct discharge, which can be stored in a pond or depression of limited extent, where it evaporates and infiltrates. In a study in Niger, Boers (1994) illustrates the efficiency of such pondings (Table 3.6); as can be seen, the concentration of rain from small areas sampled in one plot of 8 m<sup>2</sup> creates groundwater recharge, which did not exist without rain harvesting. However, this recharge is small and refers in a wet year for a 20- or 40-m<sup>2</sup> plots to 2 mm/year and 4.5 mm/year respectively.

### 3.8. WATER VAPOR-FLUXES IN THE SUBSURFACE

Water vapor-fluxes are sometimes supposed to contribute also to groundwater recharge and soil water displacement. Such vapor-fluxes are driven by air pressure, vapor pressure, and temperature gradients in the vadose zone.

Air pressure gradients in the percolation zone depend on water level fluctuations, becoming strong in low porosity rocks, or by wind entering the pore space as far as porosities are high.

Table 3.6. Efficiency of water harvesting in a wet and a dry year

	Without rain harvesting	Rain harvested from an area of	
		20 m <sup>2</sup>	40 m <sup>2</sup>
Dry year			
P	258	258	258
R <sub>sf</sub>	0	78	155
ET	138	205	277
R	0	0	0
Wet year			
P	673	673	673
R <sub>sf</sub>	0	285	571
ET	481	720	849
R	0	38	185

Predicted run-off (R<sub>sf</sub>), transpiration of a Neem tree and rain harvesting on a 20m<sup>2</sup> and a 40m<sup>2</sup> plot (Boers, 1994). All numbers in mm/year.



The establishment of a vapor pressure gradient depends on bounding of soil moisture, which is normally an unimportant factor, because vapor pressure does not change much with soil moisture suction in the water content range from field capacity to the wilting point; therefore, the suction gradient is always much higher than the respective vapor pressure gradient.

In contrast, temperature gradients may become important for changes of water vapor pressures; e.g., a temperature rise from 10–30°C increases the vapor pressure by a factor of three. Such temperature gradients always provide a flux from high to low temperature zones, albeit little at high water saturation. These fluxes, however, are always smaller than the water consumed by transpiration. Such temperature-driven fluxes may contribute in temperate climates to soil moisture in freezing soils or in arid (dry-land) areas to the soil surface according to large differences between day and night temperatures.

Temperatures in the subsurface result from the interference of a constant geothermal flux, directed conductively vertically up, and a heat import with percolation from the atmosphere vertically down; this downward flux is mainly of convective and conductive character; hence, seasonal and daily air temperature variations are transmitted to the subsurface by matrix- and preferential-flow; the penetration depth of daily temperature variations restricts to a few centimeters, whereas seasonal temperature variations can still be observed in 15–20m b.g.s. (Fig. 3.16). The depth in which seasonal temperature variations are no more measurable is called the neutral depth.

Seasonal variations of the air temperature undergo in the subsurface both a damping of the amplitude and a phase shift with depth. A respective example from two sites of Germany is presented in Fig. 3.16.

Vapor-fluxes also depend on the porosity and the tortuosity of the pores of the sediment. Marshall (1959) reports that under a temperature gradient of 3.8°C/cm and at porosities of 52 vol.%, fluxes are in the range of  $1.1 \cdot 10^{-3}$  m/day, at 25 vol.% of  $8.4 \cdot 10^{-4}$  m/day and at 10 vol.% of  $6.0 \cdot 10^{-4}$  m/day; such high temperature gradients exist only at the soil surface, where the daily temperature variations still express. At depth, such gradients are missing and, therefore, vapor-fluxes are becoming smaller than matrix-fluxes ( $<2$  m/year or  $<5.4 \cdot 10^{-3}$  m/day).

From Fig. 3.16, it can be seen that the amplitude of the yearly temperature variations close to the land surface is strong and weakens rapidly with depth; till the neutral depth the phase shift of seasonal temperature variations becomes half a year.

The liquid (w) and vapor-flux rates (v) in the vadose zone depend on hydraulic and temperature gradients

$$\frac{Q}{A} = [K_w(H) + k_v(H)] + [d_{T_w} + d_{T_v}] \frac{dT}{dz} = K_w(H) \quad (3.7)$$

Under arid and semi-arid conditions  $d_{T_w}$  is negligible as compared with  $d_{T_v}$ , and in almost all climate zones,  $K_v(H)$  is several orders of magnitude smaller and less variable than  $K_w(H)$ . Taking both these parameters into account, it is evident that

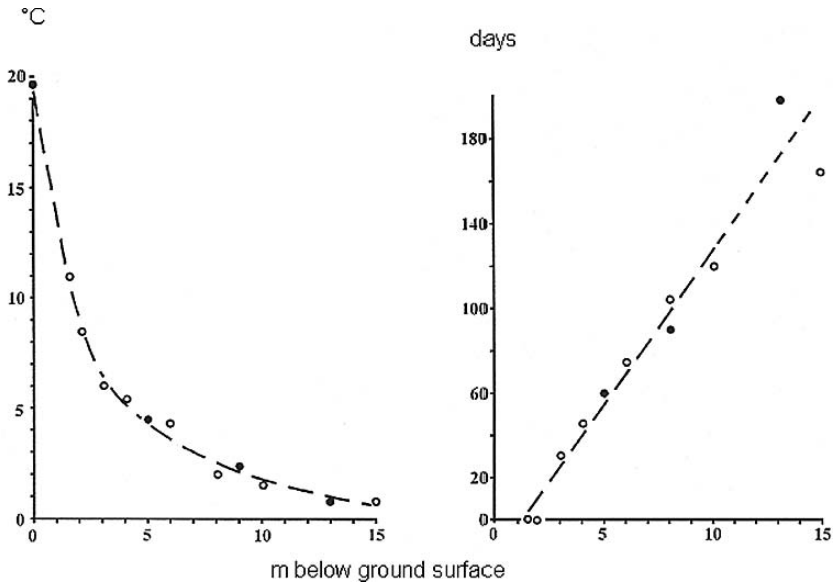


Figure 3.16. Damping of the amplitude (left) and phase shift of air temperatures (right) in different depth of the subsurface. Air temperature refers to 1 m above ground. ● Kappelmeyer (1961) from Hannover, ○ Seiler from Munich area

water contents may become significantly influenced by vapor-fluxes only close to the land surface (Campbell, 1985), where thermal gradients are highest and in-depth groundwater recharge increases by vapor-fluxes (Fayer & Gee, 1992) only by  $<0.1$  mm/year.

## CHAPTER 4

### RESEARCH TOOLS AND METHODS IN THE STUDY OF RECHARGE

Depending on the aim of investigation, groundwater recharge studies contribute to develop long- or short-term strategies on water use.

- In a first step, it must be clarified to which extent the studied hydro-geologic system discharges under steady-state respectively transient hydraulic conditions; both conditions occur naturally world wide, because of the always existing global changes in climates, vegetation, and discharge levels (chapter 1), which became accelerated through human activities since the beginning of the industrial age.
- In a second step, the scale to which results on groundwater recharge refer has to be considered, to enable a representative assessment of results.
- Finally, it should be kept in mind that virgin conditions may significantly differ from managed conditions, because groundwater recharge is not a fixed number, but may vary with the boundary conditions of the recharged system.

Long-term recharge estimates allow to developing appropriate exploration and exploitation strategies for water scarce and water excess periods of time. Short-term information on groundwater recharge is needed, to better assess the impact of floods and accidental spills on groundwater resources and to optimize irrigation.

There are six general approaches to estimate groundwater recharge:

- Mass balance methods,
- Mixing methods,
- Hydraulic approaches,
- Flux measurements,
- Methods that are based on outflow analysis, and
- Turn-over-methods.

All these methods experienced in the past modifications according to the available investigation tools, the local or regional climate, plant cover, and hydro-geologic conditions. Most common are meteorological mass balance studies, issuing bulk information on run-off, but mostly not on groundwater recharge. Methods of outflow analysis as well as hydraulic approaches that are based on numerical modeling of groundwater flow deliver approximate results on groundwater recharge. The results of all these studies always refer to the catchment scale and depend on observations

of precipitation, the energy balance, land use, river discharge and groundwater level fluctuations, and must be based on a reliable conceptual hydro-geologic model. In contrast, lysimeter mass balance studies, soil hydraulic, and tracer-based turn-over-methods always provide small-scale and instantaneous information, referring to local singularities, giving to groundwater recharge an often unknown weighing factor. Hence, both large- and small-scale methods inform about bulk respectively distinguished recharge; bulk information have to be tested if they refer to a Reference Elementary Volume (REV) of dedicated or mixed boundary conditions and small-scale results often hardly refer to any REV. Links between both types of results are transfer functions, which are, however, mostly missing.

The above-mentioned methods are frequently applied in humid climates and suffer in arid to semi-arid areas from restrictions, because

- input data for mass balances (meteorological) vary too much in time and space and are mostly not adequately known over a long run of time and in the large scale of the dry-land,
- intrinsic hydraulic parameters, the boundary conditions of aquifer systems, and fit parameters such as groundwater level fluctuations often suffer from non-precision and are often not representative for the entire catchment,
- infiltration in arid (dry-land) and tropical climates is more punctual than areal, and
- much out-flowing groundwater in dry-lands is old and therefore does not correlate with present meteorological data sets.

#### 4.1. WATER BALANCE ESTIMATES

Water balance calculations require steady-state conditions and refer to average annual means of precipitation and evapo-transpiration, hence, hiding areal variations and time-dependent effects; they heavily depend on the precision of the estimate of the actual evapo-transpiration, which is – no doubt – the most difficult parameter to determine.

Simple input–output relations on precipitation and discharge (eq. 4.1) are supposed to be linear and refer only to distinguished areas and their discharge; they obey the general form of

$$D = \beta_1(P - \beta_2). \quad (4.1)$$

The betas are fit parameters and represent unweighed system specific constants. Such an approach, however, neglects all geologic and non-linear plant, soil and climate influences on infiltration, and run-off; hence, delivers bulk information, which applies just for the catchment, in which they have been gained. Any significant change in land use, climate, and the discharge base requires the re-calibration of such a model.

The meteorological water balance for *closed basins* (eq. 4.2) relates to

$$P = (D_O + D_I + D_G) + (EP + TP) \pm \Delta S \quad (4.2)$$

and for *open basins* (eq. 4.2) to

$$P = (D_O + D_I + D_G) + (EP + TP) \pm \Delta S \pm D_T \quad (4.3)$$

In both equations, it is assumed that the surface/subsurface run-off areas of  $D_O$ ,  $D_I$ , and  $D_G$  are identical in size and for climates with high amounts of convective rains also in extent, because convective rains are local events. By experience, in catchments exceeding  $5 \text{ km}^2$  in size, the size criterion is mostly fulfilled or negligible different as far as the discharge base of neighboring rivers is similar in altitude (Fig. 4.1, left side); in catchments smaller than  $5 \text{ km}^2$ , perched groundwater could underflow orographic water divides and thus produces different sizes in surface and subsurface catchment areas. Finally in neighboring catchments with different discharge altitudes, the orographic (owd) and the subsurface water divides (sswd) may also differ in position (Fig. 4.1, right side).

If size differences in the catchments are difficult to assess, only direct run-off can be exactly determined, whereas groundwater recharge is either over- or underestimated, because the size of the subsurface catchment was either smaller or larger than the orographic catchment.

To identify and assess run-off components (eqs. 3.5 and 3.6), hydrograph analysis (Naterman 1951) (section 4.1.2), analysis of groundwater level fluctuations (section 4.1.3) or environmental (Sklash et al., 1976; Seiler et al., 2002) and artificial tracer methods have been applied (sections 4.4.2.3 and 4.4.4 respectively).

Changes in subsurface water storage ( $\Delta S$  in eqs. 4.2 and 4.3) are negligible in long-term water balances studies. This simplification, however, applies only in areas, in which an active groundwater recharge zone occurs all over the catchment (section 2.4). In arid (dry-land) zones, this is mostly invalid, because the active and passive groundwater recharge zones contribute in similar orders of magnitude to groundwater outflow to the oceans (exorhenic areas), or terminal lakes, Salares or Sabkhas (endorheic areas) or to evaporation in areas with a water table close to the surface ( $<2.5 \text{ m b.g.s.}$ ); hence, in the water balance for such areas, the consumption of stored water can never be neglected. A very useful support in quantifying such losses of long-term stored subsurface water is groundwater dating with environmental isotopes of appropriate half-lives ( $^3\text{H}$ ,  $^{85}\text{Kr}$ ,  $^{39}\text{Ar}$ ,  $^{14}\text{C}$ ,  $^{36}\text{Cl}$ ) in the active and passive groundwater recharge zone as well as in the run-off of the

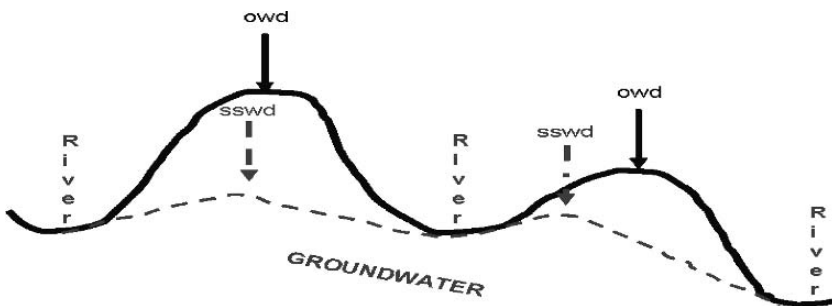


Figure 4.1. Altitudes of discharge base of rivers and the resulting differences in the position of orographic (owd) and subsurface water divides (sswd)

catchment (Mook, 2002); with these two components and the mix out of it, the run-off partitioning of old and young groundwater can be quantified (eqs. 4.59–4.62).

#### 4.1.1 Estimate of Evapo-Transpiration

Precipitation transforms on continents into evapo-transpiration, often called green water, and surface/subsurface run-off, often called blue water. Green water, basically consumed by plants, is part of blue water and accounts on an average to about 50% of the continental water cycle. Falkenmark (2001) reports that in humid tropical and temperate climates

- 57% of green water evapotranspires through forests,
- 22% through grassland,
- 10% by agro-lands,
- 2% by wetlands, and
- 9% by other areas.

These numbers and the increasing demand for water to produce food and energy for a growing world population make clear that ET is significantly open to manipulation through changes of land use (Tables 3.1, 4.2, and 4.3).

The determination of evapo-transpiration is the most crucial factor in the mass balance equation. Evaporation occurs during rain events, however, mostly from receptor interfaces (biosphere/atmosphere or lithosphere/atmosphere) and open water surfaces; in contrast, transpiration consumes water from the soil/sediment store through leaf surfaces and, therefore, the leaf area index (LAI) and plant development play an important role in the determination of transpiration. Changes of the LAI during the vegetation period of the crops are shown in Table 4.1.

ET has a climate, seasonal, land use, and human development share of contribution (Tables 4.2 and 4.3): With the shift of human activities from hunting to agriculture and recently to industrialization, crop rotation and selection, deforestation and irrigation and emissions into the atmosphere ET changed and will do so much more in the near future.

Depth reach of evaporation or vaporization of water below ground is limited to some decimeters (Fig. 4.30) and becomes increased by shrinking cracks; capillary raise of percolation water substitutes and thus increases evaporation losses from

*Table 4.1.* Mean leaf area index (LAI) values ( $\text{m}^2/\text{m}^2$ ) for different crops (Löpmeier, 1983)

Crop	LAI <sub>S</sub>	LAI <sub>B</sub>	LAI <sub>MAX</sub>
Winter wheat	0.3	0.7	3.8
Summer wheat	0	0.7	3.9
Winter barley	0.3	0.6	3.7
Sugar-beet	0	0.2	4.2

Indices S, MAX, and B refer to the beginning, maximum, and in between phase of plant development.

*Table 4.2.* Relative evaporation/evapo-transpiration in mid-latitudes (Baumgartner & Reichelt, 1975)

	ET/P in %		ET/P in %	
Wet prairies	100	Ever-green areas	65	
Water surfaces	75	Grain areas	40	
Needle forests	70	Barre soil	30	

*Table 4.3.* ET from different forests as referred to spruce (100%)

Douglas fir	111	Spruce	100
Birch	109	Beech	90
Larch	109	Pinne	56

the percolation zone. In contrast, transpiration reaches to great depth under deep rooting trees and only a few meters deep under field crops.

In areas with a closed plant cover, transpiration exceeds evaporation by far in the vegetation period; in areas with sparse plant cover evaporation dominates. Some ET data from different surfaces and trees are shown in Tables 4.2 and 4.3.

In water balance studies, the determination of ET with meteorological parameters is a special challenge. It depends on

1. Incoming and
2. Reflected solar radiation,
3. Air temperature and
4. The temperature of the evaporating surfaces,
5. Relative humidity,
6. Wind speed, and
7. Has to consider the development respectively any changes of physiologic properties of the plant cover during the vegetation period.

Parameters 1, 3, and 4 can be locally determined and transferred to the catchment scale, because they do not vary too much in space and short periods of time; all other parameters should be registered on the scale of the landscape, especially the reflected radiation, which is quite variable in the catchment scale (Table 2.4). Therefore, the parameters 4–6 are often determined by remote sensors in aircrafts, flying at 150–300 m above ground. As far as clouds and rain events do not interfere, data of one flight a day can be extrapolated to the whole day; in case of weather changes within a day, several flights are necessary to approach the real ET. As airborne measurements to determine ET are quite expensive for routine or repeated measurements, often local meteorological data are used, and calculated ET is then extrapolated to the catchment scale.

Evaporation (EP) depends on the escape of water molecules from a water surface to the air; this escape is triggered by the heat energy produced by solar radiation. Thus, evaporation depends on three processes:

- The storage of heat in water close to the surface (energy balance),
- The water vapor-flux through the interface water/air (Dalton process), and
- The air motion along the water/air interface (disturbance of an equilibration process).

As most of these data are in general not available in detail and, if available, results are often non-representative for the catchment scale, empirical or semi-empirical methods have been developed.

The energy balance equation (eq. 4.4) for the heat storage ( $E_T$ ) is known and delivers

$$E_T = (E_{ti} - E_{tr} + E_{li} - E_{lr} - E_{le}) - EP - (E_{sh} + E_{ai} - E_{ao}) \text{ [Joule/(cm}^2\text{day)]} \quad (4.4)$$

<    *Radiation balance*    >        < *Heat exchange* >

$t_i$  = total insolation,

$t_r$  = total insolation reflection,

$l_i$  = long wave insolation,

$l_r$  = long wave reflection,

$l_e$  = long wave emission from the water body,

$E$  = evaporation,

$sh$  = sensible heat,

$ai$  = advective heat income,

$ao$  = advective heat outcome.

In this equation,  $EP$  corresponds to the potential evaporation.

The driving forces for water molecules to change from the liquid into the vapor phase is the vapor pressure gradient from the liquid to the gas phase; the Dalton equation (eq. 4.5) describes this flux from the liquid to the gas phase as

$$\frac{dQ}{dt} = \frac{\chi (e_{\text{water}} - e_{\text{air}})}{p_{\text{air}}} \quad (4.5)$$

$\chi$  = coefficient, which refers to air motion.

This flux tends to decrease the water vapor gradient with time (closed system), if it was not disturbed by an export of water vapor through air motion (open system).

Even more complicated is the calculation of the transpiration (TP) from plants, which depends on the available water content in the effective root zone and its retention by capillary forces, the water take up by roots, the hydraulic conductivity along the flow path in the plant, the LAI, and the regulation of water escape through the plant stomata, which depends not only on insolation, plant development, and plant species but also on the chemical composition of the surrounding atmosphere, like, for example, the  $\text{CO}_2$ - and ozone-content (section 6.3).

According to the many data needed to quantify evapo-transpiration and the mostly missing detailed data base in most climate zones, different approaches have been developed to calculate ET on the base of empirical or semi-empirical constants, replacing missing data sets by bulk parameters. Among these the following approaches often apply:



1. *The approach of Turc (1954)* (eq. 4.6) refers to long-term annual means of precipitation (mm/year) and air temperature ( $^{\circ}\text{C}$ )

$$ET = \frac{P}{\sqrt{0.9 + \left(\frac{P}{300 + 25T + 0.05T^3}\right)^2}} \quad [\text{mm/year}] \quad (4.6)$$

2. *The approach of Albrecht (1951)* is based on mean monthly or mean daily water vapor deficits ( $e_{\text{saturation}} - e_{\text{air}}$ ) in mbar:

$$ET = 0.75\chi(e_{\text{saturation}} - e_{\text{air}}) \quad [\text{mm/month or mm/day}]. \quad (4.7)$$

The wind factor  $\chi$  is shown in Table 4.4. These values have been questioned and some authors emphasize to use always a wind factor of 16 and to refer to monthly instead of daily means of water vapor deficits (Uhlig, 1954).

3. *The Haude (1955, 1959) approach* (eq. 4.8) is widely used: it is similar to the Albrecht (1951) approach, considers the water vapor deficit in mbar of each day, measured at 2 m above the ground at 2 p.m. and introduces a calibrated factor ( $f$ ), referring to the plant cover

$$ET = \sum_1^{i\text{-days}} 0.75f(e_{\text{saturation}} - e_{\text{air-2p.m.}}) \quad [\text{mm/i-days}] \quad (4.8)$$

with

$$e_{\text{saturation}} = 6,11 \cdot 10^{\frac{17,62T}{243,12+T}} \quad \text{if } T > 0 \quad (4.9)$$

or

$$e_{\text{saturation}} = 6,11 \cdot 10^{\frac{22,46T}{272,62+T}} \quad \text{if } T < 0 \quad (4.10)$$

Table 4.4. Values of  $\chi$  (eq. 4.7) in the Albrecht equation according to wind speed

Wind speed km/h	Wind factor $\chi$ , referring to	
	Mean monthly value	Mean daily value
0–0.6	4	0.13
0.6–1.2	6	0.20
1.2–1.8	8	0.27
1.8–2.4	10	0.33
2.4–3.0	12	0.40
3.0–3.6	14	0.47
>3.6	16	0.53

Table 4.5. f-factors (eq. 4.8) in the Haude approach for different crops (from DWD Agriculture Meteorological Service, Braunschweig, Germany)

	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
1	0.26	0.26	0.33	0.39	0.39	0.37	0.35	0.33	0.31	0.26	0.26	0.26
2	0.20	0.20	0.21	0.29	0.29	0.28	0.26	0.25	0.23	0.22	0.20	0.20
3	0.10	0.10	0.20	0.25	0.40	0.40	0.60	0.60	0.40	0.35	0.10	0.10
4	0.18	0.18	0.18	0.26	0.36	0.35	0.30	0.20	0.18	0.18	0.18	0.18
5	0.18	0.18	0.18	0.20	0.25	0.35	0.36	0.25	0.25	0.18	0.18	0.18
6	0.18	0.18	0.18	0.20	0.22	0.30	0.35	0.36	0.30	0.18	0.18	0.18
7	0.14	0.14	0.14	0.14	0.18	0.26	0.26	0.26	0.25	0.23	0.22	0.20
8	0.14	0.14	0.14	0.15	0.23	0.30	0.36	0.32	0.26	0.19	0.14	0.14
9	0.18	0.18	0.18	0.20	0.25	0.32	0.36	0.34	0.25	0.18	0.18	0.18
10	0.18	0.18	0.18	0.32	0.37	0.35	0.26	0.20	0.18	0.18	0.18	0.18
11	0.18	0.18	0.19	0.26	0.34	0.38	0.34	0.22	0.21	0.20	0.18	0.18
12	0.18	0.18	0.20	0.30	0.38	0.36	0.28	0.20	0.18	0.18	0.18	0.18
13	0.18	0.18	0.18	0.25	0.35	0.36	0.34	0.30	0.20	0.18	0.18	0.18
14	0.18	0.18	0.18	0.25	0.32	0.38	0.36	0.30	0.18	0.18	0.18	0.18
15	0.15	0.15	0.18	0.25	0.30	0.36	0.26	0.18	0.18	0.18	0.18	0.18

line 1 = bare land, line 2 = grass land, line 3 = pine forest, line 4 = early potatoes line 5 = potatoes, line 6 = late potatoes, line 7 = corn, line 8 = sugar-beet, line 9 = sunflower, line 10 = winter rape, line 11 = winter wheat, line 12 = rye and barley, line 13 = pea, line 14 = bean, line 15 = summer barley and oat.

Table 4.5 presents the f factors by month for different crops as calibrated for mid-latitudes. The Haude (1955) approach has also been successfully applied in arid (dry-land) climates (Haude, 1959).

According to Table 4.5, ET is higher in the vegetation period for forests than for grass lands with a deep groundwater table; crops evapo-transpire in the vegetation period water quantities in between forests and grass lands.

ET calculations based on eq. 4.8 always refer to daily data and not to monthly mean values of the water vapor deficit at 2 p.m. A similar approach referring to crop parameters is presented by Allen et al. (1998).

4. *The Thornthwaite (1948) approach* (eq. 4.11) goes back to mean monthly temperatures, supposing a 30 days month and daily 12 hours of sunshine.

$$ET = 1.6 \left( \frac{10T_{month}}{I} \right)^a \quad [\text{mm/month}] \quad (4.11)$$

with

$$I = \sum_1^{12} \left( \frac{T_i}{5} \right)^{1.514} \quad (4.12)$$

and

$$a = 6.75 \cdot 10^{-7} I^3 - 7.71 \cdot 10^{-5} I^2 + 1.792 \cdot 10^{-2} I + 0.49239 \quad (4.13)$$

5. *The Penman (1948) approach* (eq. 4.14) refers to the potential evaporation of an open water surface and was originally expressed as

$$EP = \frac{\Delta E_0}{\Delta + \gamma} + \frac{\gamma E_{\text{air}}}{\Delta + \gamma} \quad [\text{mm/day}] \quad (4.14)$$

with

$$E_0 = \frac{1}{\zeta} [(1 - r) E_{\text{in}} - E_{\text{out}}] \quad [\text{mm/day}] \quad (4.15)$$

$E_{\text{in}}$  = Incoming radiation energy

$E_{\text{out}}$  = emitted energy

$r$  = reflection coefficient

$\zeta$  = conversion- from  $\text{J}/(\text{cm}^2 \text{ day})$  into  $\text{mm}/\text{day}$

$E_{\text{air}}$  = vapor transport through the water /air interface

$\gamma$  = psychrometer constant =  $0.65 \text{mbar}/^\circ\text{C}$

$\Delta$  = slope of the saturation vapor curve at temperature  $T$

The conversion-factor  $\zeta$  changes with the temperature range and expresses as

$$\begin{aligned} \zeta &= 59.6 - 0.0533 T & \text{at } T > 0^\circ\text{C} \\ \zeta &= 59.6 & \text{for } T = 0^\circ\text{C} \\ \zeta &= 67.6 - 0.05 T & \text{at } T < 0^\circ\text{C}. \end{aligned}$$

6. *The traditional long-term water balance* (eq. 4.16) in a closed system applies to determining a difference height ( $U$ ), if long-term registrations of run-off and precipitation are available

$$U = P - D. \quad (4.16)$$

As far as precipitation was representatively determined for the catchment (section 3.1), surface and subsurface catchments do not differ in size, and any groundwater displacement beneath the reference gauge station is negligible, the difference height in the water balance corresponds well to the actual or real ET.

Calculations of EP or ET according to methods 1–5 always result in the potential ET and EP and have an error bare of about 20%. Potential ET refers to unlimited water availability as realized along water surfaces and over wetlands. As water availability on continents is mostly limited, one is always faced with real or actual instead of potential ET, which is smaller than the potential one. Therefore, bulk correction factors have been proposed to better approach real ET or EP; these correction factors either refer to a mean annual value, which is often supposed to be 75% of potential ET in humid climates, or orient at threshold values like the field capacity of the unsaturated zone.

The still existing uncertainties in determining the actual ET for short time slots makes any short-term hydrological water balance based on meteorological data

difficult to apply. Comparison of ETs from all mentioned methods on a run of several years results normally in a quite good agreement. This comparison, however, reflects on short intervals too many parameter uncertainties contributing to the calculation of ET.

#### 4.1.2 Hydrograph Analysis

The meteorological water balance (eqs. 4.2 and 4.3) can seldom differentiate between specific run-off components (Figs. 4.2 and 4.3C). Knowing the geology of a catchment, however, allows a lumped relation between discharge and specific run-off components; only indirect run-off is a characteristic of areas with unlimited infiltration capacities (gravels, developed karst) and only direct run-off typifies areas with low storage characteristics (crystalline rocks, clays). In almost all other aquifer geologies both direct and indirect run-off are to be met. The contribution of these run-off components to surface discharge depends on

- Intensities and durations of rains,
- Catchment geology,
- Land use and plant/crop development,
- Thickness and hydraulic functions of the unsaturated zone, and
- Reservoir geometries and hydraulics.

Under dry weather conditions, the discharge of springs or rivers is fed by perched respectively regional groundwater (Fig. 2.7), named dry weather discharge, base-flow or groundwater run-off to surface discharges. As far as perched groundwater dominates base-flow, any base-flow analysis of river discharge under- or overestimates groundwater recharge rates, because the outflow from perched groundwater refers to either an excess or a too low portion of the orographic catchment size (Fig. 4.1); in the case of base-flow from regional groundwater, groundwater recharge rate is mostly underestimated because base-flow analysis refers to a threshold

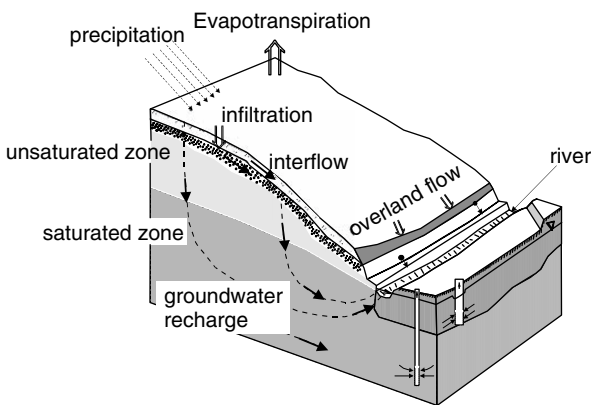


Figure 4.2. Block of a landscape with the respective run-off components

altitude, which is usually higher than the base of the aquifer or aquifer-system; hence, subsurface discharge beneath the threshold level is not considered by the base-flow analysis. Only at gauge stations of extended catchments with a very small subsurface through-flow section and with the same surface and subsurface catchment size base-flow analysis approaches well available groundwater recharge.

Any discharge surplus, produced in a limited run of time by rain events, is attributed to inter-flow and overland-flow and expresses in a characteristic sudden rise of surface run-off, followed by a slow discharge recession (Fig. 4.3C). Once all the run-off from the temporary overland and inter-flow reservoirs has gone, discharge returns to base-flow. This idealized concept on run-off neglects transmission links, which are supposed to exist, but are not well known.

Hydrograph analysis separate direct (overland- plus inter-flow) and indirect run-off (base-flow), whereas chemical/isotope discharge separation distinguishes between pre-event and event water; hence, only the combination of both methods allow a good estimate of main discharge components such as base-flow, inter-flow, and overland-flow (eqs. 3.5 and 3.6). Furthermore, hydrograph analysis of the base-flow always refers to the threshold discharge level of the gauge station, in contrast environmental dating of base-flow refers to a trench of the groundwater flow field, which penetrates beneath the mentioned threshold altitude. Therefore, both methods result in somewhat different values for base-flow.

Opposite to base-flow, the inter-flow and overland-flow reservoirs have always a discharge altitude above the receiving river; hence, both can quantitatively be determined by tracer and hydrograph-based discharge analysis.

In hydrologic regimes with dry and wet seasons, base-flow can easily be analyzed and precisely determined with respect to a threshold altitude. In regimes with frequent precipitation input (e.g., in humid areas) or with snowmelt over long runs of time in the dry season (in many temperature-driven discharge systems) an appropriate quantification of the long-term base-flow is often difficult.

The dry weather discharge characteristic of an aquifer can be constructed using hydrographs from rivers and marking in a first step sectors of dry weather discharge according to Fig. 4.3A, starting empirically about 3 days after the run-off peak; following, these curve sectors are composed to the dry weather discharge line (DWDL) (Fig. 4.3B), which covers the whole range of discharges and generally represents a trend line; the transfer of this DWDL into a semi-logarithmic scale usually results in two linear lines, which are attributed to direct and indirect discharge; often a third line appears in between, which, however, is often considered to result from the superposition of the two before mentioned lines.

The DWDL is unique in a discharge/time diagram, if porosities and hydraulic conductivities are high. In the case of low porosity fissured rocks, the DWDL may move up and down according to the intensity of groundwater recharge; here a medium DWDL of the aquifer can be determined by defining a maximum and a minimum DWDL.

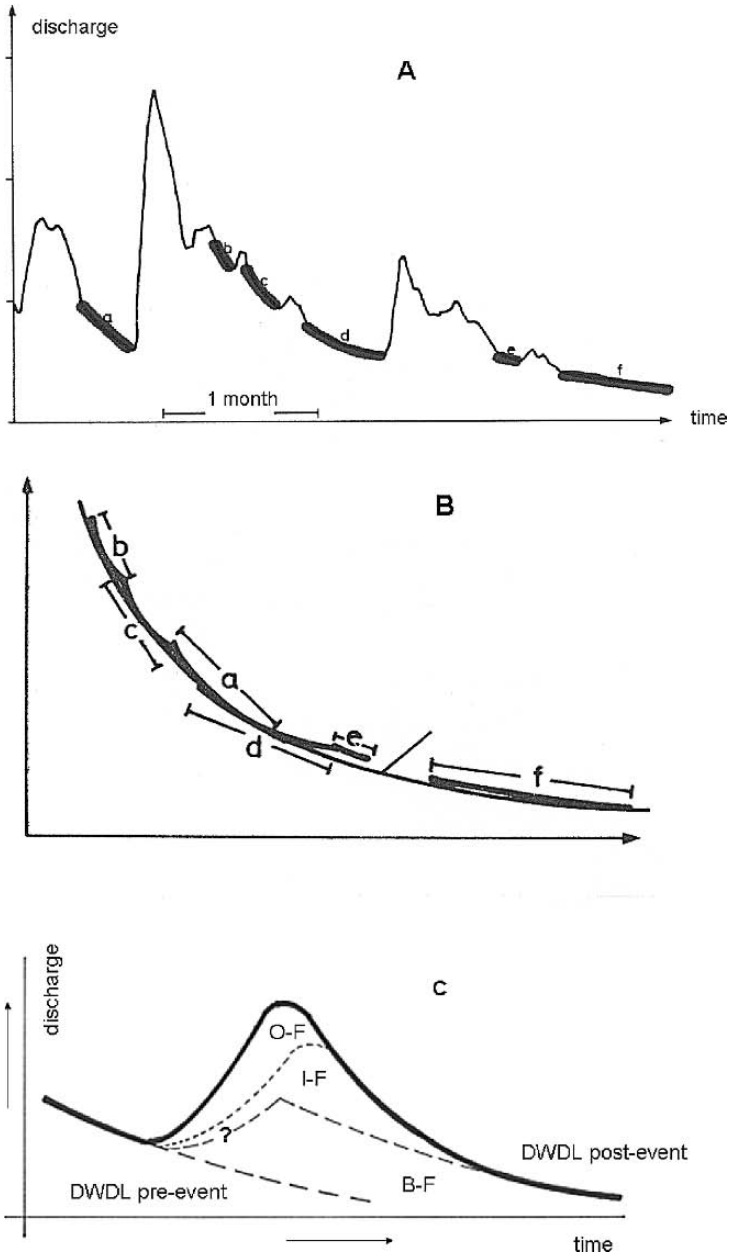


Figure 4.3. Surface discharge of a river as a function of time. (A) Sectors of dry weather discharge (curve limbs a till f); (B) Sectors of dry weather discharge are composed to a regression line (the dry-weather-discharge-line or DWDL), which generally follows an exponential function of the type of eq. 4.17; (C) Surface discharge is composed of O-F = overland-flow, I-F = inter-flow, B-F = base-flow

The outflow of a reservoir (eq. 4.17) can be characterized by an exponential function

$$Q_t = Q_0 e^{-\frac{t}{MTT}} \quad (4.17)$$

During rain events activated reservoirs with low mean-turnover-time superimpose base-flow and add to (Fig. 4.3C) eq. 4.18

$$\begin{aligned} Q &= Q_{tG} + Q_{tI} + Q_{tO} \\ Q &= Q_{0G} e^{-\frac{t}{MTT_G}} + Q_{0I} e^{-\frac{t}{MTT_I}} + Q_{0O} e^{-\frac{t}{MTT_O}} \end{aligned} \quad (4.18)$$

G, I, and O refer to groundwater, inter-flow, and overland flow, respectively.

In this equation, the bulk geometries and hydraulic properties of reservoirs G, I, and O are defined by the mean turn-over time (MTT) (eq. 4.19), which just corresponds to a one time water replacement in the respective reservoir:

$$MTT = \frac{AT'p'}{AD} = \frac{T'p'}{D} \quad (4.19)$$

Typical MTTs in the active groundwater recharge zone are for

- Base-flow in unconsolidated aquifers 1–75 years,
- Base-flow in consolidated aquifers 1–5 years and an additional >20 years if matrix porosities come into game (sandstones, chalk, reef carbonates, diagenetic dolomites) and
- For overland- and inter-flow hours respectively days.

As a rule, groundwater reservoirs have constant MTTs, because in a first approximation aquifer geometries and hydraulics are constant and hydraulic heads generally change slowly; only subsidence, triggered by natural or anthropogenic water level changes, alter geometries, and hydraulics on a long run of time, hence, produce an increase of MTTs. Such hydraulic changes never recover completely if boundary conditions return to initial water level stages.

In contrast, bulk hydraulics of the inter-flow and overland-flow reservoirs may change seasonally according to growth and decay of the vegetation cover as well as the intensities of soil biologic and agriculture activities. As a consequence, it is often observed that rain events produce in the summer or dry season less tailing of direct run-off than in the winter or rainy season; this relates to seasonal changes of MTTs of inter-flow, because of a seasonality of infiltration and through-flow capacities in hilly terrains (Fig. 4.4).

Hydrograph evaluations differentiate between quick and slow reservoir responses, respectively, high and low MTT; no intermediate MTT is distinguished; hence, hydrograph methods separate direct (overland-flow + inter-flow) and indirect run-off (groundwater run-off); any further separation exceeding two or even three components is mostly arbitrary, because of interferences of the components. Some examples for the portion of direct and indirect run-off in river discharge are shown in Table 4.6.

With the meteorological water balance (eqs. 4.2 and 4.3), bulk discharge is determined, and using hydrograph evaluations, run-off with short MTT can be

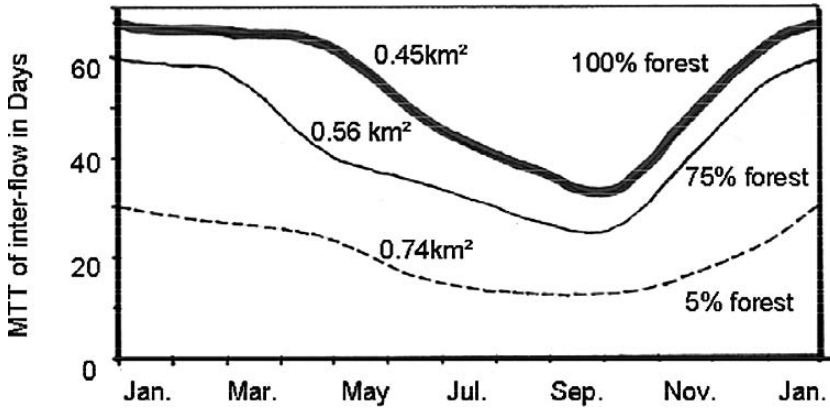


Figure 4.4. Seasonal changes of the mean turn-over time (MTT) of inter-flow in Tertiary sediments of south Germany (Scheuern). Catchment sizes are similar, but forest cover is changing

subtracted from surface discharge; hence, groundwater recharge in humid and cold areas is approximated by eq. 4.20

$$D_G = P - ET - (D_O + D_I) \pm \Delta S \tag{4.20}$$

Preconditions to apply this relation are:

- Surface and subsurface catchment areas are known in size,
- Changes in stored water ( $\Delta S$ ) can be neglected, and
- A long-term average for direct run-off is available.

In arid (dry-land) areas, it is approximated by eq. 4.21

$$D_G = P - EP \pm \Delta S. \tag{4.21}$$

To successfully proceed in hydrograph analysis, continuous discharge records and not daily means must be analyzed to determine direct run-off and its MTT; only

Table 4.6. Ratios of direct ( $Q_{I+O}$ ) and indirect discharge ( $Q_G$ ) as referred to the mean river discharge

River	$D_{O+I}$	$D_G$
Colorado/USA	0.40	0.60
Danube/D + A	0.64	0.36
Elbe/CZ + D	0.59	0.41
Mississippi/USA	0.64	0.36
Mosel/D	0.72	0.28
Neckar/D	0.70	0.30
Potomac/USA	0.46	0.54
Rhine/CH + A + D	0.57	0.43
Sacramento/USA	0.35	0.65
Weser/D	0.58	0.42



for base-flow also daily discharge means lead to representative MTTs. Monthly means or once a day records are unsuitable for this analysis.

As the knowledge of discharge generation is still limited and has a scale dimension, other simplified approaches based on discharge records have been proposed:

- Given the above-mentioned assumptions on base-flow, Wundt (1953, 1958) proposed to take for each month the lowest daily mean of discharge and to calculate the arithmetic mean for the summer and winter season. Since during summer (the vegetation period) present groundwater recharge is lower than in winter, the summer mean represents a minimum of manageable groundwater. If applied in arid to semi-arid areas, this method does not result in any reliable number of groundwater recharge, because discharge also includes a high portion of transient components from historic or even geologic times, which can be recognized applying water dating with environmental tracers (section 4.2.2).
- Natermann (1951) proposed a more optimistic approach to determine manageable groundwater. He used continuous discharge records, put a wrapping curve at low discharge points and extrapolate a smoothed curve to the hydrograph of the rainy or snowmelt season. Determining the mean of the adopted curve and subtracting it from the mean discharge results in a good approximation of manageable groundwater quantities. This method is easy to handle and delivers reliable data for long runs of continuous discharge observations.

Hydrograph analysis based on environmental tracers such as isotopes, silicate, or DOC are also named “end member mixing methods (EMMM)”, which allow analyzing surface flow as a composition of two end members. As far as these end members are non-reactive tracers (section 4.4), their partitioning in surface run-off is proportional to the respective discharge component (eq. 4.59). A typical example for such an EMMM is shown in Fig. 4.5 for an area without base-flow; the example shows that at the beginning of the discharge event, pre-event water does not measurably contribute to the discharge of both fields, however, after September 29, 2002, it does for each plot in a different manner.

In EMMM, the environmental isotope tracers  $^{18}\text{O}$ ,  $^2\text{H}$ , ( $^3\text{H}$ ) (sections 4.4.2.3 and 4.4.2.2) and the weathering products  $\text{Si}(\text{OH})_4$  and DOC are often applied.

- Silicon is considered a geogenic tracer from the weathering zone of sediments and rocks; its dissolution is rather quick (Kennedy, 1971), dissolution kinetic is high, and once dissolved, it maintains this concentration (Hendershot et al., 1992),
- Dissolved organic carbon (DOC) is the part of TOC passing through a filter of  $0.45\ \mu\text{m}$ ; it is produced in soils by weathering of the organic detritus and underlies in the effective root zone strong mechanical filtering (White, 1998; Seiler et al., 2002); therefore, it is abundantly available within the soil zone ( $>4\ \text{mg/L}$ ) and traces lateral flow and decreases rapidly in the unsaturated zone to  $<2\ \text{mg/L}$ , thus tracing groundwater recharge; typical groundwater concentrations of DOC are  $0.5\text{--}1.5\ \text{mg/L}$  (section 5.1.1).

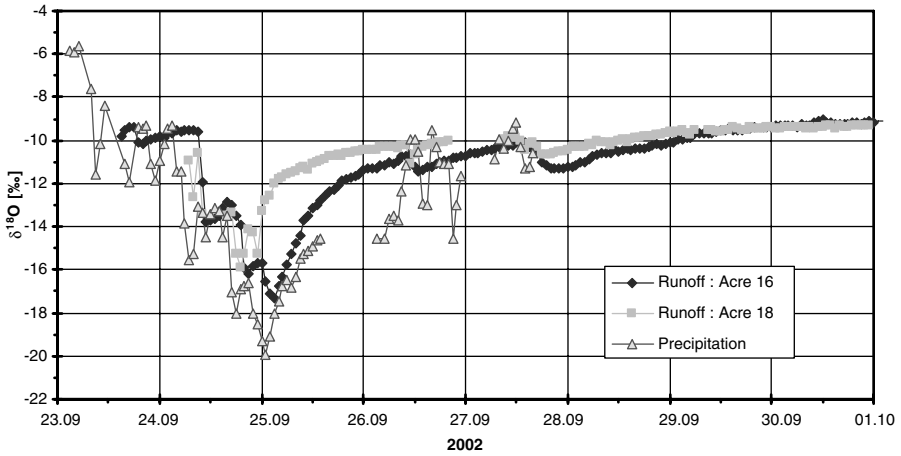


Figure 4.5. Direct run-off from two agro-fields (acre 16 and 18) as produced by a precipitation event in the area of Scheyern, Germany. The figure shows the variations of  $^{18}\text{O}$  in precipitation (grey) and direct run-off (light grey and black); the response function is at the beginning of the rain event similar and differs in a more advanced stage of rain

### 4.1.3 Groundwater Level Fluctuations

Groundwater levels fluctuate according to atmospheric pressures, the compression of rocks during earth-quakes and tides, and as a response to groundwater recharge/discharge. Atmospheric pressures and rock compressibility result in measurable groundwater level fluctuations only if the porosity is low and the groundwater is confined.

Regional groundwater levels rise if groundwater recharge exceeds groundwater consumption and decline if evaporation and horizontal fluxes consume stored groundwater. Given that groundwater fluxes are quite constant, groundwater level fluctuations, hence, express groundwater recharge. Taking mean groundwater levels per month over a run of many years results in an average amplitude of groundwater fluctuations with high groundwater levels following recharge times and low groundwater levels following dry weather conditions. These average fluctuations mark the recharge space in an aquifer.

Taking this amplitude and supposing that groundwater fluxes do not change significantly with water levels, allows to calculate (eq. 4.22) groundwater recharge if the porosity ( $p'$ ) of that part of the aquifer is known

$$R' = \Delta h p' \tag{4.22}$$

$S_c$  is not constant, because it might be reduced by entrapped air in the groundwater fluctuation zone. Therefore, it is always lower than total and sometimes also than effective porosity; under-wetting conditions, it is often smaller than under-draining conditions, because of hysteretic effects. Some values of  $p'$  are listed in Table 4.7.

Table 4.7. Range of porosities  $p'$  of aquifers, which are relevant to calculate groundwater recharge from fluctuations of groundwater levels

Material	$p'$ in %	Material	$p'$ in %
Fluvial gravels	10–18	Clay sand	10–15
Medium sands	25–30	Clay	> 10
Fine sands	20–25		
Loamy sand	15–20	Karst	1.5–4.5
Loam	13–17	Fissured aquifer	0.5–1.5

The range of data in Table 4.7 is due to both the air entrapment and the degree of uniformity in grain size distribution in the groundwater fluctuation zone.

As the groundwater table is the first contact of recharge with groundwater, observations of groundwater fluctuations in this zone are most relevant. To depth, groundwater recharge distributes uneven (section 2.4), resulting in a first approximation in an exponential decline of groundwater recharge with depth, and groundwater level fluctuations are rather caused by a pressure equilibration than a mass transport.

This method of mean groundwater level fluctuations results in an underestimate of groundwater recharge, because it does not consider natural groundwater fluxes.

## 4.2. LYSIMETER STUDIES

Lysimeter studies are known since the end of the 17th century. The prime concept in using this tool was to better estimate actual evapo-transpiration and through-percolation; through-percolation and precipitation have been volumetrically measured in lysimeters, and EP or ET was equated by the difference of both. Later, lysimeter studies have been directed to investigate transport as well as physical, chemical, and microbial transformation processes of pollutants in the vadose zone. No doubt, as compared with the bulk determination of groundwater recharge through water balances or discharge analysis, lysimeter studies give a more detailed insight in the role of geology, soil, vegetation, and climate factors on recharge mechanisms.

Lysimeter investigations, however, generally suffer from

- high construction and maintenance costs,
- the small scale as compared to inhomogeneities in soil/sediment fabrics,
- the missing transfer functions to reliably apply lysimeter results in the catchment scale (Blöschl & Sivapalan, 1995), and
- the mostly non-representative vegetation cover.

Therefore, today lysimeter studies mostly aim to investigate transformation processes, being more complex than in the microcosm or laboratory scale, but still not as complex as under field conditions.

There exist two basic types of lysimeters:

- Natural and
- Constructed lysimeters.

*Natural lysimeters* often refer to springs with a known catchment size, discharging perched groundwater of a known areal extent. Such springs occur at the outcrop of inclined low permeable layers, mostly clays or marls, which are supposed to have negligible leaching losses to the underground and no diffuse groundwater consumption by evaporation along the outcrop area. The catchment of such springs is usually high above the valley, small in extent ( $<1 \text{ km}^2$ ) and often linked to inselbergs. Such natural lysimeters can only be used to set up input/output relations; process-oriented studies are difficult to execute.

In recent times, natural lysimeters have been constructed in the field by drilling horizontal full-tubes with an open end at different depths from a vertical shaft into the percolation zone (Fig. 4.36) (Seiler et al., 2002; Juren et al., 2003). At the open end tensiometers, TDRs or suction cups can be inserted to study quality and flow of water in the vadose zone. These lysimeters do not disturb soil/sediment fabrics, but influence natural water contents, hence, local percolation do not need any adaptation time to start investigations, but suffer from not well-known boundary conditions and intrinsic hydraulic parameters to study input/output relations or to set up a water or matter balance, but refer to investigation scales exceeding the reference elementary volume (REV).

In fissured and karst rocks, cave or tunnel studies apply as natural lysimeters (Veselic & Cencur Curk, 2001; Grasso et al., 2003). Such studies allow quantifying real processes, without knowing the real hierarchical process structure and boundary conditions. Linking these observations with discharge, spring, and groundwater observations allows setting up a reliable conceptual model on recharge, flow, and transport mechanisms in the percolation zone (Grosso et al., 2003).

The *constructed lysimeter* consists of a cylindrical pot, mostly 1.5 m long and 1.13 m in diameter, with open surfaces on the cylinder top and base. Either the cylinder is filled up with sediments, ending on top with a soil cover, or the cylinder was used to dig out a cylindrical undisturbed monolith. Such lysimeters can be used to study the influence of small plants on percolation, transport, and transformation. To investigate the influence of trees on percolation, lysimeters must have surfaces of several  $100 \text{ m}^2$  (e.g., Castricum/Netherlands and St. Arnold/Germany), which are rectangular in size and 3–5m deep; sediments and soils are always filled into such giant lysimeters.

- Lysimeter lengths are usually selected according to the thickness of the effective root zone, depth of plant rooting, and the thickness of the closed and open capillary fringe (Fig. 4.6) in the studied sediment,
- Large lysimeter diameters approach much better the REV of the vadose zone. A diameter of 1.13 m, corresponding to  $1 \text{ m}^2$  surface, makes sense for an easy data comparison but not for the representativeness of results for a landscape,
- Lysimeter cylinders usually surpass the ground floor by some centimeters, hence, overland-flow ( $D_0$  in eqs. 4.2 and 4.3) is suppressed and consequently enhances infiltration in coarse grained and ET in fine-grained soils/sediments.

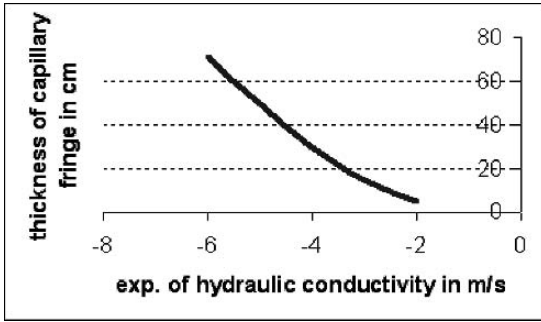


Figure 4.6. Thickness of the capillary fringe as a function of the hydraulic conductivity of unconsolidated rocks

- The 1-m<sup>2</sup> soil/sediment surface is bare, covered with grass, or used for crops. To avoid any island or oasis effects, the vicinity of the lysimeter should be cultivated as the lysimeter itself, which is not easy to realize.
- Within lysimeters, any lateral flow ( $D_l$  in eqs. 4.2 and 4.3) is suppressed; therefore, lysimeter results always refer to a forced one-dimensional infiltration and percolation process, which is characteristic for flat lands but not for any three-dimensional percolation flow in hilly terrains, where lateral flow comes into the game (section 3.5).
- The outflow on bottom of lysimeters always happens through a capillary fringe, which might become thick in fine-grained and thin in coarse grained, unconsolidated sediments; this capillary fringe controls the percolation/storage process within the length of the lysimeters in terms of speeding up fluxes in wet and suppressing the capillary rise of water ( $H_c$  in eq. 4.26) in dry seasons. This capillary fringe can be broken, but not completely eliminated, introducing a coarse grained porous drainage (sands and gravels) or suction plates.

Knowing all these influences on water storage and percolation, lysimeters have respectively been modified in size and equipment according to the investigation goal.

- Groundwater tables and suction plates have been introduced at the lysimeter base to rule in respectively out the influence of any groundwater table on percolation and capillary rise of water.
- Some are staffed with tensiometers, TDRs, and suction cups in replicates at different depth to better assess the role of inhomogeneities on water and matter fluxes and to better follow dynamic transformation processes.
- More sophisticated lysimeters are mechanically or electronically balanced and thus refer to changes of storage ( $\Delta S$  in eq. 4.2) and further allow a better approach to dew formation, effective precipitation, and evaporation.

Lysimeters are mostly transported from a place of interest to an experimental side. These lysimeters are either filled with unconsolidated sediments, which still compact at the beginning of the investigation, or have been digged; in both cases, the water content

from the side of interest does not fit with the one of the experimental side, because of non-representative precipitation distributions and quantities. As the unsaturated hydraulic conductivity changes approximately with the square of the porosity, both the unstable porosity condition and the not yet adapted water contents express in transient flow. From this point of view, lysimeter experiments need months or years to achieve equilibrium conditions in soil/sediment fabrics or water contents, before delivering reliable local results. As percolation velocities are rather low (section 3.4), it takes in 1.5-m long lysimeters about 1–2 years to reach water contents, which are representative for the climate conditions at the lysimeter station

Taking all limitations, manipulations and eqs. 4.2 and 4.3 into account, it can be stated that

- Constructed lysimeter results refer only to unconsolidated rocks,
- Non-weighable lysimeters without suction plates deliver reliable results only on a long run of time, when  $\Delta S$  can be taken as constant; they apply only for through-percolation or bulk process studies in areas with a groundwater table close to the surface;
- Weighable lysimeters provide good results on changes of  $\Delta S$  and thus apply also for short-term water balances; all liquid, solid, and gas gains and losses can be determined with a precision of 0.1 mm, if equipped with respective probes on top, base, and within the column of the lysimeter. They contribute to detailed process studies;
- Lysimeters with a fixed water table deliver similar results like weighable lysimeters;
- All lysimeter results exaggerate groundwater recharge or under/overestimate evapo-transpiration according to soil/sediment fabrics;
- Most lysimeters suppress capillary rise in extended dry periods, because it does not refer to an 'inexhaustible' groundwater source and
- The transformation of local lysimeters results to the landscape is semi-quantitative.
- Natural lysimeters allow a better qualitative coupling with catchment results on percolation and matter transport than traditional lysimeters do.

Traditional lysimeter studies produce excellent relative values on the water balance, and results are generally expressed as infiltration/precipitation or ET/precipitation ratios. The transfer of these data to the landscape leads often to an overestimation of groundwater recharge and an underestimation of the actual ET. Nevertheless long-term and relative data from lysimeter studies bring a good orientation in groundwater recharge studies.

In a non-weighable lysimeter,  $P$  and  $D_G$  is measured volumetrically, and  $ET$  is calculated assuming a constant  $S$ ; this assumption approaches reality in wet climates for time series of more than half or one year; for shorter time intervals, results are questionable. In semi-arid and arid climates  $S$  can become so significant that no percolation occurs; therefore, lysimeters studies apply in arid (dry-land) areas only for special goals, for example, Wadi infiltration into the subsurface (Issar et al., 1984).

From lysimeter studies result a good estimate on groundwater recharge for different soils/sediments and vegetation covers. As expected, these data have a high variability, because they neglect REV, special fabrics, preferential-flow, local climate and soil hydraulic features, inter-flow and overland-flow. Hence, all numbers reported in Table 4.8 can only be considered as an orientation.

Systematic evaluation of lysimeter studies show that there exists for selected sites (eq. 4.23) an approximate linear relation between yearly means of precipitation and groundwater recharge

$$R' = m(P - c) \quad (4.23)$$

In this equation,  $c$  and  $m$  are constants, and any correlation coefficient becomes close to one if vegetation is missing, but very low if needle trees grow on lysimeters; for leaf trees and agriculture crops, this relation stretches in between these extremes. Shorter time discretisations than one or half a year enlarges significantly the error bar.

In Table 4.9, the parameters  $c$  and  $m$  from lysimeter studies in Germany are listed. From these data, it can be seen that precipitation, geology, and vegetation are not the only influencing parameters; others intervene such as rain intensities,

*Table 4.8.* Groundwater recharge ( $R'$ ) as referred to precipitation ( $P$ ) in typical sediments out of a temperate climates ( $P = 500\text{--}700$  mm/year)

Sediment	$R'/P$ in %	Sediment	$R'/P$ in %
Fluvial gravel	40–60	Loamy sand	31–40
Dune sand	75	Loam	20–23
Sand	45–55	Loamy clay	8–10

All sediments without vegetation cover.

*Table 4.9.* Lysimeter constants (eq. 4.23) from groundwater recharge studies in Germany (Matthess & Ubell, 1983)

Sediment/Place	Vegetation	$m/c$	Sediment/Place	Vegetation	$m/c$
Sand/Senne	grass	0.784/–162	Sand/Steyerberg	Cereals + sugar beet	0.784/–220
Sand/Norderney	grass	0.859/–108	Sand/Barme III	Cereals + sugar beet	0.623/–182
Sand/St Arnold	grass	0.621/–146	Sand/St. Arnold	pinus	0.858/–443
Loamy sand/Berlin	grass	0.734/–386	Sand/Dortmund	pinus	0.582/–296
Sandy loam/Infeld	grass	0.311/–533	Loamy sand/Raumental	cereals	0.960/–473
Loess/Senne	grass	0.546/–67	Loamy sand/Berlin	bare	0.770/–226
Loess/Dortmund	grass	0.912/–306	Loess/Bonn	Cereals + sugar beet	0.289/–185
Clay/Senne	grass	0.521/–296			

Table 4.10. Monthly ET as referred to the yearly mean in percent (1967–1971) from sand in Eberswalde/Berlin (Dyck, 1980)

Month												Vegetation	Sediment
I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII		
0.8	1.9	8.7	10.5	15.7	17.2	13.4	10.8	10.6	6.9	2.5	1.0	Bare	Sand, fine grained
0.6	1.6	4.4	10.1	17.1	19.0	19.6	11.0	8.6	5.1	2.3	0.6	Grass	Sand, fine grained
0.7	1.8	6.3	9.2	14.6	16.5	15.5	11.3	10.5	6.8	4.2	2.6	Pine	Sandy loam

summer to winter rain ratios, preferential-flow, disturbed fabrics of sediments, and many more.

Taking the monthly ET as related to the yearly mean for different land use close to Berlin delivers the data in Table 4.10. From this table, it can be seen that in comparison to bare soils/sediments grassland both reduces and increases ET in the non-vegetation, respectively the vegetation period.

### 4.3. HYDRAULIC METHODS IN THE VADOSE ZONE

There exist sharp water–air and water–solid interfaces in the unsaturated zone. This is basic to apply the classical equations on filter flow also to percolation. In contrast to saturated flow in aquifers, however, capillary forces intervene in unsaturated flow and cause some modifications of Darcy’s law (eq. 3.1).

Flow in the unsaturated zone of unconsolidated and decompressed media is directed perpendicular to bedding; by contrast, groundwater flow mostly parallels bedding. This difference in flow orientation toward bedding expresses in a stronger transverse flow component and hydrodynamic dispersion (Behrens et al., 1980; Seiler & Baker, 1985) in the percolation zone than in aquifers (Seiler, 1985).

Similar to groundwater flow in bi-porous media, there exists in the unsaturated zone a quick (preferential-flow) and slow flow (matrix-flow) component, which usually expresses in the unsaturated zone in greater differences of flow velocities than in aquifers; this is related to the fact that in the vadose zone hydraulic gradients can reach from close to zero till one and hydraulic conductivities may differ by several orders of magnitude; in general, this range of gradients and hydraulic conductivities is smaller in aquifers. As preferential-flow is not yet well quantifiable (section 3.4) on the catchment scale and as the vadose zone is hydraulically more inhomogeneous than the groundwater zone, mathematical or numerical approaches on percolation are more difficult to achieve than on groundwater movement.

According to climates and soil/sediment fabrics, matrix-flow in the unsaturated zone ranges from few meters to less than few millimeters per year (section 3.4). In humid areas, it is dominantly directed vertical down and in semi-arid to arid climates also vertical up according to the duration of drying and wetting cycles. In all climate zones, however, percolation can transform along beddings or ground-ice into



inter-flow or perched groundwater, if high differences in the unsaturated hydraulic conductivities occur along these interfaces (section 3.5).

Infiltration of precipitation generates in the vadose zone water storage, matrix- and preferential-flow (Beven & Germann, 1982; Nielsen et al., 1986; Glass et al., 1989; Kung, 1990a, 1990b; Baker & Hillel, 1991). Preferential-flow interacts with matrix-flow by mass and ion exchange and often transforms partly or completely into inter-flow; it typically occurs in the upper part of the vadose zone of unconsolidated rocks and can by-pass the barrier function of soils for contaminants.

The volumetric water content (eq. 4.24) in unsaturated sediments refers to the ratio water volume  $V_w$  and the sum of soil/sediment and pore volumes ( $V_T$ )

$$\theta = \frac{V_w}{V_T} \geq 0. \quad (4.24)$$

Water saturation ( $S'$ ) (eq. 4.25) refers to the ratio water volume ( $V_w$ ) and void volume ( $V_v$ )

$$S' = \frac{V_w}{V_v} \leq 1$$

or (4.25)

$$\theta = \frac{S' V_v}{V_T}$$

With respect to the water content in the vadose zone two types of flow occur in the unsaturated zone:

- Gravitational flow vertical down dominates at water contents close to or higher than field capacity and
- Capillary flow in potentially all directions prevails at water contents below field capacity.

In the vadose zone, the dominance of gravitation flow is limited in depth reach (section 3.4) except artificial groundwater recharge through rivers and ponds intervene; in contrast, capillary-flow occurs all over the unsaturated zone.

In water saturated sediments no capillary forces exist. Expressing the capillary forces (eq. 4.26) by the capillary head ( $H_c$ ) and referring it to the potential energy per water weight results in

$$H_c = \frac{-2\sigma \cos\beta}{\rho_w r g}. \quad (4.26)$$

$\beta$  expresses the angle of the water meniscus against the capillary wall (angle of internal friction). For fresh-water at ambient temperatures ( $\rho \approx 1 \text{ tm}^{-3}$ ) the height of capillary rise can be approximated by (eq. 4.27)

$$H_c = \frac{0.15}{r}, \quad (4.27)$$

because the surface tension of water ( $\sigma$ ) at 0°C and 30°C (common range of subsurface water temperatures) is  $75.6 \times 10^{-3} \text{Nm}^{-1}$  and  $71.2 \times 10^{-3} \text{Nm}^{-1}$  respectively, the specific weight  $9.998 \times 10^2 \text{kgm}^{-3}$  and  $9.956 \times 10^2 \text{kgm}^{-3}$  respectively, hence, differ little, and  $\cos \beta$  is close to 1. In eq. 4.27,  $H$  and  $r$  express in cm.

In this approximation, the pore radius ( $r$ ) represents for sediments and soils a weighted or equivalent capillary radius. Small pores are characteristic for uniform fine-grained and little-sorted coarse grained sediments; in contrast, large pores stand for uniform coarse grained sediments. Small pores pull water with higher capillary forces and often at higher hydraulic conductivities against gravity than large pores do; therefore, in many exposures with sands and clays, the fine-grained clays always appear wetter than sands or gravels and the nomenclature of high and low conductivity media differ from saturated to unsaturated conditions (Fig. 3.10).

Equation 4.26 can also be used in combination with tensiometer experiments to approximate the pore size distribution of sediments under wetting or draining conditions (Figs. 3.9 and 4.9).

The height of the *capillary fringe* above the groundwater table is negatively correlated to hydraulic conductivities of an aquifer; it approximates some centimeters to few decimeters in gravels, half to one meter in medium to coarse-grained sands (Fig. 4.6) and an increasing number of meters from fine-grained sands to silts and clays. Finally, capillary fluxes (Fig. 4.7), which are co-responsible for crop yields (Fig. 4.8), diminish with an increase of the distance of the capillary fringe.

*Field capacity* ( $\theta_{fc}$ ) refers to a maximum water content retained in soils/sediments against gravity forces over the run of 3 days. At water contents exceeding field capacity, gravity drainage dominates, below it, gravity drainage continuous, but

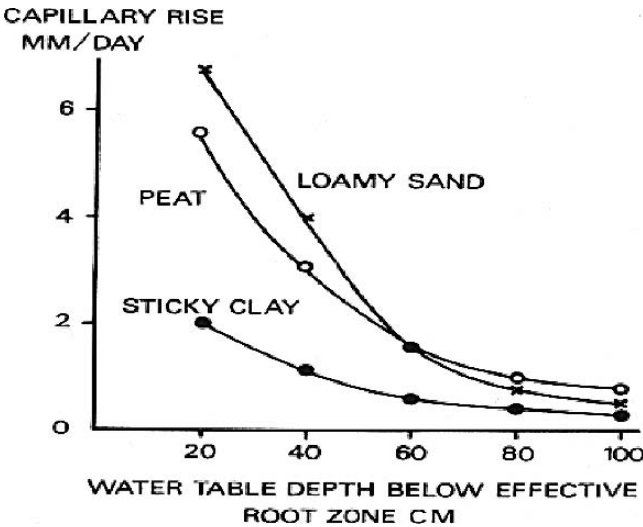


Figure 4.7. Capillary rise rates as a function of depth of the water table beneath the effective root zone (Rijtema, 1968)

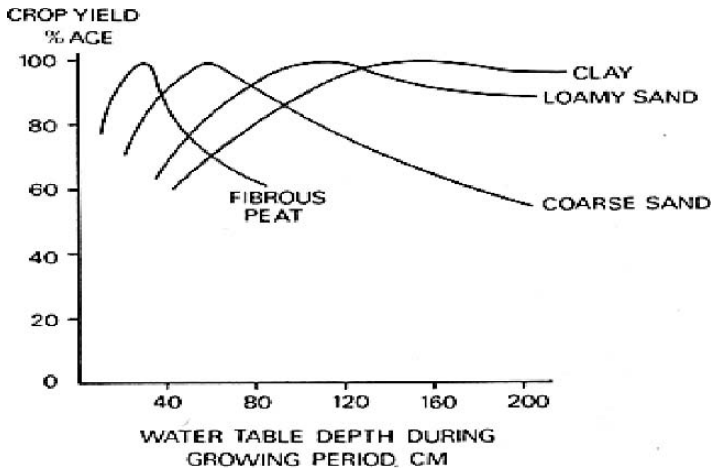


Figure 4.8. Crop yields as a function of water table depth (Wesseling, 1958)

becomes less efficient, because capillary forces intervene (eq. 4.26). From this definition, it becomes clear that the field capacity concept is to some extent vague, but nevertheless proved a useful tool in unsaturated zone hydrology.

Water content at field capacity refers to an average suction of 100 hPa and covers the range from 50 (uniform sand) to about 150 hPa (clay). Water contents at field capacity range from about 5 vol.% in Quaternary gravels, 8 vol.% in uniform coarse, 10 vol.% in uniform medium, 20 vol.% in uniform fine grained sands and rises to about 45 vol.% in heavy clays. Young organic matter in soils/sediments binds as much water at field capacities as clays do; montmorillonites develop higher water contents at field capacities than illites. A discussion on methodologies to determine field capacities on the field and laboratory scale is presented by Cassel and Nielsen (1986).

The water content at the *permanent wilting point* ( $\theta_w$ ) refers to suctions, at which plant roots cannot take up any more water; hence, plants wilt and then may die. This suction is assigned to about 15 bar but may reach somewhat higher or lower values according to plant physiologic properties.

The *residual water content* ( $\theta_r$ ) occurs at a hydraulic conductivity of “zero” or by another definition, when the slope of the water/soil/sediment tension characteristic approaches a slope of zero; it often is equated with the water content at the wilting point.

Classical hydraulic methods to calculate percolation are based on the modified Darcy law, also known as the Richards equation (eqs. 3.1 and 3.2) with the total pressure head (eq. 4.28)

$$\psi = H_c + H_g + H_o \quad (4.28)$$

In eq. 3.1, the hydraulic conductivity depends upon water content  $[K(\theta)]$  or water suction  $[K(\psi)]$ ; both these functions are difficult to determine in place or representatively by laboratory experiments and undergo a hysteresis under wetting or drainage conditions (Fig. 4.9); this hysteresis results from pore geometries, which require more energy for water to withdraw than for water to be replaced. Therefore, an empirical solution (eqs. 4.29 and 4.30) for an average  $K(\theta)$ -function has been proposed by van Genuchten (1980), which refers to effective water saturation ( $S_e$ ) of the soil or sediment

$$S_e = \frac{\theta - \theta_r}{\theta_s - \theta_r} = [1 + (\alpha H_c)^n]^{-m} \tag{4.29}$$

$$K_{S_e} = K_{S_{at}} (S_e)^\gamma \left[ 1 - \left( 1 - S_e^{\frac{1}{m}} \right)^m \right]^2 \tag{4.30}$$

$s_{at}$  = hydraulic conductivity at  $S_e = 1$

$\gamma$  in eq. 4.30 is often taken to be 0.5 (Mualem, 1976), but may rise up to 2;  $\alpha$ ,  $n$ , and  $m$  refer to the shape of the water retention curve and  $m$  and  $n$  interact approximately as eq. 4.31:

$$m = 1 - \frac{1}{n} \tag{4.31}$$

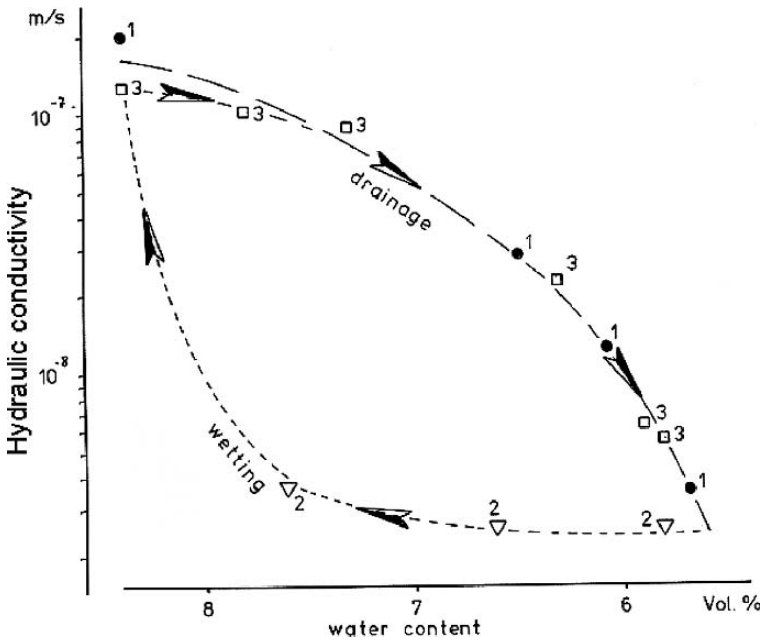


Figure 4.9. Hysteresis in hydraulic conductivities in the percolation zone according to wetting or draining conditions. Quaternary gravels of south Germany

The van Gnuchten (1980) approach does not consider any hysteresis in unsaturated hydraulic conductivities (Fig. 4.9); it formulates an average wetting/drainage behavior.

Table 4.11 presents commonly known ranges of hydraulic conductivities at saturation and at field capacity (Mualem, 1976).

Applying eqs. 3.1 and 3.2 for any numerical calculation of percolation requires

- an appropriate conceptual model on percolation,
- an estimation of the hydraulic functions, and
- measurements of suctions and water contents under field conditions over the run of minimum 1 year (Figs. 4.10 and 4.11).

These measurements can be performed continuously using fixed point tensiometers for the registration of capillary suction (Fig. 4.10) and TDRs to determine water contents (Fig. 4.11).

In hydraulic models on percolation, the real range of porosities, unsaturated hydraulic conductivities, water contents, and water tensions in an REV can only be approached; therefore, the real system is generally characterized as a media with statistically equivalent properties. As a consequence, for the simulation of percolation and the determination of groundwater recharge, conceptual models suppose uni-directed fluxes, for example, vertical down and homogeneous equivalent hydraulic properties. This approach leads to compartment or box models (Belmans et al., 1983), each with equivalents properties.

The hydraulic functions for REVs of the vadose zone are in temperate climates a good approach, but often do not equivalently apply under semi-arid and arid climates. In permafrost areas additionally to capillary and gravitation forces, gradients related to the formation of ground-ices also influence the direction of fluxes; these crystallization induced gradients lead in the neighborhood of ground-ices to a shrinking of unconsolidated and decompressed sediments by dewatering and above ground-ices to a respective doming. All these specific boundary conditions in very cold and warm climates can hardly be controlled by means of statistical evaluations of suction and water content measurements and therefore, often remain theoretical.

Analytic models on percolation offer first cuts of flow and transport in the unsaturated zone; numerical models can provide more real world results but require more detailed data sets than analytic models need. As such voluminous data sets often

*Table 4.11.* Ranges of hydraulic conductivities of some uniform soils/sediments at a water content at field capacity [modified after Mualem (1976)]

Material	Hydraulic conductivity in m/s	
	At saturation	Close to field capacity ( $\theta_{fc}$ )
Clay	$10^{-8}$ – $10^{-7}$	$10^{-8}$ – $10^{-7}$
Loam	$10^{-7}$ – $10^{-6}$	$10^{-7}$ – $10^{-6}$
Fine sand	$10^{-6}$ – $10^{-5}$	$10^{-7}$ – $10^{-6}$
Medium sand	$10^{-5}$ – $10^{-4}$	$10^{-6}$ – $10^{-5}$
Coarse sand	$10^{-4}$ – $10^{-3}$	$10^{-6}$ – $10^{-4}$
Gravel	$10^{-3}$ – $10^{-2}$	$10^{-5}$ – $10^{-4}$

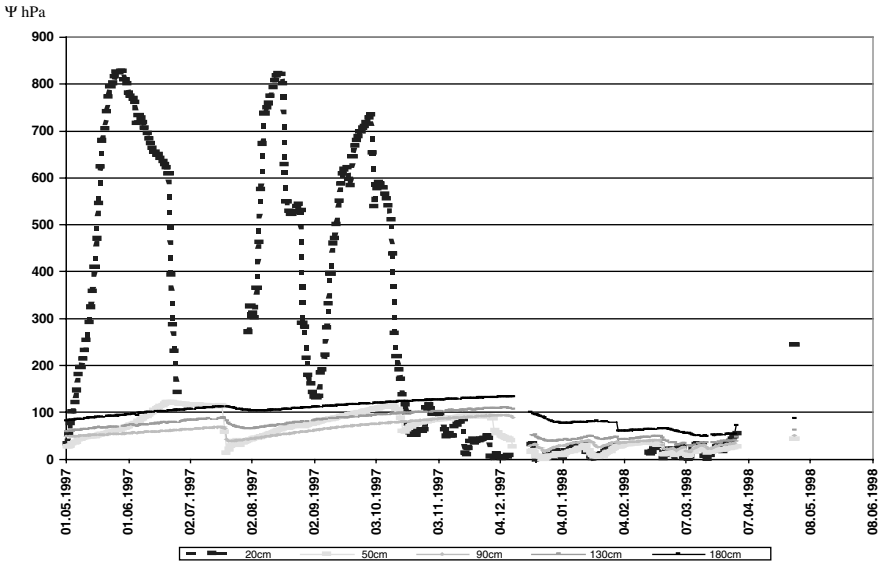


Figure 4.10. Changes of suction in depths between 20 cm (black with great variations) and 180 cm (black with little variations), measured during one vegetation period, followed by a bare soil period in gravely sands of Scheuern, South Germany. Measuring period June 1, 1997, to June 6, 1998

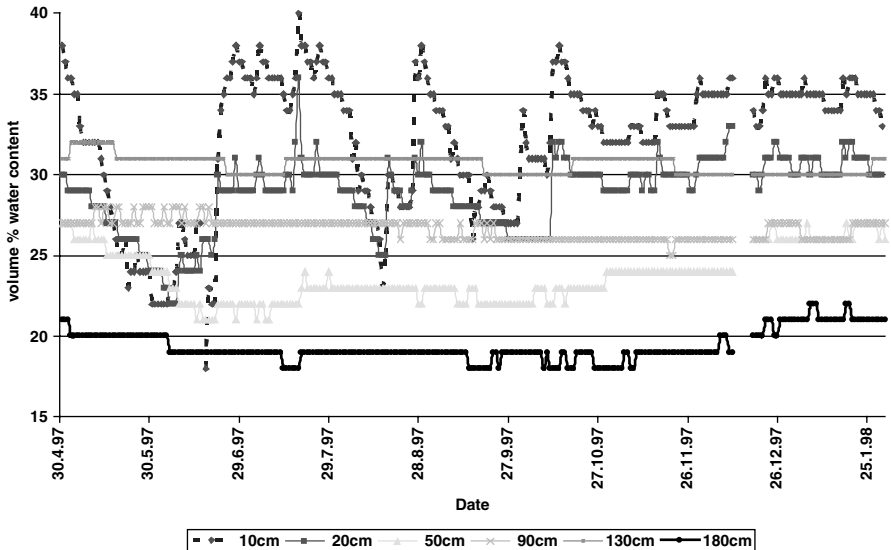


Figure 4.11. Changes of water contents in depths between 10 cm (black with great variations) and 180 cm (black with little variations), measured during one vegetation period, followed by a bare soil period in gravely sands of Scheuern, South Germany. Measuring period April 30, 1997, to January 25, 1998

do not exist, but real world approaches are the choice, Monte Carlo simulations as a special type of stochastic simulations are applied by re-running a deterministic model with probabilistic spatially parameter distributions and boundary conditions; the results of all these runs characterize a range of coincident and excluding outcomes, which have to be assessed with real world observations.

Typical parameters required for vadose zone numerical models are

- Bulk and particle densities,
- The hydraulic conductivities from saturation till the residual water content,
- Water contents and suctions at field capacity and at the wilting point,
- Effective and total porosities for both saturated and unsaturated conditions,
- Time series of water suctions and water contents at fixed places,
- Climatologic data to determine evapo-transpiration,
- Infiltration and overland-flow.

All these data underlie scale and heterogeneity influences and have to be transferred into representative data of a representative elementary volume (REV).

Considerable discussion exists as to the validity of many assumptions and theories to model percolation, and sometimes field measurements do not contribute to a satisfactory understanding of physical, chemical, and microbial processes in the unsaturated zone. As a consequence, prediction and forecasting of flow and much more of transport and transformation in the unsaturated zone is often not transferable. However, if based on reliable conceptual models, mathematical models contribute much to control the intrinsic logic and the data set applied, to launch for further measurements and developments.

As preferential-flow is still difficult to quantify (section 3.4) and, therefore, is mostly not considered, all hydraulic methods to determine groundwater recharge or percolation velocities refer only to matrix-flow and often result in an over- or underestimate of both groundwater recharge and percolation velocities.

To reduce the uncertainty in analytic and numerical modeling, artificial and environmental tracer methods have been applied to support and improve hydraulic evaluations (section 4.4).

If percolation velocities have been measured by means of tracer experiments (section 4.4.4), the apparent flow velocity ( $v_a$ ) (eqs. 4.32 and 4.33) refers to the filter velocity ( $v_f$ ), groundwater recharge ( $R'$ ) and the water content ( $\theta$ ) by

$$v_f = v_a \theta = R' \quad (4.32)$$

or

$$v_a = \frac{R'}{\theta}. \quad (4.33)$$

This equation implies that no dead end pores or stagnant water occurs; otherwise an effective water content lower than the measured water content must be introduced.

Knowing  $\theta$ , which can be determined with neutron probes, TDRs or gravity methods and the specific groundwater recharge of the catchment (eq. 4.33), matrix-flow velocities can be calculated and then be compared with measured flow velocities. Table 4.12 shows results of such a comparative study in Quaternary loess,

Table 4.12. Apparent percolation velocities ( $v_a$ ) as calculated through water content ( $\theta$ ) and groundwater recharge ( $R'$ ) and from tracer experiments of the same test site

Site	Lithologic/soil unit	Depth cm b.g.s.	$V_a$ in m/year	
			$R'/\theta$	Tracer experiment
2-18	Loess	10	0.5	0.09
		10		0.80
		10		0.31
		20	0.5*	1.10
		90	0.5	0.60
		90		0.67
9-3	Tertiary sand with clay lenses,	10	0.6	0.44
		10		0.44
		10		0.49
		10		0.88
		50	0.4*	1.10
		50		16.64
12-9	Tertiary fine to medium grained sand	180	1.0	1.24
		10	0.7	0.34
		20		0.78
13-16	Tertiary fine to medium grained sand	20	0.6	0.73
		20		0.62
		10	0.7	1.14
		10		0.27
		20	0.7	0.24
	90	0.4	0.78	

For the variations of water contents see Table 4.16.

\*preferential-flow was not recognized by hydraulic calculations, but by tracer experiments.

sand with clays, and Tertiary sands in South Germany. Both the water balance/water content and the artificial tracer method result in similar flow velocities; tracer experiments, however, may indicate higher apparent flow velocities than hydraulic calculations do (Table 4.12), because tracer results are independent from total as compared to effective water contents and may be influenced by preferential-flow.

#### 4.4. ISOTOPE AND CHEMICAL TRACERS

Water balance and hydraulic methods sometimes fail in determining groundwater recharge in extreme climates (arid, semi-arid, or cold), because of missing knowledge on the catchment extent, on reliable input/output and intrinsic data, hysteretic hydraulic functions, little knowledge on transient hydraulic conditions,



in-homogeneities, and on transfer functions to overcome scale problems; hence, they do sometimes not fit the precision required for a good estimate of groundwater recharge. Under such conditions, tracer methods offer a valuable support for traditional groundwater recharge studies.

In hydrology, tracer methods are often applied, because they are basically an independent method from hydraulics on filter flow and, therefore, enable to complement hydraulic methods on calculations of subsurface flow, groundwater recharge, or mixing of waters of different origins (e.g., in the case of river-infiltration).

Tracer investigations deliver valuable information on subsurface through-flow systems, as far as

- A good conceptual model has been adopted,
- The tracer input, transformation, and output functions are known,
- The geochemical behavior of the tracer in the subsurface is quantitatively understood, and
- The tracer amount was balanced from the input to the output.

Tracer evaluations refer to geometries of break-through-curves (TBT) at the system's output as a response to the geometry of an input signal. TBTs are evaluated (eq. 4.63) in terms of fluxes, flow directions, hydrodynamic dispersion, and contribute together with water fluxes to tracer balances (eq. 4.65).

Most hydraulic exercises provide local and instantaneous information; in contrast, artificial tracing leads to time integrated and sectorial, and environmental tracers to time and space integrated information on the catchment scale; however, it should be kept in mind that environmental tracers often characterize a sequence of different REV's, hence, do not represent homogeneous answers to any tracer input. Therefore, a combination of tracer and hydraulic methods is recommended for those groundwater areas, in which long-term climate and discharge observations are missing or scarce in number or where scale problems play an important role; such a combination of methods supports any elaboration and assessment of sustainable groundwater management and protection strategies much better than one method can do all alone.

Among tracer techniques, one distinguished between artificial and environmental tracer methods.

- Artificial tracers (in general chemical, dye, particle, and activable tracers) are applied to receive information along individual subsurface flow paths, groundwater motion, and hydrodynamic dispersion. Artificial tracing is always performed parallel to the potential field; therefore, the hydraulic and the traced flow vectors coincide.
- Tracing by environmental indicators starts all over the catchment, however, always nearly perpendicular to the potential field; therefore, the hydraulic and traced flow vectors do not necessarily coincide.

All tracing contributes to the determination of flow vectors (eq. 4.34) according to

$$\vec{v}_t = \frac{ds}{dt}, \quad (4.34)$$

in contrast, hydraulic evaluations (eq. 4.35) lead to

$$\vec{v}_a = \frac{k_f}{p} \frac{dH}{ds}. \tag{4.35}$$

As far as the traced and hydraulic flow vectors do not coincide, flow velocities, determined by means of isochrones, become in the discharge area too small and are exaggerated in the recharge area.

In hydrology, environmental indicators receive a characteristic signature in well-known sections of the water cycle (Fig. 4.12); these sections may be positioned above the earth’s surface, in the atmosphere ( $^2\text{H}$ ,  $^{18}\text{O}$ ,  $^3\text{H}$ ,  $^{14}\text{C}$ ,  $^{39}\text{Ar}$ ,  $^{85}\text{Kr}$ ,  $^{36}\text{Cl}$ ) or in the subsurface ( $^{15}\text{N}$ ,  $^{13}\text{C}$ ) or potentially everywhere ( $^{34}\text{S}$ ,  $^3\text{He}/^4\text{He}$ ,  $\text{Cl}$ ). Some of the environmental tracers are radioactive ( $^3\text{H}$ ,  $^{14}\text{C}$ ,  $^{39}\text{Ar}$ ,  $^{85}\text{Kr}$ ,  $^{36}\text{Cl}$ ), others stable

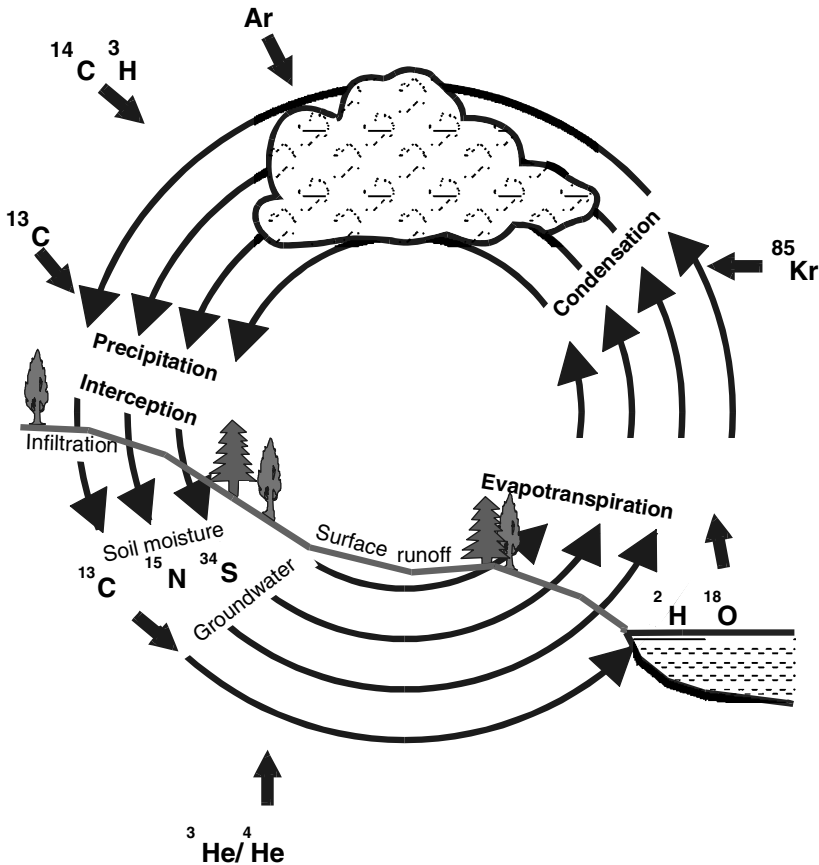


Figure 4.12. The water cycle and sections where some selected environmental tracers receive their typical signature, which can be interpreted in terms of mixing, MTTs and water origins

isotopes ( $^2\text{H}$ ,  $^{18}\text{O}$ ,  $\text{Cl}$ ,  $^{15}\text{N}$ ,  $^{13}\text{C}$ ,  $^{34}\text{S}$ ,  $^3\text{He}/^4\text{He}$ ), and among all these tracers,  $^2\text{H}$ ,  $^{18}\text{O}$ ,  $^3\text{H}$ ,  $\text{Cl}$ ,  $^{14}\text{C}$  (and  $^{36}\text{Cl}$ ) have often been analyzed; only some of these tracers will here be discussed with respect to groundwater recharge.

Temperature cannot be considered a conservative tracer, because it is controlled by various factors; it is, however, often used as a qualitative indicator to differentiate between overland-/inter-flow and base-flow, shallow and deep groundwater, and so on.

Any tracer application to determine flow vectors are based on a non-reactive, ideal, or conservative (conservative with respect to water flow) tracer behavior. This means, the typical tracer signature, once received, does not change any more by physical, chemical, or microbial means, hence, underlies only processes, linked to subsurface water flow and refers to

- A defined magnitude of the tracer input,
- Defined hydraulic initial conditions, and
- Known boundary conditions of the flow field.

To interpret environmental tracer signals from the input to the output (section 4.4.2.2) in terms of intrinsic parameters of the through-flow system, a transformation function applies, which refers either to bulk parameters (black-box- or lump-parameter-models) for the whole system or to compartment parameters (compartment models) or to a detailed space and time distribution of hydraulic parameters (discretising models); a common characteristic of all these models is that they are balancing mass fluxes.

Before processing traditionally monitored and analyzed tracer input/output signals with mathematical models, special attention has to be paid to

- Processes at the interface atmosphere/biosphere/lithosphere, which may change the magnitude of the atmospheric input signal (sections 3.1 and 3.2),
- Geochemical particularities within the soil and effective root zone,
- The electric charges of solid surfaces in the subsurface,
- The input season, which may be governed by storage or drainage of infiltration or be characterized by enhanced or reduced chemical or microbial activities both in the effective root zone, and
- Plant-uptake, plant-release of tracers as well as any tracer export with biomasses through harvesting.

All these processes may produce tracer concentration changes aside from mere hydrodynamic concentration changes.

At the interface *between atmosphere/biosphere/lithosphere* solute matter deposition and retention on receptors is enhanced. Solid matter can be deposited (e.g., dust) both in dry and in wet form, to be later flushed by rain or fog deposition. As the surface accumulated water then evaporates, the solute matter accumulates in the residual. In contrast, the heavy stable isotope species initially enrich in the residual surface water as evaporation proceeds, following the law of the Raleigh distillation (eq. 4.36), are at later stages of the evaporation conserved; hence, the evaporate isotope composition equals that of the residual water and then finally is completely lost, when the surface water pool on receptors is completely drying out

and leaving behind the residues of accumulated solid matter.

$$\frac{R}{R_0} = \left(\frac{N}{N_0}\right)^{\alpha-1}$$

*or · in ·  $\delta$  - notation*

$$\delta = (+\delta_0) \left(\frac{N}{N_0}\right)^{\epsilon} - 1 \quad (4.36)$$

In a more general way, evaporation increases the concentration of solute matters in water more than fractionation of the water isotopes does. Both, however, are related processes and provide, if correlated, a clear qualitative and often also quantitative answer on water losses by evaporation.

In the *soil/sediment zone*, water is preferentially stored by capillary forces and to some extent by sorption at surfaces of organic matter and clay minerals, and it becomes charged with C- and N-gases from the microbial decay of litters, thus increasing the chemical reactivity of percolation water. All these processes contribute in the effective root zone to preferential sediment weathering, in other words to the formation of new, stable minerals and the liberation of nutrients for plants and thus also to the quality characteristic of percolation and groundwater.

The bulk parameter *electric surface charge of sediments (zeta potential)* is mostly negative in the whole pH-range of silicate sediments (Fig. 4.13); however, individual minerals such as carbonates change from negative to positive surface charges when the pH drops from 11 to 10 (Fig. 4.13). As a bulk consequence for tracing, anionic indicators are better tracers in sediments than cationic indicators, because of the prevailing negative charge of most sediments, however, in carbonate and carbonate containing sediments, which characterize substantially Mesozoic and Cenozoic sediments, also anionic tracers may undergo some retardation by positively charged, carbonate islands within the sediment; such positive-charged island do not show up in the bulk number of the zeta-potential. This makes the decision to apply appropriate tracers for artificial tracing crucial.

Apart from the electric charge, tracers, applied for the determination of hydrodynamic parameters of subsurface flow, should

- not be toxic for life and health,
- have a low natural background concentration, and
- high solubility, and
- should be detectable in very small concentrations with routine analysis.
- applying them in small quantities avoids density induced flow;
- they should not interact with solid inorganic or organic phases,
- not undergo species changes by chemical and microbial processes,
- not be taken up or released by plants, and
- should not change significantly the ion balance in subsurface water as far as tracer studies are an integrative part of geochemical studies.

The *season of artificial tracing* is important for any quantitative tracer breakthrough interpretation. In temperate and tropical climates, the fluxes to groundwater are high in the non-vegetation respectively rainy season, because of a dominance of

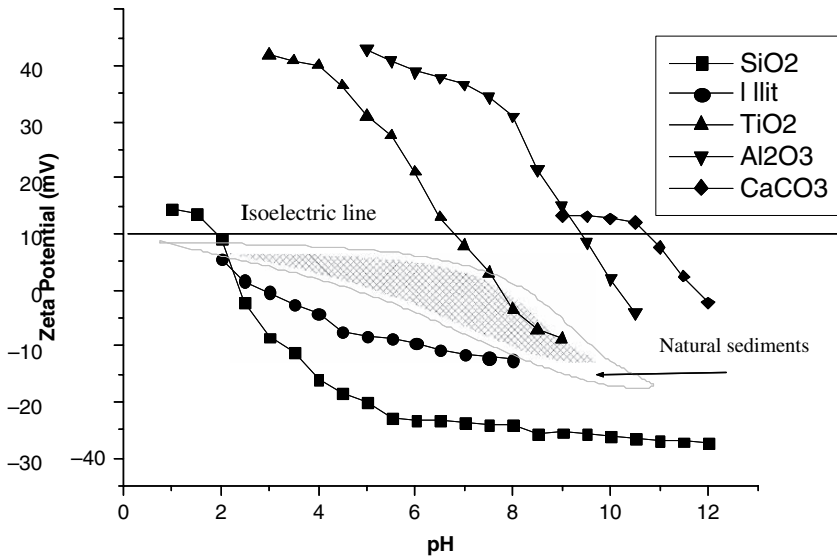


Figure 4.13. Zeta-potential of sediments and of some minerals in the pH-range of 1–11 (elaborated by Dr. H. Lang, GSF-Institute of Hydrology)

vertical down percolation; during the vegetation period, storage of soil water controls water movement in the root zone beneath the infiltration interface, because of the transpirative water losses. In semi-arid and arid climates recharge and consumption by evapo-transpiration occur also in the dry, irrigation season, whereas in the dry, non-irrigation season, water losses by capillary upraise dominate and recharge becomes negligible. In cold climates, tracer experiments in the percolation zone may become hindered during total ground freezing or favored, when ground-ice produces frost shrinking and frost upheaval in the winter season, which both open pathways for preferential short cuts between the ground and groundwater surface (section 5.5).

*Plant uptake and release* of tracers may restrict the determination of flow velocities and any tracer balance, if tracing was performed with too low input concentrations. Bromide uptake by plants is reported from Kung (1990b).

The isotopes of the water molecule ( $^2\text{H}$ ,  $^3\text{H}$ ,  $^{18}\text{O}$ ), the halogens Br and Cl and some dye tracers (Berg et al., 2001) proved to be most appropriate indicators to trace the percolation zone. If these tracers are used for artificial tracing, it is recommended that they be preferentially apply in the recharge season, which corresponds

- In temperate climates to the end of the cold and beginning of the snowmelt season when the ground is no more frozen, water contents at the infiltration interface are high, evaporation is low and thus infiltration becomes high;

- In humid tropical and semi-arid climates to the mid of the rainy season, when water contents are close to field capacity, allowing the infiltrate to move quickly away from the evaporation interface;
- In cold climates to the summer season.
- Only in arid climates, it is difficult to recommend any special season for tracing, because recharge depends on rain intensities, line and point infiltration.

The results of such tracer exercises always refer to the season or boundary condition of main groundwater recharge and lead with respect to any percolation forecast of the behavior of contaminants to a worst-case assessment. Hence, before applying such tracing results in groundwater recharge and contaminant studies, a careful pre-assessment is necessary.

#### 4.4.1 Stable and Radioactive Environmental Isotopes

Isotopes are always analyzed as isotope ratios  $R$  ( $^2\text{H}/^1\text{H}$ ,  $^3\text{H}/^1\text{H}$ ,  $^{18}\text{O}/^{16}\text{O}$ ). With routine methods, the stable isotope contents are never measured in absolute concentrations, but always refer to the per mille deviation of the isotope ratio in the sample to a standard (delta notation):

$$\delta = \left( \frac{R_{\text{sample}}}{R_{\text{Standard}}} - 1 \right) 1000 \quad [\text{‰}] \quad (4.37)$$

This definition implies that  $\delta$ -values may be positive and negative as well. The isotope content of a sample may be indicated as  $^2\delta$  or  $\delta^2\text{H}$ ; for all other stable isotopes, this notation applies respectively.

Often used standards for the stable water isotopes are shown in Table 4.13. Standard materials can be ordered from the Isotope Hydrology Section of the IAEA in Vienna.

The natural *variability of stable water isotopes* is in the range of

$$\begin{aligned} -450\text{‰} < \delta^2\text{H} < +100\text{‰} \\ -50\text{‰} < \delta^{18}\text{O} < +50\text{‰} \end{aligned}$$

This range of variation is basically due to isotope fractionation during phase transitions over large temperature intervals (see *Isotope Fractionation* in this chapter).

Table 4.13. Isotope standards commonly used to analyze stable isotope contents

Reference	Material	$\delta^2\text{H}$ ‰	$\delta^{18}\text{O}$ ‰
VSMOW	Water	0.0	0.0
GISP	Water	-189.7	-24.79
SLAP	Water	-428.0	-55.50

*Isotope fractionation* occurs as a result of physical or chemical phase transitions and becomes measurable for isotopes with high, but not for isotopes with low abundance. The greater the mass differences of isotopes the stronger isotope fractionation can develop; it finally leads to a partial separation of light from heavy isotopes, accumulating in the high respectively low energy phase and following a Rayleigh process (eq. 4.36). The greatest mass differences of isotopes exist at the beginning (hydrogen), the smallest at the end of the periodic system of elements (uranium). Therefore, and because of the analytic sensitivity of mass spectrometer analysis, stable isotopes from the beginning of the periodic system of elements are more frequently analyzed in hydrology than those from the end.

In the water cycle, two kinds of isotope fractionation can be distinguished:

- Transport fractionation, which emanates from irreversible physical processes, and
- Equilibrium or thermodynamic fractionation, which has a reversible component.

Most fractionation processes in nature belong to combinations of these two processes.

The equilibrium isotope fractionation (eq. 4.38) is quantified by the isotope fractionation factor  $\alpha$ :

$$\alpha = \frac{R_{\text{low-energy-phase}}}{R_{\text{high-energy-phase}}} > 1 \quad (4.38)$$

Fractionation factors as a function of temperatures are shown for the stable isotopes of the water molecule in Fig. 4.14; as can be seen, the fractionation factor  $\alpha$  is about 10 times higher for  $^2\text{H}$  than for  $^{18}\text{O}$  and inversely related to the temperature; hence, isotope fractionation increases with the mass difference and decreases with temperature.

This temperature dependence of isotope fractionation expresses in high and low isotope contents in precipitation

- During warm respectively cold season (*seasonal effect*),
- At low respectively high altitudes (*altitude effect*), and
- On a large scale in low as compared with high latitudes (*latitude effect*).

All these effects frequently apply in hydrology to obtain information on the origin of percolation and groundwater by places and seasons.

The stable isotope signatures of the water in the hydrological cycle originate from phase transitions in the atmosphere before infiltration and follow the world around a meteoric water line (Fig. 4.15). In the subsurface, this stable isotope composition is conservative and can only be changed under special, well-known boundary conditions (Fig. 4.15).

- The  $^{18}\text{O}$  content of the groundwater recharge changes at low temperatures ( $< 100^\circ\text{C}$ ) only by
  - mixing of waters from different origins,
  - evaporation, and
  - excess  $\text{CO}_2$ , bubbling through the water, like in volcanic areas, depleting  $^{18}\text{O}$  in subsurface water.

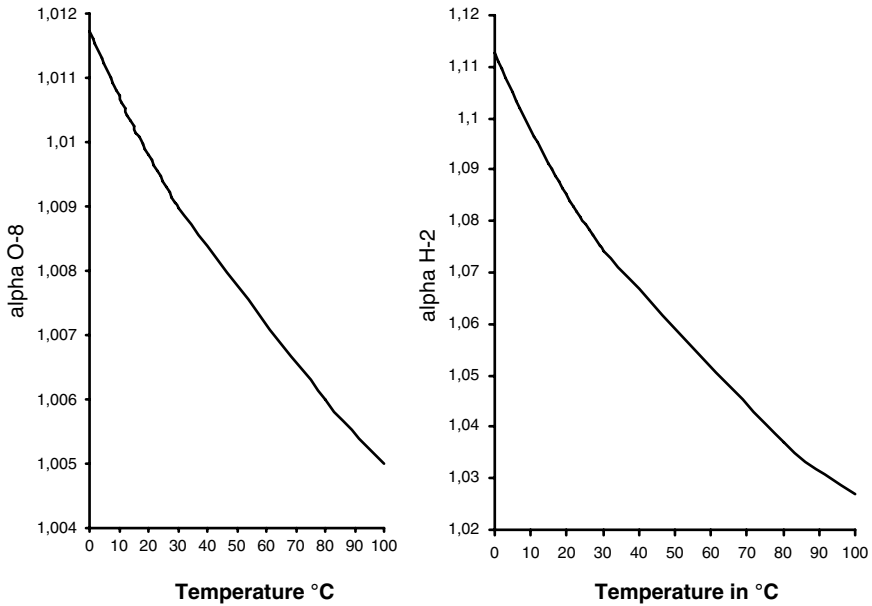


Figure 4.14. Equilibrium fractionation factors alpha for the isotope ratios  $^2\text{H}/^1\text{H}$  and  $^{18}\text{O}/^{16}\text{O}$  as a function of temperature

- In contrast, the oxygen isotopes of the water molecule may exchange in medium and high enthalpy systems with mineral oxides, which always have higher  $^{18}\text{O}$  contents. Therefore, exchanges with mineral oxides always increase the  $^{18}\text{O}$  content of the subsurface water (water rock exchange in Fig 4.15).
- The  $^2\text{H}$  content of groundwater does also not change its isotope signature after infiltration except by
  - evaporation and

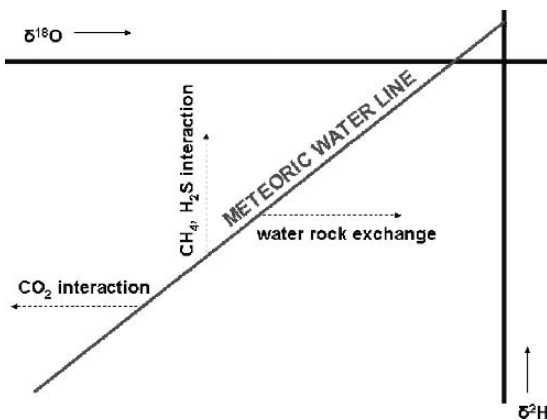


Figure 4.15. Changes of the stable water isotope signature by special water/rock/gas interactions in the subsurface



– any  $\text{CH}_4$  or  $\text{H}_2\text{S}$ , occurring with the disintegration of local organic contaminants, in contact with groundwater. Both gases increase the  $^2\text{H}$ -content of the water (Fig. 4.15).

- When subsurface boiling of water occurs in geothermal high enthalpy areas, another fractionation comes into the game.
- All these processes of stable isotope enrichment or depletion follow straight lines in a  $^2\text{H}/^{18}\text{O}$ -diagram and, therefore, may also include mixing processes. These straight lines (Fig. 4.15) always start from the meteoric water line; hence, allow reconstructing the original stable isotope contents of both  $^2\text{H}$  and  $^{18}\text{O}$ .

Radioactive isotopes of hydrologic interest are produced in the outer atmospheric or in the lithosphere environment; in between these, the atmospheric production is more efficient and less of local character than the lithosphere production:

- Cosmic radiation represents a wide range of particles (photons, neutrons, electrons, mesons), reaching the outer earth's atmosphere. It varies in intensity according to solar flares on short and according to changes in the earth magnetic field on long terms. High energy reactions with atmospheric N, O, and Ar produce  $^3\text{H}$ ,  $^{39}\text{Ar}$ , and  $^{36}\text{Cl}$ , low-energy reactions with N produce  $^{14}\text{C}$ .
- Neutron fluxes from the radioactive decay of U and Th in rocks produce in special cases  $^3\text{H}$ ,  $^{39}\text{Ar}$ , and  $^{14}\text{C}$ ; this production is, however, only of local importance and quite variable according to the amount of U and Th, accumulated in rocks. Dating with environmental radioactive isotopes applies in two different ways.
- If the input concentration varies in well-known ranges, as the stable isotopes of the water molecule do, the damping (eqs. 4.49 and 4.50, section 4.4.2.2) or the phase shift of the input as compared to the output signal can be used for dating; this method, however, covers mostly time spans of less than 5 years or
- According to the radioactive decay law and the element typical half life (Table 4.14).

Opposite to dating in geochronology, in hydrological studies, the initial concentration of radioactive environmental isotopes cannot be re-calculated by summing up the still available radioactive substance and a specific decay product to the initial concentration, because all radioactive environmental isotopes, applied in hydrology, decay into abundantly occurring isotopes (Table 4.14). Therefore, in hydrology, the input concentration, to which dating refers, is either supposed to be constant ( $^{36}\text{Cl}$ ,

*Table 4.14.* Routine measuring methods and half-lives of radioactive environmental isotopes

Isotope	Measuring Method	Half-life in years	Decay	Decay product
$^{36}\text{Cl}$	AMS	301,000	$\beta^-$	$^{36}\text{Ar}$
$^{14}\text{C}$	LSC, GPC, AMS	5,730	$\beta^-$	$^{14}\text{N}$
$^3\text{H}$	GPC, LSC	12.3	$\beta^-$	$^3\text{He}$

The analytic precision for radioactive isotopes refers to the  $2\sigma$  or 95% confidential interval.

AMS = accelerator mass spectrometry, LSC = liquid scintillation counting, GPC = gas proportional counting.

$^{14}\text{C}$ ) in the earth magnetic Brunhes period, which stands for the late Pleistocene and the Holocene, or was monitored by or can be extrapolated from results of the Global Network of Isotopes in Precipitation (GNIP) (IAEA, 1992).

In archeology, dating relates to unique ages, in hydrology always to an age distribution, expressed as mean-turn-over- or mean-transit-time (MTT). The reason is that hydrologic systems

- Undergo hydrodynamic dispersion,
- Are traced by environmental markers along an arbitrary plane in the ground-water flow field instead of along a potential plane as hydraulic tracing does (section 4.4), and
- Are always sampled in groundwater profiles.

Consequently, the MTT has to refer to an age distribution, representing the mean time of water exchange (section 4.4.2.2) of

- A whole reservoir, when sampling refers to pumping from fully penetrating wells, or
- An aquifer sector that has been sampled by operating partly penetrating wells or at selected well depths.

This time distribution (eq. 4.47) may start from present (exponential age distribution) or historic times (dispersive age distribution) and always ends—mathematically spoken—at infinite.

In contrast to the radioactive environmental tracers  $^3\text{H}$ ,  $^{14}\text{C}$ , and  $^{36}\text{Cl}$ , the radioactive gas isotopes  $^{85}\text{Kr}$  and  $^{39}\text{Ar}$  underlie after infiltration a phase partitioning in the vadose zone according to their molecular diffusion coefficients. According to this exchange, any radioactive noble gas clock starts when percolation reaches the groundwater table, whereas the isotope clock of chemical solute radioactive tracers starts with infiltration. As percolation velocities in unconsolidated rocks and in the matrix of hard rocks are very low, analyzed ages from radioactive environmental gases with short half-life (e.g.,  $^{85}\text{Kr}$ ) may differ significantly from  $^3\text{H}$  ages although their half-lives are similar. The same applies for other gas tracers.

With radioactive environmental isotopes, a time span of 25,000 years can be covered, using routine sampling, preparation, analysis, and interpretation techniques. Dating of groundwater exceeding 25,000 years refers to  $^{36}\text{Cl}$  and needs special geochemical considerations and AMS techniques. All existing dating methods, however, do not well overlap; hence, every method in hydrology covers an individual time slot (Fig. 4.16).

In the late 20th century, man-made produced radioactive isotopes superimposed the natural radioactive isotope production: In the north hemisphere,  $^3\text{H}$  (Fig. 4.17) and  $^{14}\text{C}$  (Fig. 4.18) and  $^{36}\text{Cl}$  have been emitted by the many open air nuclear weapon tests during the years 1955–1965 into the troposphere and stratosphere as well; following that time,  $^{36}\text{Cl}$ ,  $^3\text{H}$ , and  $^{14}\text{C}$  were higher than normal in precipitation over about two decades. Because of a stronger and more rapid atmospheric mass exchange in west–east than in north–south directions, these ‘man made environmental isotopes’ played a greater role in the north or source than in the south hemisphere and appeared delayed in the south

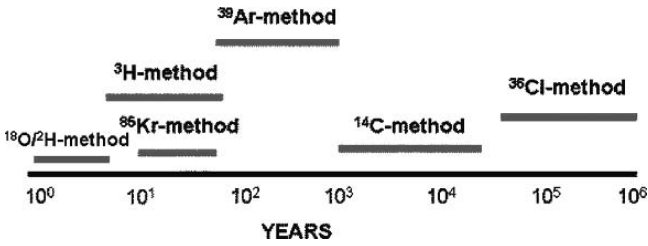


Figure 4.16. Dating intervals covered by the mostly used radioactive environmental tracers. Dating with stable environmental tracers see eq. 4.49

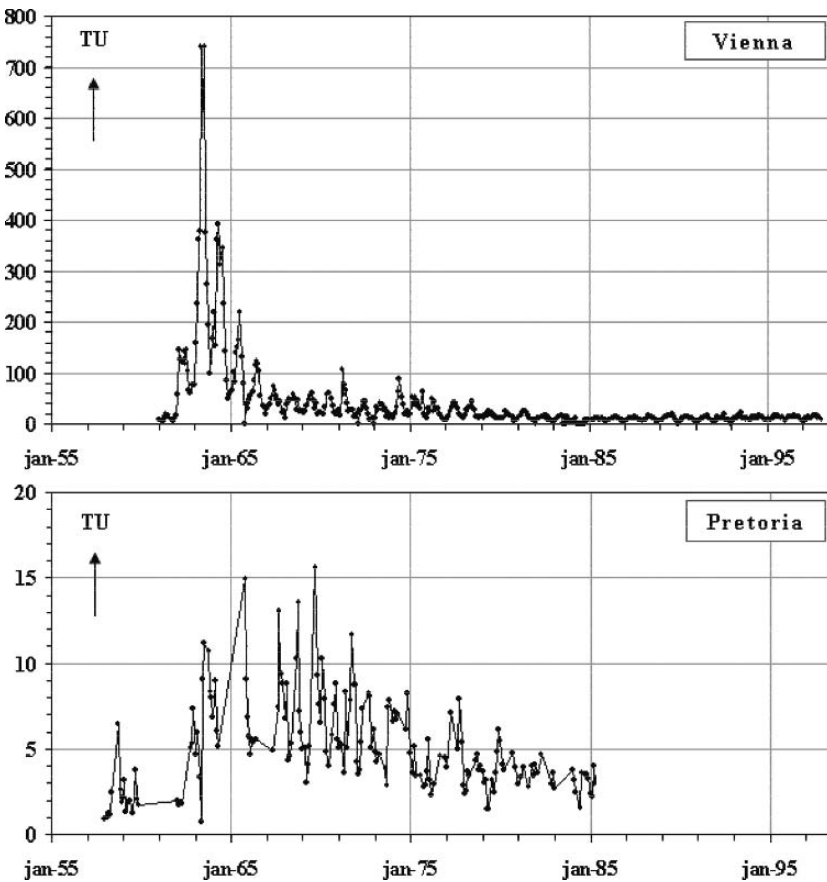


Figure 4.17. Average increase of the  $^3\text{H}$  content in both hemispheres related to the open air nuclear weapon test in the years 1955–1965. Since the end of the 80th/90th of the last century, tritium approached again natural concentration levels (Mook, 2001)

hemisphere (Figs. 4.17 and 4.18); this uneven global distribution pattern by means of the existing global atmospheric circulation pattern became enhanced by the uneven ocean/land partitioning in the two hemispheres and the respective differences in the intensity of atmosphere/ocean exchanges; this exchange acts more efficient in the south than in the north hemisphere, because of the larger ocean surfaces.

Concentrations of radioactive environmental isotopes also refer to standards, except for  $^3\text{H}$ .

- For  $^3\text{H}$ , it makes no sense to define a standard, because of its short half-life; therefore, activity ratios are measured and a tritium unit (TU) has been defined as

$$1 \text{ TU} = 10^{-18} \text{ } ^3\text{H}/^1\text{H} \equiv 0.118 \text{ Bq/L.}$$

The TU is well known to hydrologists, but little to other scientists.

- The  $^{14}\text{C}$  activity ratio ( $^{14}\text{C}/^{12}\text{C}$ ) relates to the oxalate standard with 13.56 dpm/g C. This standard refers to the  $^{14}\text{C}$  concentration at the beginning of the industrial age.  $^{14}\text{C}$  concentrations are calculated as percent modern carbon-14 (pmc), expressed as (eq. 4.39)

$$\text{pmc} = \frac{\left(\frac{^{14}\text{C}}{^{12}\text{C}}\right)_{\text{sample}}}{\left(\frac{^{14}\text{C}}{^{12}\text{C}}\right)_{\text{Standard}}} 100 \quad [\%] \quad (4.39)$$

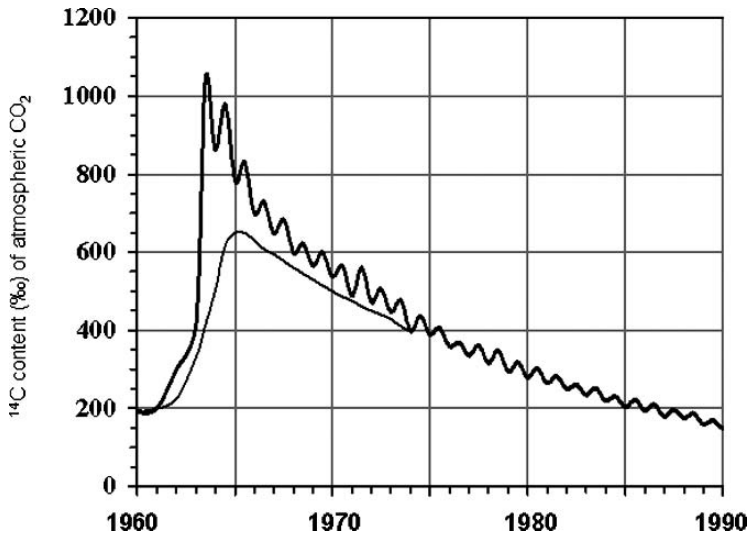


Figure 4.18. The increase of  $^{14}\text{C}$  in the atmosphere because of the open air nuclear weapon test in the years 1955–1964 in the north (upper curve) and the south hemisphere (lower curve)

From 1890 to 1950, the pmc decreased from 100% to about 90% because of the combustion of fossil hydrocarbons and the respective reduction of the  $^{14}\text{C}/^{12}\text{C}$  ratio in the atmosphere. Although the nuclear weapon tests (1955–1965) increased the natural  $^{14}\text{C}$  input signal (Fig. 4.18) to some extent, this has no implications for dating of old groundwater, but can be used under special hydrogeological conditions for short-term dating.

Most of the radioactive environmental tracers are physically or chemically soluted in groundwater; they either have its initial concentration already at the infiltration interface ( $^3\text{H}$ ,  $^{36}\text{Cl}$ ) or receive it in the effective root zone ( $^{14}\text{C}$ ).

Within groundwater the

- $^{14}\text{C}/^{12}\text{C}$  signature can change by any admixture of  $^{12}\text{C}$  from
  - $\text{CO}_2$ -gas emanations out of magma chambers or coal deposits,
  - The microbial supported oxidation of sulfides, thus enhancing the dissolution of rock carbonates, which is free of  $^{14}\text{C}$  or
  - By changes of the carbonate species through ion exchange.
- Atmospheric  $^{36}\text{Cl}$  input concentrations can change by
  - excessive evaporative respectively wind blown Cl accumulations at the infiltration interface in arid (dry-land) areas (section 4.4.2.1),
  - the application of fertilizers in agriculture,
  - the solution of Cl from evaporitic rocks or
  - any subsurface  $^{36}\text{Cl}$  production.
- $^3\text{H}$  can also be produced subsurface in U-Th-bearing sediments or crystalline rocks.

#### 4.4.1.1 Preparation techniques

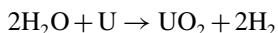
Preparation and measuring techniques have been reported in detail by Moser and Rauert (1980) and Mook (2001, 2002).

In routine analysis, the stable isotopes  $^{18}\text{O}$  and  $^2\text{H}$  are measured by mass spectrometry in the gas phase, because liquid water imposed serious memory effects through sorption on metals.

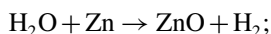
- $^2\text{H}$  is measured as  $\text{H}_2$  gas, and
- $^{18}\text{O}$  becomes coupled with  $\text{CO}_2$ ,

To do so

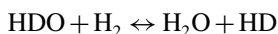
- About 10  $\mu\text{L}$  of  $^2\text{H}^1\text{HO}$  is reduced to  $^2\text{H}^1\text{H}$  with uranium at  $800^\circ\text{C}$



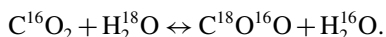
or with Zn at  $400^\circ\text{C}$



or with metallic catalysts (e.g., Pt) at room temperature



- About 10 mL of water is equilibrated in a water bath with CO<sub>2</sub> of known isotope composition for the <sup>18</sup>O measurement according to the reaction



This equilibration reaction depends on time, free-O<sub>2</sub>, pH, and temperature. The temperature in the water bath should vary by less than 0.2°C; the sample is typically shaken 4–8 h to reach an optimal equilibration between H<sub>2</sub>O and CO<sub>2</sub>. To remove O<sub>2</sub> and other gases before equilibration, the sample is either frozen and gas was removed by pumping or the water is pumped through a capillary. The pH should be in the range of 6–7 to have abundant CO<sub>2</sub> and HCO<sub>3</sub><sup>-</sup>.

To reach reliable results on both <sup>2</sup>H and <sup>18</sup>O contents in water samples, the water standard and the water sample are always prepared and measured in exactly the same way; thus, any preparation error becomes non-significant for the mass spectrometer result.

<sup>3</sup>H is normally enriched by electrolysis from about 500 mL of water, to increase the measuring accuracy and thus to improve the detection limit. <sup>3</sup>H concentrations are analyzed by either liquid scintillation counting (LSC) or by proportional gas counting (PGC). It can also be determined by measuring the decay product <sup>3</sup>He at the beginning and end of storage of the sample over a given period of time; this method delivers the highest measuring accuracy.

<sup>14</sup>C is conventionally measured in DIC, which consists of HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, and CO<sub>2</sub>. There are two methods to obtain DIC under field conditions from groundwater:

- Sampling groundwater quantities according to the total inorganic carbon (CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, CO<sub>2</sub>) of the water and the analytic requirements (3–5 g C) or
- Precipitating DIC in the field as carbonate after adding NaOH.

Often, precipitation methods are preferred in the field to avoid the transport of huge volumes of water from the field to the laboratory. With the introduction of the AMS analysis, sampling of groundwater for <sup>14</sup>C analysis simplified, because this method needs only 1 mg C.

The measurement of the <sup>14</sup>C activity ratio is performed applying

- PGC filled with CO<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>6</sub> or CH<sub>4</sub>,
- LSC with C<sub>6</sub>H<sub>6</sub>, which is condensed by acetylene and mixed with a scintillation fluid or
- AMS starting from CO<sub>2</sub>, which is reduced to graphite at 600°C using Fe as a catalyst.

For the analysis of <sup>36</sup>Cl, about 10 mg Cl is needed. The quantitative measurement of <sup>36</sup>Cl by low-level techniques was difficult, because of the very low specific activity ratio; therefore, it is always measured by AMS and with a detection limit of <sup>36</sup>Cl/Cl = 10<sup>-15</sup>.

According to the storage, preparation, and measurement techniques, the following maximum quantities are recommended to sample for analysis:

- <sup>2</sup>H and <sup>18</sup>O 50 mL, water,
- <sup>3</sup>H 500 mL water,
- <sup>14</sup>C 5–3 gr C mostly precipitated carbonate in the field, LSC,

- 500 mL C water for AMS,
- $^{36}\text{Cl}$  10 mg Cl AMS.

The water volumes to be sampled and treated for environmental C- or Cl-isotope analysis can be calculated on the base of a chemical analysis of the water of concern.

#### 4.4.1.2 Measuring techniques

The relative abundance of stable isotopes is measured with mass spectrometers (MS). In the MS, the measured gas is first ionized by ion sources, than the ions are accelerated by high voltage and enter a magnetic field. The pathway of the ions in the magnetic filed becomes circular, because of Lorenz forces and the circle radius depends on the ion mass; light ions follow a pathway with a smaller radius than heavy ions (Fig. 4.19). The thus separated ions can be collected by adjusted Faraday collectors, in which the electric charge is proportional to the number of incoming ions. This measurement is performed alternatively with a sample and a standard using a double inlet system, to insure a high precision delta notation.

The measuring accuracy ( $2\sigma$ -error) by mass spectrometer is:

$$\delta^2\text{H} < \pm 1.0$$

$$\delta^{18}\text{O} < \pm 0.1$$

Radioactive environmental isotopes of hydrologic interest are all  $\beta$  radiating, hence, measurement takes place with low-level counting techniques; these measurements refer to a special shielding of the measuring devices to keep the natural background of radioactivity as low as possible and to measure the low radiation energy of the isotopes of concern as precise as possible. As an alternative to low-level counting, AMS applies; the principle of this measurement is shown in Fig. 4.20.

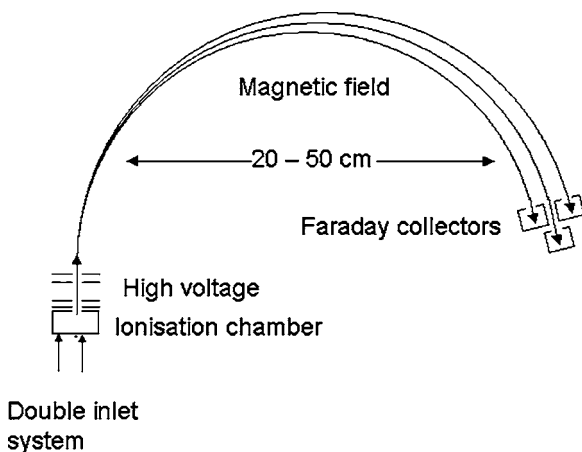


Figure 4.19. Principle sketch of mass spectrometry measurements

The upper and lower limit of dating through radioactive isotopes depends on the sample preparation and the design of the counter; these analytic errors are summed up as  $2\sigma$ -errors. As the interpretation of such analysis depends from an appropriate knowledge of the input concentration and a good conceptual model on the fate of the isotopes from entering to leaving the subsurface, water ages are often named model-ages, which refers to the applied conceptual model. Uncertainties of the input concentration of these radioactive isotopes often limit the application over short periods of times; such uncertainties, however, can be reduced if time series of analysis are interpreted.

#### 4.4.2 Environmental Tracers for Recharge Determination

##### 4.4.2.1 Environmental chloride

Under natural conditions, chlorides in percolation and groundwater are of atmospheric origin; other sources intervene under special climate, land use, geologic, or hydrogeologic conditions.

As compared to many other solute matters, chloride is a non-reactive ion, hence, underlies no freight changes along the different flow paths within the water cycle, except if the water came in contact with new Cl-sources. Chloride, however, undergoes in the water cycle concentration changes, when the water volume reduces by evaporation along the interface atmosphere/lithosphere/biosphere. This has been recognized by H. Schoeller (1941), Eriksson (1952) and M. Schoeller (1963), who studied first chlorides in the water cycle to determining groundwater recharge. In the following decades, this method was further elaborated (e.g., Edmunds & Walton, 1980) and meanwhile may be considered a standard application.

Evaporation produces distilled water vapor from fresh-water and ocean surfaces, which both contribute to the air humidity on continents, mixes in the ocean environment with chlorides from sea spray (aerosols) and gets in contact with atmospheric dust and gases, emitted into the atmosphere by either natural

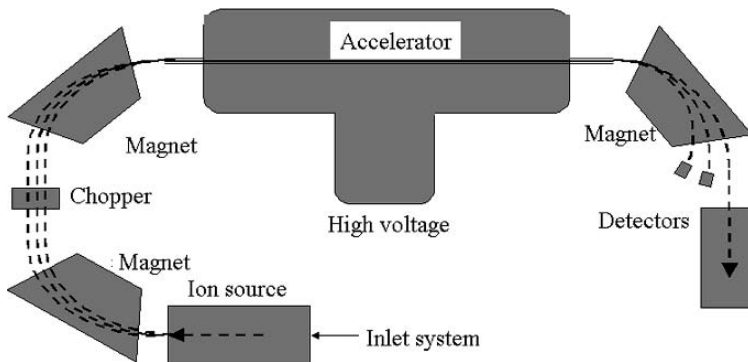


Figure 4.20. Principle of AMS measurements



(volcanism, wind/water or wind/sediment interaction) or man-made processes (industry, agriculture, urbanization, traffic). These natural and man-made components reach the interface atmosphere/lithosphere/biosphere by precipitation or interception deposition (Fig. 3.4), accumulate at this interface before becoming incorporated into canopy discharge or infiltration and finally reaches surface and subsurface flow paths.

Although active volcanoes may add close to the emitting source several 100 mg/L (known maximum about 500 mg/L) of chloride to precipitation, such emissions dilute on a global scale to an average of about 0.2 kg/(ha year). Other chlorides in precipitation and percolation originate from the combustion of coal [about 0.01 kg/(ha year)], industrial/agricultural emissions [about 3 kg/(ha year)] and the alteration of sediments [about 0.04 kg/(ha year)]. All these sources amount to about 3.3 kg/(ha year). With respect to the global mean of continental precipitations of 925 mm/year (section 2.2), this constitutes an average concentration of chlorides in precipitation on earth of about 0.3 mg Cl/L. As compared to often measured natural chloride concentrations in precipitations (1 to more than 5 mg Cl/L), it becomes evident that most chlorides in precipitations are from other sources than the previously mentioned: They primarily originate from sea spray and dust.

Chloride concentrations in regional, single, and consecutive rain events significantly differ according to

- The distance from the source area of chlorides,
- Weather trajectories (see below),
- Re-evaporation,
- The regional condensation altitude (section 3.2), and
- Rain intensities.

Similar to the stable isotopes of the water molecule (section 4.4.2.3), chloride concentrations show a continental effect, which expresses in an exponential decrease of mean chloride concentrations in precipitation with the travel distance of the air humidity from the source area (Fig. 4.21), mostly the coast. In contrast, however, to stable isotopes in precipitation, chlorides undergo only dilution by re-evaporation along the continental weather trajectory and stable isotopes of the water molecule fractionation at phase transitions (evaporation and condensation) and mixing with re-evaporated fresh-water. Therefore, chloride depletes in precipitations more than stable isotopes with the distance from the coast.

According to the intensity, rain events often start with high and continue with low chloride concentrations and consecutive rain events may differ in mean chloride concentrations by a factor of 50. Therefore, representative chloride input data (eq. 4.40) should always refer to weighted input concentrations in precipitation over a long enough period of time (minimum 1 month to 0.5 years).

$$Cl_{\text{weighted}} = \frac{\sum Cl_i P_i}{P}. \quad (4.40)$$

A precondition in using individual rain events for determining groundwater recharge was that it follows a linear proportionality between precipitation and

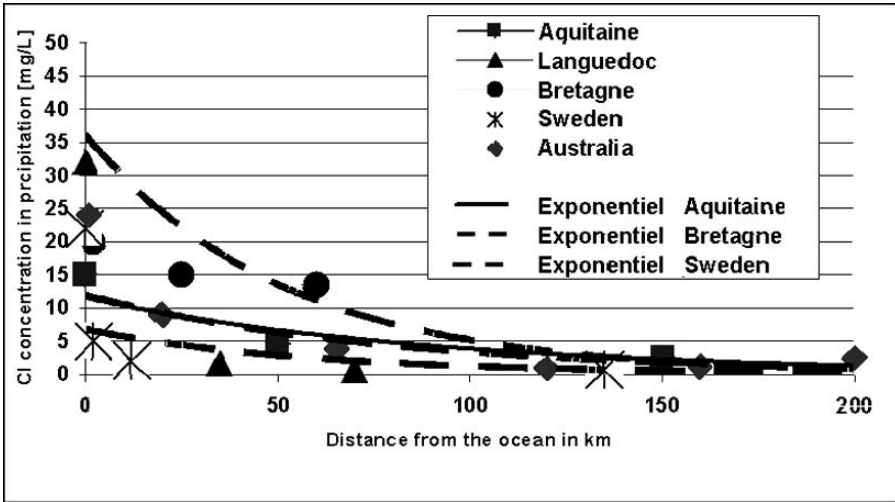


Figure 4.21. Mean chloride concentrations, decreasing with the distance from the ocean (modified after Schoeller, 1963)

infiltration amounts; this linear relation, however, is almost never realized, because temporary clogging of the infiltration interface, surface tensions of dry or wet sediments/soils, and the hydraulic functions of the unsaturated zone govern the beginning and intensity of the infiltration/percolation process during rain events; only in a more advanced stage of infiltration (e.g., after reaching water contents close to field capacity at the infiltration front) a proportionality between infiltration/percolation and precipitation occurs and accounts its maximum value when infiltration capacity is reached. As a consequence, concentration variations in chloride profiles may have many reasons, hence, imposes restrictions in applying the chloride method to determine groundwater recharge for short periods of time; in contrast, averaging a Cl-profile of the vadose zone over significant thickness delivers an excellent approximation on groundwater recharge with only small interferences from special infiltration conditions.

Seasonality of chloride concentrations in precipitation must also be taken into account in calculating groundwater recharge through the chloride balance. Eriksson (1952) found for the meteorological station of Rothamsted the following relation:

$$\begin{aligned}
 Cl_{\text{winter}} &= 0.5 + \frac{75}{P} \\
 Cl_{\text{summer}} &= 2.0 + \frac{75}{P}
 \end{aligned}
 \tag{4.41}$$

(P measured in mm/half year).

Using only the winter mean of chloride concentrations in precipitation in humid temperate climates is problematic, although winter is the main recharge season. All

observations from the unsaturated zone prove that during the vegetation period, percolation stagnates in the effective root zone, because of significant water losses by transpiration. Then, after harvesting, in late summer, water storage and evaporation dominate (Fig. 4.29), because plant transpiration stopped with harvesting. During this period, the soil solution at the evaporative interface enriches chlorides from summer precipitation, which are later washed out or pulled down with the groundwater recharge of the winter season. Consequently, there is some summer chloride, contributing to winter recharge (section 4.4.2.3, Fig. 4.29). Therefore, in semi-arid and humid climates, it is often observed that discharge from catchments is higher mineralized at the beginning of the recharge season than in the following months and in temperate climates stable isotopes of groundwater ( $^2\text{H}$ ,  $^{18}\text{O}$ ) often group somewhat below the local meteoric water line (Fig. 4.29).

Applying the law of mass conservation (eq. 4.42), the freight of non-reactive chloride input equals to the chloride output, both in  $\text{mg}/(\text{m}^2 \text{ time})$ .

$$\begin{aligned} Cl_{\text{input}} &= Cl_{\text{output}} \\ Cl_P * P &= Cl_R * R' \\ \frac{Cl_P * P}{Cl_R} &= R' \end{aligned} \quad (4.42)$$

From eq. 4.42, it can be seen that

- Chloride concentrations in groundwater close to the input concentration result in high and
- High Cl-outputs as compared to the precipitation input in low groundwater recharge rates.

Equation 4.42 applies, if there are no chloride sources on soils and in sediments, no dry deposition and no direct run-off occurs. Taking these factors also into account, a more general application of eq. 4.42 can be recommended (eq. 4.43) by replacing

- Precipitation through an effective precipitation, contributing to groundwater recharge

$$P_{\text{effective}} = P - D_o - D_i \quad (4.43)$$

This correction overestimates groundwater recharge to some extent, because  $D_i$  may export some Cl to surface run-off, because it exchanged with the stored water in the percolation zone;

- The output concentration through an effective output concentration of

$$Cl_{R' \text{ eff}} = Cl_{R'} + Cl_{\text{plant-uptake}} - Cl_{\text{plant-disintegration}} - Cl_{\text{rock-weathering}} - Cl_{\text{anthropic}} \quad (4.44)$$

Accounting on eq. 4.42 and the natural variability of Cl in precipitation, it becomes evident on the one hand that high chloride concentrations in groundwater, which are not related to solution processes along the subsurface flow path, deliver much lower errors in determining groundwater recharge than very low chloride

concentrations. On the other hand, in humid climates, low groundwater recharge is often associated with high overland- and inter-flow, which can only be quantified by a continuous discharge analysis (section 4.1.2, eqs. 4.2 and 4.3). In semi-arid and arid areas, groundwater recharge can be determined with high accuracy if the groundwater table is deep (>10 m), and capillary rise of groundwater to the surface becomes negligible. In the case of a groundwater table at shallow depth, saline groundwater disturbs any application of the chloride method.

Although the chloride method applies well in determining groundwater recharge rates in arid (dry-land) zones, special care is recommended, because groundwater is often from historic times and does not necessarily correlate with the chemistry of present precipitation. Therefore, groundwater from the last glacial period in the south German Molasse basin has a lower chloride concentrations (1–2 mg/L) than present groundwater (5–7 mg/L), because of a lower evaporation rate during glacial times than today, but probably also because of a low Cl concentration input; similar results have been reported by Stute et al. (1993) for the Carrizo Aquifer in Texas.

To differentiate between natural Cl-inputs by precipitation, anthropogenic, or geogenic emissions, the atmospheric  $^{36}\text{Cl}/^{34}\text{Cl}$  ratio in precipitation has been used (Magaritz et al., 1990); this ratio keeps constant in the active groundwater recharge zone from infiltration till detection times, because of the  $^{36}\text{Cl}$  half-life, which is 301,00 years; all other Cl sources, however, have  $^{36}\text{Cl}/^{34}\text{Cl}$  ratios differing from atmospheric; thus anthropogenic or geogenic chlorides dilute the atmospheric  $^{36}\text{Cl}/^{34}\text{Cl}$  ratio. Hence, evaluating Cl-concentration changes in subsurface water as compared to precipitation should be first assed by the  $^{36}\text{Cl}/^{34}\text{Cl}$  ratio before it is transformed into groundwater recharge calculations.

In the unsaturated zone, chloride profiles proofed a valuable method to study average recharge and to quantify recharge as a function of climate changes. Cook et al. (1992) found such recharge histories in thick unsaturated profiles of Senegal and Cyprus and report that the resolution in such profiles depend on effective groundwater recharge; climate changes within decades or centuries express very well even at recharge rates lower than 100 mm/year; in contrast, yearly or even seasonal recharge changes express only at recharge rates >100 mm/year.

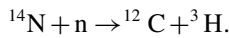
On the one hand, missing chloride data in precipitation for long periods of time are an often encountered handicap in determining present groundwater recharge through the chloride-balance method. On the other hand, the advantage of this method is that it does not depend on sophisticated meteorological or soil hydraulic measurements to calculate actual evapo-transpiration respectively water fluxes vertical down.

Chloride based recharge studies have been executed extensively in Australia (Allison & Hughes, 1978), North and Central Africa (Edmunds et al., 1988, 1992), France (Schoeller, 1961; Vachier et al., 1987), North America (Wood & Sanford, 1995), Central and South America (Baldison et al., 1995; Alvarado et al., 1996). On a global scale, the comparison of the chloride with the tritium (Fig. 4.22) method (section 4.4.2.2) (Prych, 1998) often provides

- Good agreements when recharge exceeds 25 mm/year,
- In semi-arid areas (5–50 mm/year of recharge) higher recharge rates with tritium than with the chloride mass balance method, and
- Often too low groundwater recharge rates with the chloride-balance method in arid areas (recharge rate <5 mm/year).  
To interpret these observations, it can be argued that
- The chloride input function is mostly not as well known as the tritium input function,
- The tritium method provides time information to calculate recharge, but chloride method delivers process information,
- Excessive evaporative salinization of soils has often more than one source, and
- Apart from precipitation, aeolian dust often imports chlorides to the infiltration interface.

4.4.2.2 Environmental tritium

Tritium is produced in the upper atmosphere by the interaction of cosmic rays and <sup>14</sup>N



According to the earth magnetic field, cosmic radiation is more incident at the magnetic poles than at the equator; thus, the intensity of the natural <sup>3</sup>H production decreases from the polar to the equatorial zones; this situation prevailed during most of the present Brunhes magnetic epoch (0–690 000 B.P.). Consequently, the natural production of environmental tritium is considered constant over historical

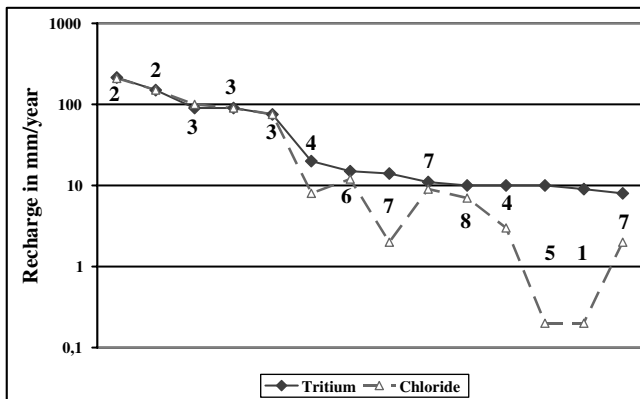


Figure 4.22. Comparison between groundwater recharge determined with the chloride and the tritium method. The numbers refer to: (1) Tyler & Walker (1994), (2) Allison & Hughes (1978), (3) Edmunds et al. (1988), (4) Allison & Hughes (1983), (5) Phillips et al.(1988), (6) Gieske et al. (1990), (7) Foster et al. (1982), (8) Cook et al.(1992)

and recent geologic periods of time with some variations parallel to changing sun activities.

Natural tritium is stored in the stratosphere and reaches in mid latitudes through a temperature inversion along the tropopause, occurring in both hemispheres in the respective spring time, the troposphere, becomes mixed and precipitates by wash-and-rain-out. This yearly injections and subsequent rain- and wash-out produces seasonal variations of  $^3\text{H}$  in precipitation with high values in most of the vegetation period and low values in winter (Fig. 4.17).

From natural production mechanisms and the seasonal short cut between troposphere and stratosphere result mean annual  $^3\text{H}$  concentrations in precipitation ranging from 5 TU at the equator to 20 TU in mid-latitude precipitations and seasonal  $^3\text{H}$  variations by a factor of 2 to 4. Since production, storage and short cuts between the stratosphere and the troposphere have the same importance for  $^{14}\text{C}$  and  $^{36}\text{Cl}$ , they undergo similar seasonal variations (Fig. 4.18).

In the south-hemisphere, average tritium concentrations in precipitation are lower than in the north-hemisphere, because of the different ocean/land partitioning; oceans act as a sink for tritium and  $^{14}\text{C}$  as well.

The open-air nuclear weapon tests produced during 1955–1963/1964  $^3\text{H}$  (as well as  $^{14}\text{C}$  and  $^{36}\text{Cl}$ ), which reached the stratosphere, the store of naturally produced tritium. Maximum man-made input of  $^3\text{H}$  occurred in 1963/1964 in the northern part of the north-hemisphere (Fig. 4.17), followed by the test moratorium, which set an end to the nuclear weapon input of radioactivity to the atmosphere. This weapon input appeared dampened and with a delay of about 2 years also in precipitation of the south-hemisphere; it increased the tritium concentrations in the north-hemisphere by a factor of hundred to thousand and in the south-hemisphere of fifty. From the maximum  $^3\text{H}$  concentrations in precipitation on, it decreased first exponentially, later slower and approached in the late 1980s asymptotically values close to natural.

Tritium has a half-life of 12.34 years and decays ( $\beta^-$  decay) to  $^3\text{He}$ ; the measuring accuracy ( $2\sigma$ -error) amounts to

- $\pm 0.7$  TU with routine LSC,
- $\pm 0.003$  TU applying the  $^3\text{H}/^3\text{He}$  method, and
- $\pm 0.3$  TU with the PGC method.

After three to four half-lives, the input of naturally produced tritium to groundwater is no more detectable with the routine LSC. This corresponds to mean residence times of 40–70 years.

Tritium meets subsurface water through infiltration of precipitation (Fig. 4.12). As  $^3\text{H}$  production in the subsurface is restricted, if ever, to areas with radioactive minerals like in some crystalline rocks and in areas with re-sedimented weathering products of crystalline rocks, tritium information is quasi always from atmospheric origin; this and its occurrence in the water molecule makes tritium to a very valuable hydrologic tracer to determine MTTs and groundwater recharge.

Tritium was used to determine qualitatively and quantitatively groundwater recharge.

- In areas with a huge deficit in precipitation as compared to potential ET, it is often doubtful if groundwater recharge occurred or not. In such areas, however, heavy rainfall can produce within a short period of time groundwater recharge, which is qualitatively documented by measurable  $^3\text{H}$ -concentrations in the percolation zone or in shallow groundwater. The assessment of such  $^3\text{H}$  evidence in groundwater of arid (Sinai, Kalahari, Djibouti, Oman, Saudi Arabia, Sahara, Gobi) and semi-arid areas (Sahel) is generally attributed to exceptional rain events or to the snowmelt (Gobi), but it does not necessarily prove that a net recharge over long periods of times comes into game. Similar observations exist from permafrost areas, where  $^3\text{H}$  was found in groundwater beneath permafrost (Michel & Fritz, 1978).
- Following tritium on its flow path from infiltration through the vadose zone to the groundwater, it can also be used to quantify groundwater recharge by the peak, mass balance or mean transit time method.

The tritium peak of 1963/1964 (Figs. 4.17) spiked percolation water in the vadose zone (Fig. 4.23) and was first used by Münnich (1983) to determine groundwater recharge. The mass balance method compares the variable input with the tritium profile in the unsaturated zone to calculate in an inverse manner groundwater recharge using bulk transport models. Later the mean transit time in the active groundwater recharge zone was also used to quantify groundwater recharge with  $^3\text{H}$ .

On short distances (1–5 m) percolation can be considered as of piston-flow type (eq. 4.47, Fig. 4.23). Under these conditions, the 1963/1964 spike was a very good time marker to calculate groundwater recharge; knowing the water content between the ground surface and the tritium spike, the groundwater recharge (eq. 4.45) results from an integration of the water contents ( $\theta$ ) above the spike as related to the time span between 1963/1964 ( $t_1$ ) and the sampling year ( $t_2$ ).

$$R' = \frac{\sum_0^h \theta_i h_i}{t_2 - t_1} \quad (4.45)$$

With respect to percolation velocities of 2–0.2 m/year, which are quite common in humid temperate, tropical, and semi-arid areas, the tritium spike of the year 1963/1964—reduced in amount by the radioactive decay—was in 2005 at a depth of maximum 70 m b.g.s. in humid respectively 7 m b.g.s. in semi-arid areas. This spike was still detectable if

- Flow in the unsaturated zone was homogeneous,
- No preferential-flow occurred, and
- The input was strong enough.

However, if flow in the unsaturated zone is inhomogeneous and preferential-flow occurs, the  $^3\text{H}$  information becomes smeared over the profile according to the

- Depth reach of preferential-flow (section 3.4),
- Magnitude of mass exchanges (Fig. 4.5), and
- Molecular diffusion between slow and rapid moving water.

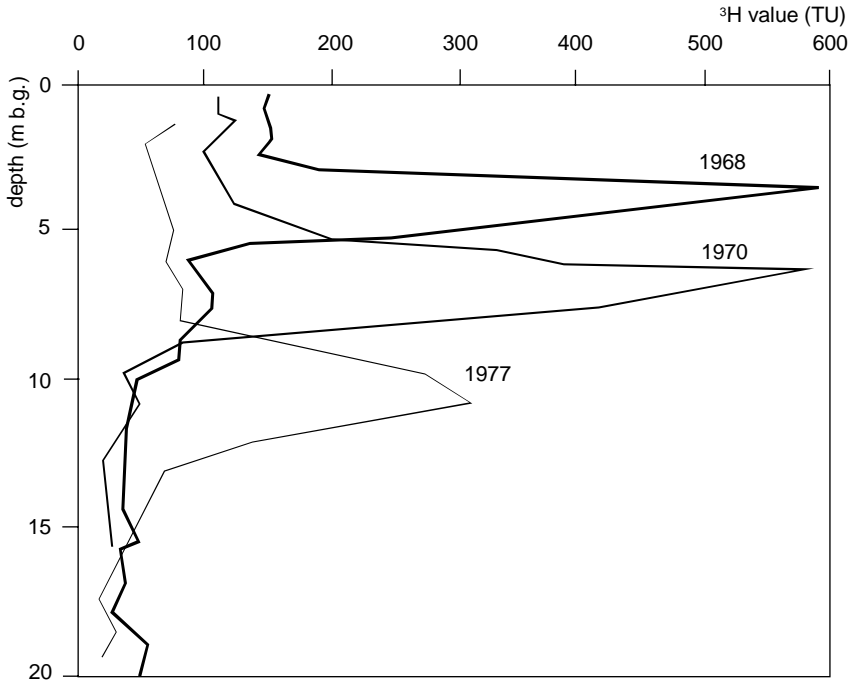


Figure 4.23. Displacement of the tritium peak in the unsaturated zone of Cretaceous chalks (Foster & Smith-Carrington, 1980)

When using the tritium peak of the years 1963/1964, no correction for seasonality of groundwater recharge is necessary, because tritium in precipitation dropped within the first 1.5 years so much that peak recognition is unambiguous. However, using tritium profiles to determine groundwater recharge by comparing the input with the output function and introducing a transformation function on flow and radioactive decay (eq. 4.46), a weighting factor must be taken into account to assess low recharge in the warm and high recharge in the cold season.

The environmental  $^3\text{H}$ -peak method applied well in temperate, tropical, and semi-arid areas; it was cautiously used in arid (dry-land) zones, because under these climates precipitation is scarce in time, and not well distributed within the catchment area. Therefore, and, because of the seasonal variability of tritium in precipitations, a tritium maximum in the vadose zone may or may not correlate with the 1963/1964 peak in precipitation and the occurrence of tritium in the percolation zone may be considered a hazard or not.

The tritium mass balance method (eq. 4.46) refers to

$$C_{\text{out}} = \int_0^t C_{\text{in}}(\Delta t)g(t')e^{-\lambda t} dt \quad (4.46)$$



(convolution integral) or the transport equation (eq. 4.63).

According to the hydraulic initial and boundary conditions, three basic bulk approaches (eq. 4.47) exist for the transformation function  $g(t')$  (Maloszewski & Zuber, 1982);

- The piston-flow model (PFM) assumes that flow paths with different residence times, hydrodynamic dispersion, and molecular diffusion do not play any role along the propagation path,
- The exponential model (EM) implies an exponential distribution of travel times, beginning with zero, but no hydrodynamic dispersion, and
- The dispersion model (DM) accounts an exponential distribution of travel times, starting with any time and includes hydrodynamic dispersion, thus accounting to heterogeneities of aquifer systems.

$$\begin{aligned}
 g_{PFM}(t') &= 1 \\
 g_{EM}(t') &= \frac{1}{t'} e^{-\frac{t'}{\tau}} \\
 g_{DM}(t') &= \frac{1}{\sqrt{4\pi \frac{D'}{v_a x} t'}} \frac{1}{t'} e^{-\left[\frac{1-t'}{\tau} + \frac{D'}{4v_a x} \frac{t'}{\tau}\right]}
 \end{aligned} \tag{4.47}$$

From PFM to DM, the number of unknown parameters increases, hence, the error bar in calculating groundwater recharge too. The same holds, if applying the transport equation (eq. 4.63) to fit inversely groundwater recharge from known input and output functions.

Often, model combinations are used by introducing weighing factors of  $\eta$  and  $(1 - \eta)$ . The precision of these approaches increases, if response functions of different environmental tracers (e.g.,  $^3\text{H}$ ,  $^{85}\text{Kr}$ , CFC-12) can be analyzed and fitted with the respective input function. Results, calculated with eq. 4.47, do not differ, if MTTs are in the range of few years. At higher MTTs, the choice of the model plays an important role (Maloszewski & Zuber, 1982). A model comparison between numerical and lump sum parameter models has been presented by Seiler et al. (1995); it shows no significant differences in results.

EM and DM deliver

$$\text{MTT} = t',$$

which translates to recharge using the mean water content in the vadose zone (eq. 4.33) or applying the transport equation (eq. 4.63), recharge is included in the flow velocity parameter  $v_a$ .

A special situation is given in the percolation zone of bi-porous media, to which belong reef and dolomitized limestones, the Upper Cretaceous Chalk and many types of sandstones. Here a slow flow of decimetres or meters per year occurs in matrix pores and a quick flow in exchange with matrix-flow exists in fissures

or even solution channels. Knowing only matrix-flow leads to an underestimate of groundwater recharge. Vachier et al. (1987) determined the recharge in chalk sediments of the Champagne (France) to be 250 mm/year, which was in good agreement with hydraulic calculations; this recharge refers to a precipitation of 630 mm/year.

Using the tritium peak method for the determination of groundwater recharge requires only one sampling campaign some years after the peak concentration percolated to a depth that excludes vertical up return to the land surface; recharge results, always referring to matrix-flow, are the more representative as the time interval between the infiltration of the tracer peak and the sampling is long. However, to also consider preferential-flow, an artificial tracing is required (section 3.4) and an intensive and repeated sampling must be performed just after the infiltration of the tracer signal.

Today, the environmental tritium peak and mass-balance methods are of little use, because no new  $^3\text{H}$  signal was produced since the years 1963/1964, and the present tritium input is quasi constant. Therefore, more than environmental tritium, artificial tritium has been applied in India (Gupta & Sharma, 1984; Sukhija et al., 1996), Africa and Australia (Sharma, 1989) (Fig. 4.22) (section 4.4.4).

In closed hydrologic aquifers, the  $^3\text{H}$  method can be combined with  $^3\text{He}$  measurements;  $^3\text{He}$  is the decay product of  $^3\text{H}$  and accumulates in the closed system. When helium sources other than from the decay of tritium can be quantified and the system is closed, the  $^3\text{He}$  content increases with time proportional to the input and half-life of  $^3\text{H}$ .

Another application to determine groundwater recharge with  $^3\text{H}$ ,  $^{14}\text{C}$ , or potentially with  $^{36}\text{Cl}$  refers to the MTT of groundwater in the active as well as passive groundwater recharge zone (section 2.4). By definition, the MTT is the average time to exchange once the water volume of an aquifer through groundwater recharge (Nir & Lewis, 1975; Zuber, 1986) (eq. 4.48).

$$\begin{aligned} \cdot MTT_w &= \frac{V_{\text{aquifer}}}{R' A} \\ V_{\text{aquifer}} &= p' T' A \\ R' &= \frac{p' T'}{MTT_w} \end{aligned} \quad (4.48)$$

When using eq. 4.48, the question of the geometry of the active recharge zone often arises. Taking the TNL, which separates tritiated from non-tritiated water and referring to a routine measuring accuracy of  $\pm 0.7$  TU, water of the active groundwater recharge zone (section 2.4, Fig. 2.11) relates to a MTT of maximum 40 years at the equator (natural input 5 TU) and maximum 70 years in the mid latitudes (natural input 20 TU). According to results of numerical simulation (section 2.4), the TNL expresses the thickness of the active groundwater recharge zone below the groundwater table. If the porosity of the aquifer is known, groundwater recharge can be calculated. For example, in the Molasse basin of south Germany with

unconsolidated sands and gravels the active groundwater recharge zone becomes 50 m thick, porosity is about 0.25, and the natural tritium content stands for an MTT of 70 years. From these data, groundwater recharge was calculated to amount 0.18 m<sup>3</sup>/year or 180 mm/year, which is in good agreement with traditional water balance studies (section 5.1.2).

In <sup>3</sup>H recharge studies, based on MTTs, the depth of the TNL should be determined in extended areas between and not beneath receiving rivers or subsurface water divides. Another limitation in applying this method may rise, if

- Shallow groundwater is overexploited; then the active groundwater recharge zone becomes too thin, because of a groundwater level decline and an upconing of deep groundwater;
- Groundwater is exploited from the passive groundwater recharge zone, and then the TNL might be determined too deep (Fig. 2.10B).

The determination of groundwater recharge through MTT and the geometry of the active groundwater recharge zone do not apply in bi-porous aquifers, unless the relative portion of groundwater recharge of both media is known by discharge analysis.

MTT can also be determined with the stable isotopes of the water molecule. These isotopes undergo seasonal variations, which can be used for short-term dating as far as the input variations have not been dumped in the subsurface to zero by hydrodynamic dispersion. Supposing a constant yearly mean of <sup>2</sup>H or <sup>18</sup>O concentrations and a sinusoidal seasonal variation with a phase of  $\omega = 2\pi$  the variation ( $f$ ) from the input to the output concentration applies to calculate the *MTT* (eq. 4.49):

$$MTT_w = \frac{1}{\omega} \sqrt{\frac{1}{f^2} - 1}$$

with

$$f = \frac{\Delta\delta^{18}O_{\text{output}}}{\Delta\delta^{18}O_{\text{input}}} \tag{4.49}$$

This method provides MTTs of month to several years according to the measuring precision and the extent of the existing seasonal variations of the stable isotope content and implies that age distributions always start from zero.

Often, CFCs have been applied to determine mean residence times (Busenberg & Plummer, 1992; Oster et al., 1996) instead of tritium, because tritium concentrations from nuclear weapon tests decreased to the low natural tritium production in the atmosphere till the end of the 1980s, and CFCs show still rising concentrations. In between CFCs, CFC-11 and CFC-113, are easy degradable in an anaerobic environment, only CFC-12 behaves conservative in both aerobic and anaerobic environment.

Mean residence times can also be determined using environmental chloride as a tracer. If the chloride input function is known over a long run of time, from the chloride distribution in the unsaturated zone follows:

$$MTT = \frac{1}{PC_{Cl,P}} \int_0^z \theta(z) C_{Cl}(z) dz \quad (4.50)$$

If preferential-flow plays an important role in the studied profile, it should be thick enough (>5 m) to produce reliable results.

#### 4.4.2.3 Environmental $^2H$ and $^{18}O$

The gas composition of the atmosphere evolved parallel to life processes, tectonic activities and the changing ocean/land distribution. Among the minor gases, carbon dioxide, water vapor, methane, nitrous oxide, and hydrogen are outstanding, because they significantly co-regulate the production, retention, and transfer of heat as well as the filtering capacity of the atmosphere for cosmic radiation.

Heating of the earth surface is quite uneven and results in a significant convective mixing within the troposphere (0–10 km heights, Fig. 4.24), leading for gases with high MTT to a homogeneous distribution; water vapor, however, is uneven distribution in the troposphere (Fig. 4.24), because it has an average MTT of only 10 days and, thus, not sufficient time to become homogeneously mixed.

Processes at the ocean surface, the main source of the water vapor in the water cycle, and within the atmosphere provide the main signature of the stable water isotopes  $^2H$  and  $^{18}O$  in precipitation. At the interface ocean/atmosphere, evaporation fractionates the stable isotopes of water according to the prevailing temperature and humidity gradients across this interface; this process of evaporation leads to distilled water vapor and fractionation of the isotopes of the water molecule, hence, to an increase of the

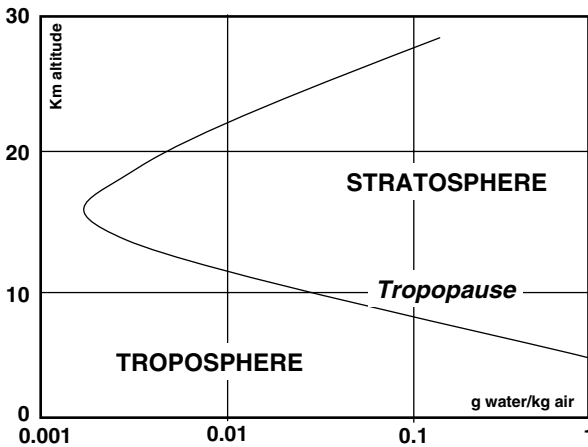


Figure 4.24. Average water vapour in the atmosphere as a function of altitude (Junge, 1963)

heavy stable water isotope species in the ocean water (the low energy phase) and the light isotope species in the water vapor (the high energy phase).

The turbulent troposphere hosts sea spray, gases, particles, organic and inorganic components of natural and man-made origin; thus, the distilled water vapor from ocean evaporation becomes physically, chemically, and isotopically charged according to the exchange intensity between vapors and air, respectively, according to chemical and photochemical processes. Finally, this mixture undergoes a dynamic exchange with the ocean water, forming the isotope composition of the atmospheric water vapor (Craig & Gordon, 1965).

Distilled water has an electric conductivity of about 10  $\mu\text{S}/\text{cm}$  (25°C) and air moisture as well as precipitation range often from 30 to 200  $\mu\text{S}/\text{cm}$ ; under vegetation covers with a high LAI or in desert areas, this electric conductivity is even higher, because of transformation processes at plant surfaces or high dust concentrations in the atmosphere reacting, for example, with the acids of precipitation.

Following ocean evaporation and atmospheric mixing, the atmospheric water vapor condenses, hence, fractionates again the stable isotopes of the water molecule to a degree, depending on the super saturation of vapor in the cloud, geographic, and elevation boundary conditions for the rain-out process; thus, all individual rain-outs represent a selective event (Fig. 4.25), but follow on the monthly or yearly average mean local and regional fractionation intensities.

At the beginning of condensation, cloud droplets are believed to be in a local isotope equilibrium composition with the moisture in the warm part of the cloud because of a rapid exchange between the droplets and the air moisture. In the cold part of the cloud, however, an additional isotope fractionation occurs by diffusion of the super cooled vapor molecules on solid surfaces (Jouzel & Merlivat, 1984).

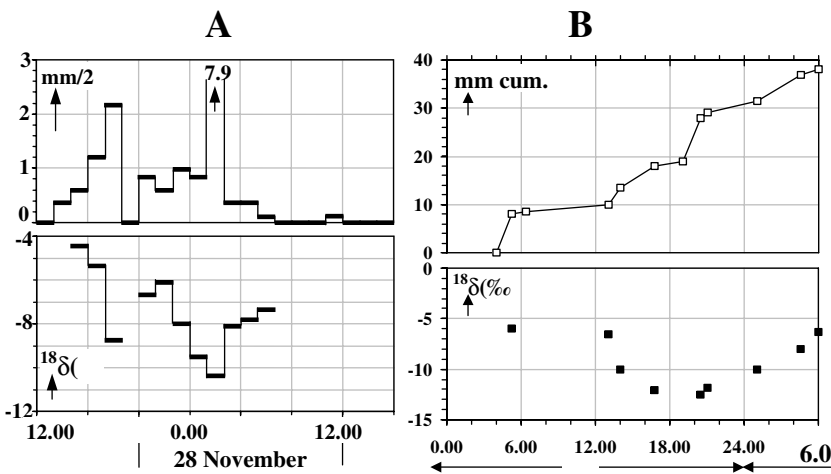


Figure 4.25. Changes of the  $\delta^{18}\text{O}$  composition of precipitation during two convective storm events ... (A) Rain intensity in mm/2 h (Mook et al., 1974); (B) Cumulative rain over variable periods

As droplets aggregate and fall through the cloud column, an exchange of isotopes between the liquid drop and the ambient air takes place, thereby approaching isotopic equilibrium between the two water phases as long as the air remains saturated with respect to water vapor at the prevailing temperature.

Below the cloud base, when the rain drops fall through unsaturated air, the water exchange is accompanied by evaporation from the droplets with the result that the heavy isotopes become enriched in the remnant drop just as the case for evaporation from lakes. Such losses of rain between the cloud base and the land surface are known from, for example, the Himalaya, where precipitation is high in high altitudes, whereas in the adjacent valleys steppe vegetation stands for low rain quantities. Under more arid conditions, this may result in complete evaporation of the droplets before reaching the land surface and the re-cycling of the water vapor into the cloud system.

The size of the raindrops, which affect the fall velocity, and thus the duration that exchange or evaporation occurs, will control the degree of achieving equilibrium conditions by the exchange within the cloud or below the cloud.

- Bolin (1958) calculated that only high intensity showers ( $>10$  mm/h) represent the relatively unmodified composition of the precipitation at the cloud base, and
- Woodcock & Friedman (1963) observed a correlation between drop sizes and  $^2\text{H}$  contents of precipitation.

There are still insufficient data to fully characterize isotope changes during single precipitation events; such variations span a range of 10‰ in  $\delta^{18}\text{O}$  (Fig. 4.25B). Early studies by Epstein (1956), Bleeker et al. (1966), and Matsuo and Friedman (1967) indicated also differences between precipitation produced by convective and frontal precipitation. These studies also showed that at the beginning an enrichment of most rain showers in the heavy isotopes occurs, because of partial evaporation during the fall of rain droplets through the air column. Consequently, Leguy et al. (1983), Rindsberger and Magaritz (1983), Gedzelman et al. (1989), Rindsberger et al. (1990), Pionke and DeWalle (1992), and McDonnel et al. (1990) report that these variations reflect the source of moisture and its rain-out history, and only to a smaller extent the local rain intensity. However, a notable exception to this rule is given by very strong tropical rains, associated with the ITCZ and its towering clouds, when precipitation with extremely depleted isotope values is found at the peak of the downpour (Matsui et al., 1983).

Generally, there is a recurring seasonal pattern (Fig. 4.26), but individual rain events show large variabilities, as is the case for the evolution of the isotope composition during a rain shower. Therefore, only averaged variations of stable isotopes in precipitation can be used to trace the seasonal/geographic origin of water, provided that no further changes in the isotope composition occur

- Along the interface atmosphere/biosphere/lithosphere and
- During the subsurface transition.

As long as the precipitated water is not subject to long residence times on the way from continents back to the oceans, equilibrium of stable isotopes of the water molecule establishes between the ocean and the continental fresh-water.

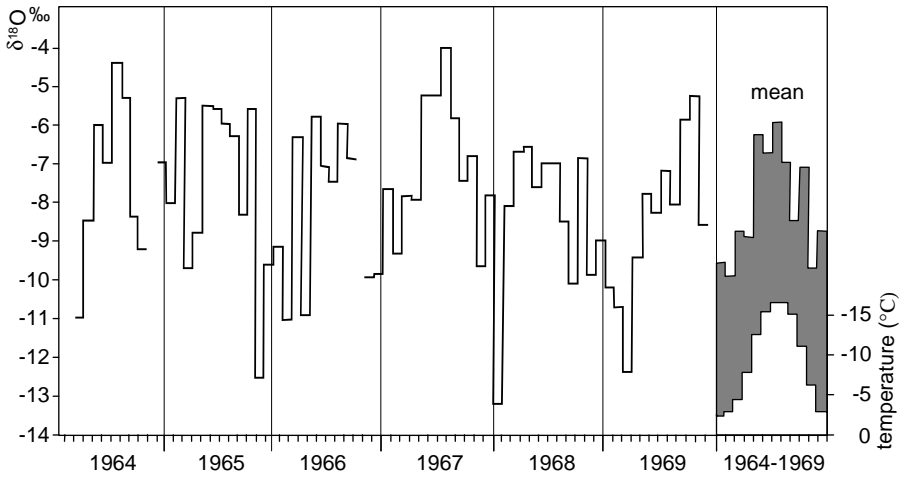


Figure 4.26. Seasonal variation of the  $\delta^{18}\text{O}$  in precipitation at Groningen and the correlation of the mean  $\delta^{18}\text{O}$  values with the respective mean monthly temperature (from Mook, 1970)

This equilibrium, however, was repeatedly disturbed during Cenozoic glacial and interglacial periods, because of accumulation in or releases of fresh-water from ice shields, glaciers, and aquifers. Retention typically occurred

- In ice covers and shields during glacial periods,
- In aquifers at the transition from glacial to interglacial times.

A release happens

- From melting ice shields and
- From aquifers at the transition from interglacial to glacial times.

This storage and release of water of the water cycle on continents expressed in connection with temperature changes in low stable isotope concentrations of fresh-water during glaciations respectively high stable isotope contents in interglacial ages; stable isotope contents of ocean water behaved just opposite to fresh-water. Thus, the stable isotopes of water are the best relative temperature indicators for climate changes during the last millions of years in the ocean and fresh-water environment as well.

The present, long-term averaged stable isotope composition of the precipitation at any given location can be rather well specified by the key stations of the GNIP network (Global Network on Isotopes in Precipitation, IAEA, 1992). A geographic pattern is observed that was summarized by Dansgaard (1964) as

- A latitude effect by decreasing stable isotope contents in precipitation from the equator to polar regions, which is paralleled by a decrease of mean air temperature and approximated as

$$\delta^{18}\text{O} = 0.34T - 11.99\text{‰} \text{ by Dansgaard (1964), or}$$

$$\delta^{18}\text{O} = (0.521 \pm 0.014)T - (14.96 \pm 0.21) \text{ by Yurtsever (1975).}$$

- A seasonality with mean low and high stable isotope contents in the cold and warm season, respectively (Fig. 4.26),
- An altitude effect with mean low and high stable isotope contents in precipitation of high and low altitudes respectively, because of a decline of the air temperatures with the altitude (Fig. 4.27), which is closer, correlated for rain than for snow (Fig. 4.27) (Gat & Dansgaard, 1972). The observed  $^{18}\text{O}$  altitude effect generally amounts  $-0.1\text{‰}/+100\text{ m}$  to  $-0.6\text{‰}/+100\text{ m}$  of altitude.
- Stable isotope variations in one single rain event according to rain-out/wash-out interchanges, condensation speeds, and elevation (Fig. 4.25),
- A mass effect on islands by an increase of the stable isotope concentrations with the precipitation amount; on island in oceans with small temperature variations, a dependence of  $^{18}\text{O}$  on rain intensity is observed to the extent of  $-1.5\text{‰}/100\text{ mm}$  of monthly precipitation, and
- A continental effect along weather trajectories from the coast to inland by a decrease of mean stable isotope concentrations due to the successive rain events.

With the distance from the coast a progressive  $^{18}\text{O}/^2\text{H}$ -depletion in precipitation is observed (continent effect; see also section 4.4.2.1), which varies considerably by regions and with seasons. It depends both on the topography and on the climate regime. For example, from the Irish coast to the Ural mountains, an average depletion of  $7\text{‰}$  in  $\delta^{18}\text{O}$  is observed; this effect is in summer only one-fourth of the effect in winter and is attributed to the re-evaporation of summer rains (Eichler,

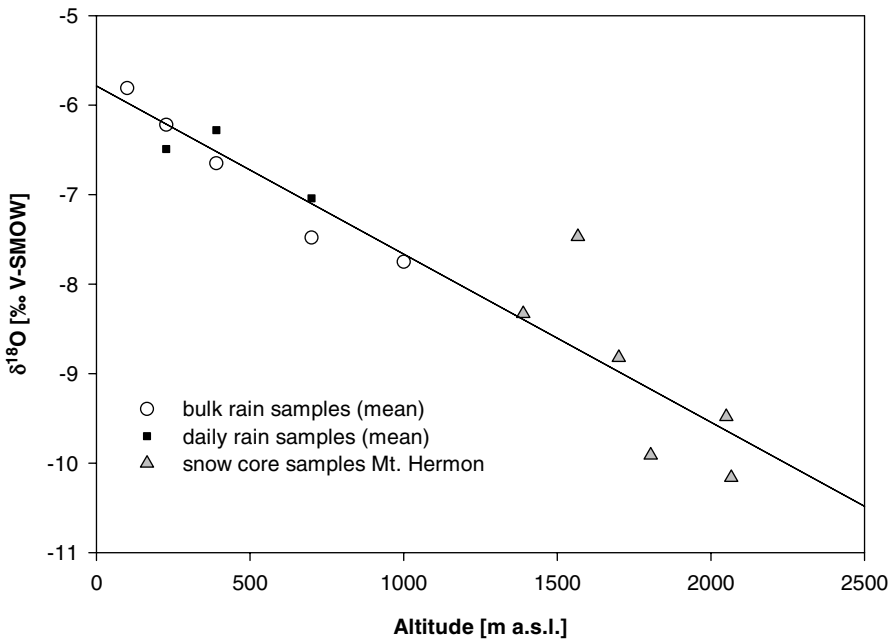


Figure 4.27. Change of stable isotope composition of precipitation with the sampling altitude in the Jordan River spring area in North Israel. Stable isotope composition increases by  $0.19\text{‰}$  in  $^{18}\text{O}$  with a decrease of the altitude of  $100\text{ m}$  (data from H. Brielmann, GSF-Institute of Hydrology, Neuherberg)



1964). In contrast, over the Amazon basin, the absence of a continent effect over thousands of kilometers was reported (Salati et al., 1979); this is attributed to the return flux of moisture by (non-fractionating) transpiration.

Continental stations away from the coast portray a seasonal change in the isotope composition of precipitation, which correlates with temperature. In contrast, at oceanic islands the seasonality of the isotope composition of precipitation practically disappears, because of the small seasonal temperature variations.

Therefore, precipitation over the ocean has a relatively small seasonal range of variation in the stable isotopes of the water molecule. There is, however, a relatively large variability in the value of the deuterium excess.

In temperate and semi-arid climates, it has regularly been observed that the  $\delta^{18}\text{O}/\delta^2\text{H}$  values of rain samples over periods of a day or less and at locations close to one another agree well within measuring accuracy. At larger distances (Fig. 4.28), especially in areas with frequent convective storms, however, large differences exist. Although over a periods of months, stable isotopes in precipitation have a similar pattern over distances of a few hundred kilometers; by contrast, single monthly samples might differ largely one from another.

Average  $\delta^{18}\text{O}/\delta^2\text{H}$  values vary from year to year. In temperate climates, this variation is small (less than few permilles), and a significant part of this spread is caused by variations in the average annual temperature. In semiarid climates, with a less regular precipitation distribution in time, large variations occur. Here, only weighted means of precipitation inputs (eq. 4.53) over many years can be correlated with the discharge response.

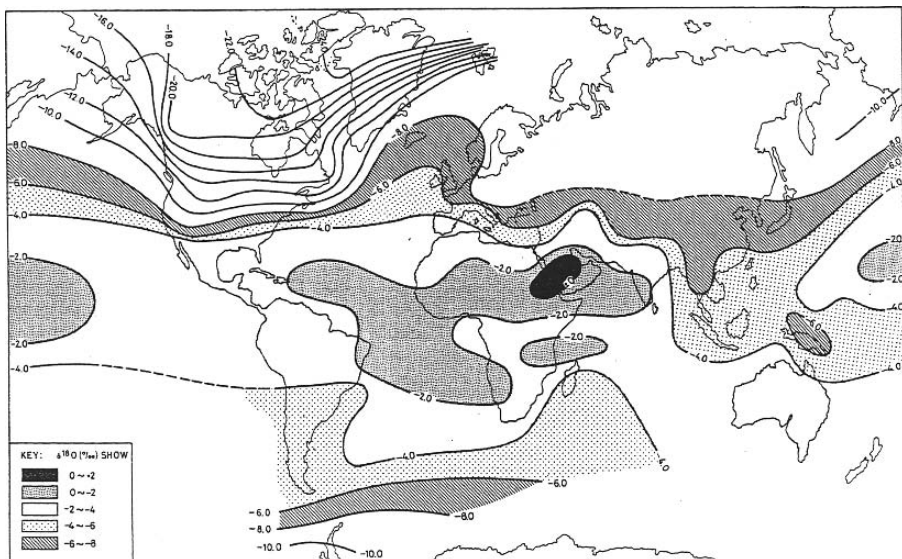


Figure 4.28. World-wide distribution of the annual means of  $\delta^{18}\text{O}$  in precipitation (Yurtsever & Gat, 1981)

The 30-year time series of the GNIP program has enabled to identify a trend of increase in  $\delta^{18}\text{O}$  in parallel with mean air temperatures in continental European stations (Rozanski et al., 1992). Contrary, fluctuations in the isotope composition of precipitation in shorter times than this proved to coincide either with changes in weather trajectories or the course of the condensation/fractionation process mentioned before.

Changes in the stable isotope composition of hydrogen and oxygen in the atmospheric part of the water cycle as expressed by the deuterium-excess ( $d$  in eq. 4.52) may differ from 10‰ of the Global Meteoric Water Line (GMWL, eq. 4.51); the known mean deuterium excesses of the MWL range from about  $d = +5\text{‰}$  to  $d = +22\text{‰}$ , depending upon humidity and temperature in the source area of atmospheric vapor; individual rains may even exceed this range. On the contrary, in accompaniment of evaporation from open waters the isotope composition of both hydrogen and oxygen in the water changes along so-called evaporation lines (Fig. 4.29) which differ from the MWL in that their slope in  $\delta$ -space is smaller than 8 (Gat, 1995). When evaporation occurs into a stagnant air layer such as the void space in the soil (unlike the turbulent layer above an open water body), the slope of the evaporation line is even lower (Allison et al., 1983), so that these two situations can easily be distinguished by means of their respective isotope signatures.

$^2\text{H}$  and  $^{18}\text{O}$  in precipitation are correlated (eq. 4.51) by the GMWL (Craig, 1961)

$$\delta^2\text{H} = 8\delta^{18}\text{O} + 10(\text{‰}) \tag{4.51}$$

A more general correlation (eq. 4.52) relates to

$$\delta^2\text{H} = 8\delta^{18}\text{O} + d(\text{‰}) \tag{4.52}$$

and is named regional meteoric water line.

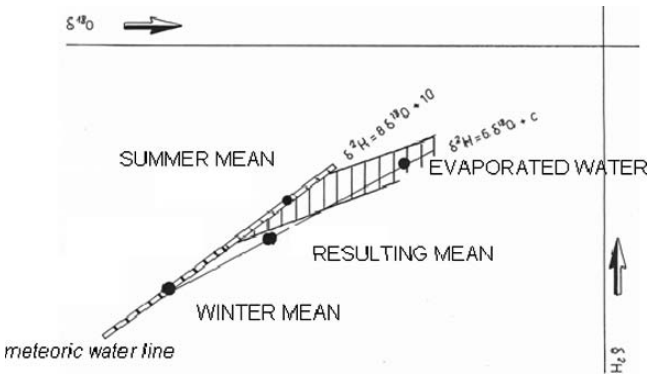


Figure 4.29. Change of the stable isotope composition from precipitation to percolation by evaporative enrichment and following mixing of non-evaporated winter with evaporated summer water; soil water with an isotope summer mean evaporates at the end of the crop season, hence, enriches along an evaporation line and mixes in the recharge season with the winter mean of non-evaporated water to a resulting mean isotope content

A typical long-term stable isotope pattern in precipitation is shown in Fig. 4.28; it underlies short-term seasonal and interannual variations and on a long run of time varies with climate changes.

A comprehensive review of the isotope composition throughout the water cycle can be found, among others, in Mook (2001, 2002).

The stable isotope composition in discharge from a watershed does not necessarily equal the amount-weighted isotope composition (eq. 4.53) of the open air input

$$\delta_{\text{input}} = \frac{\sum \delta_i P_i}{P}, \quad (4.53)$$

because as the rain falls to the ground and transforms to run-off, two basic isotope effects are often recognized. First that of selection between water of different isotope composition on a seasonal basis or by preferential routing of different parts of a rain shower into various run-off components and compartments. Special attention has to be paid to the situation at low temperatures, characterized by the precipitation of snow on ice covered surfaces, because the precipitation is then not mixed immediately with the antecedent moisture at the surface and may be lost or modified before melting occurs. The second isotope effect refers to isotope fractionation at phase transition from liquid to vapor such as evaporation from an open water body, receptors, or soil surfaces.

At the beginning of rain events and up to the point of reaching infiltration capacity, no isotope change is involved in the infiltration process; however, in the more arid (dry-land) terrain where significant surface flow usually precedes the process of infiltration, a slight enrichment of the heavy isotopes by evaporation can be noted. Once the evaporation capacity has been reached, evapo-transpiration from the land surface and from ponded water starts; as this zone dries up gradually by water losses through plants and evaporation, moisture, and isotope gradients established (Allison et al., 1983). There is, however, a significant difference between the effect of the water uptake by the plant cover (the transpiration flux) and the diffusive evaporation of the soil water from the porous medium, which can be recognized in the isotope composition of the residual water. Transpiration takes place essentially without changes of the isotope composition, whereas the diffusive flux through a non-turbulent air layer results in a residue, enriched in the heavy isotopes; this isotope enrichment follows a low-slope evaporation line in a  $^2\text{H}/^{18}\text{O}$ -diagram (slopes 4 to 6). These two mechanisms of soil water losses lead to a situation of having less isotope fractionation in a plant covered terrain as compared with a bare soil surface, although the water loss by transpiration is higher than by evaporation.

Later, isotopically enriched water mixes with non-evaporated infiltration water (Fig. 4.29), which results in the enrichment of the groundwater recharge flux relative to the mean isotope composition of rain. The degree of enrichment, which can reach values as high as several permille in  $\delta^{18}\text{O}$ , depends on the relative amounts of the rainfall and that of the antecedent moisture content of the soil, as discussed by Gat and Tzur (1967) and Gat (1987).

The magnitude of deviation of the stable isotope content of groundwater recharge from the precipitation input depends in all climates on infiltration capacities and increases with the mean air temperature. As a consequence, rivers in cold and humid areas have a stable isotope composition ( $^{18}\text{O}/^2\text{H}$ ) close to the GMWL, because evaporation from river water is not strong enough to measurably change the precipitation signal by isotope fractionation. In contrast, rivers from arid (dry-land) areas often have some evaporative signature, which results mostly from evaporation of direct run-off along the river course.

As rain falls on the land surface, it is partitioned into overland-, inter-flow-, groundwater recharge, and a return flux to the atmosphere by means of evaporation and transpiration. Thus, the stable isotope composition is modified by evaporative processes at surfaces as well as by selective responses of run-off on rainfall with different isotope composition. This shift in the isotope composition that accompanies the run-off process has been named the Isotope Transfer Function (ITF) (Gat, 1998). These shifts are especially significant under two extreme environmental situations:

- In lakes and wetlands and
- In an arid (dry-land) environment.

Isotope separation in open surface processes has first been quantified by Craig and Gordon (1965); later Gat and Tzur (1967) described the evaporation process for a mixed surface water body containing  $N_L$  moles of water per unit area expresses as

$$\frac{dN}{dt} = EP + IN \quad (4.54)$$

or

$$\frac{dN_{L,i}}{dt} = EP_i + \frac{dN_{L,i}}{dN_L} IN.$$

Using the  $\delta$ -notation leads to

$$\frac{d \ln(1 + \delta_L)}{d \ln f} = \frac{h(\delta_L - \delta_A)}{(1 + \delta_L) - \varepsilon} \cdot \frac{1}{(1 - h' + \Delta\varepsilon)(1 + \frac{IN}{EP})}, \quad (4.55)$$

with  $f$  the fraction of the liquid left

$$f = \frac{N_L}{N_{0,L}} = \left(1 - \frac{EP + IN}{N_0}\right).$$

As the liquid will not achieve a steady-state stable isotope composition, eq. 4.54 is integrated within the limits  $f = 1$  to  $f = f$  and rearranged to obtain

$$\ln \left[ 1 + \frac{h'(\delta_L - \delta_{L,0})}{h\varepsilon^* - \varepsilon} \right] = \frac{(h' - \varepsilon)}{(1 - h' + \Delta\varepsilon)(1 + \frac{IN}{EP})} \ln f,$$

$$(\delta_L - \delta_{L,0}) = \frac{(h\varepsilon^* - \varepsilon)(f^u - 1)}{u}$$

with

$$u = \frac{(h' - \varepsilon)}{(1 - h' + \Delta\varepsilon) \left(1 + \frac{IN}{EP}\right)}$$

or

$$\frac{(\delta_L - \delta_{L,0})}{(\delta_L - \delta_{L,0})} = \frac{\int_1^0 (\delta_L - \delta_{L,0}) df}{\int_1^0 df} = \frac{h'\varepsilon^* - \varepsilon}{1 + (1 + h') \frac{In}{EP}} \quad (4.56)$$

The stable isotope content in soil profiles of arid (dry-land) zones is usually divided into two parts by an enrichment peak (evaporating front) (Fig. 4.30): In the upper, shallow part only vapor moves to the surface. In the part below the evaporating front liquid transport, driven by capillary forces, dominates. Under steady-state conditions, the ascendant flux of moisture rise equals the flux of water vapor lost by evaporation.

The steady-state condition of the isotope profile is a final state. First rainfall infiltrates and freely available water evaporates at the surface; subsequently, with decreasing water contents evaporation slows down and reaches steady-state conditions when capillary rising water vaporizes in equilibrium with evaporation along the evaporation front. This cumulative evaporation is inversely proportional to the square root of time (eq. 4.57).

$$t = \frac{D}{E^2} \quad (4.57)$$

Along the evaporating front, water is converted into vapor, issuing an isotope fractionation in an open system. Therefore, the isotope composition at the evaporating front deviates from that of precipitation as well as that of the groundwater; it depends on the following parameters:

- Temperature of the atmosphere,
- The isotope composition of the atmospheric vapor,
- The moisture deficit of the atmosphere,
- The isotope composition of the reservoir water below the capillary fringe,
- Equilibrium fractionation between liquid and vapor, and
- The kinetic fractionation in the dry soil layer above the evaporation front.

At evaporation rates of 10 mm/day, the evaporation profile can reach already within 1 day steady-state conditions. In the field, especially in humid areas, evaporation profiles rarely reach steady-state unless the water table is quite close the surface.

Stable environmental isotopes of the water have often be studied

- to determine recharge areas in mountains,
- to separed and quantify discharge components in surface run-off, produced by rain events or the snowmelt,

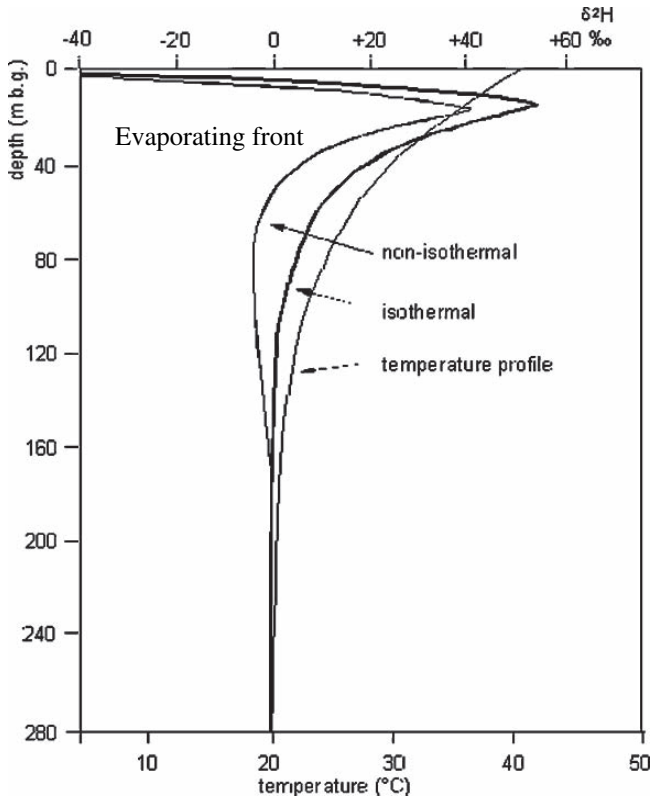


Figure 4.30. The distribution of deuterium in the percolation zone under arid climate conditions, supposing isothermal and non-isothermal steady-state deuterium conditions (after Barnes and Allison, 1988)

- to calculate MTT for determining groundwater recharge (section 4.4.2.2), and
- to investigate mechanisms and quantities of river-infiltration into aquifers.

The determination of the *mean altitude of recharge areas* in mountains refers to the altitude effect. As the measuring accuracy for  $\delta^{18}\text{O}$  is in the range of  $\pm 0.1\text{‰}$ , altitude differences should exceed 200 m in a catchment, to reasonably apply this altitude effect in delineating catchment areas.

The SW of the Dominican Republic (Pedernales Province) (Fig. 4.31) is a coastal area, flat and dry and exceeds the sea level only by some decameters. This area, however, borders in the north with the karstified Sierra de Bahoruco with altitudes of 2,000 m a.s.l., which receives lots of rain and thus is a potential recharge area for the Pedernales Province. North of the Sierra Bahoruco follows the Neiva Valle with the Enriquillo Lake, having a lake level of about 40 m b.s.l.

The goal of the isotope studies in the Pedernales Province (Febrillet et al., 1988) was to investigate the water balance, to use groundwater resources for irrigation.



Figure 4.31. The investigation area (shaded) in the southwest of the Dominican Republic

This investigation had two components: the delineation of the subsurface catchment area as compared to the surface catchment area and the determination of the recharge rate. Following, only the delineation of the subsurface catchment will be discussed.

In a first step, existing and some new precipitation stations have been equipped to sample weighted means of precipitation; this has been performed by sampling all precipitation over a given run of time and to measure the respective precipitation amount; the analytic result on stable isotopes of each bulk sample was then calculated to get yearly weighted means (eq. 4.53). The correlation of these yearly stable isotope means with the sampling altitude allows to determine the decrease of stable isotopes with the increase of the altitude, which was in the order of  $-0.25\text{‰}+100\text{ m}$  (Fig. 4.32A).

Parallel to precipitation, all springs and wells along the north and south slope of the Sierra de Bahoruco have been sampled repeatedly, to get the mean isotope

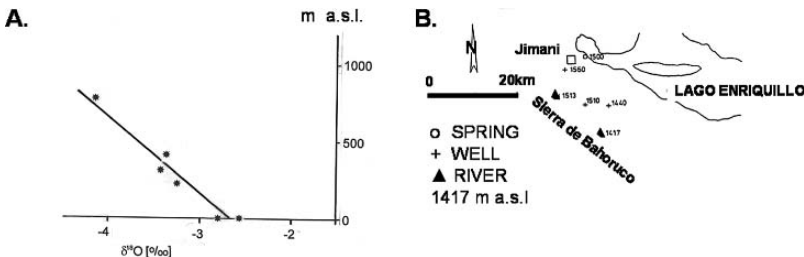


Figure 4.32. The change of  $\delta^{18}\text{O}$  with the altitude in the Sierra de Bahoruco (A) and the mean altitude recharge of groundwater (B). From the Sierra de Bahoruco down to the Lago Enriquillo the mean recharge altitudes should increase according to the geometry of the groundwater flow field

composition of the respective groundwater. To calculate the mean recharge altitude, the stable isotope content ( $\delta$ ) of the sampling point (i) as compared to a base station (0) is divided by the general change of isotopes with the altitude ( $-0.x$ ) and referred to the altitude ( $h_0$ ) of the base station (eq. 4.58)

$$h = h_0 - \frac{\delta_i - \delta_0}{-0.x} 100 \text{ m a.s.l} \quad (4.58)$$

Results of this exercise showed that in the Pedernales Province no groundwater from high altitudes occurred; however, it was found that along the north slope of the Sierra de Bahoruco sampled springs decreased in stable isotope content with decreasing sampling altitude—as expected—but then increased with further decreasing altitudes. This can only be interpreted in terms of a subsurface catchment of the Valle Neiva, which reaches over the surface water divide between the Neiva Valle and the Pedernales Province into the Pedernales Province: hence, the surface catchment area of the Neiva Valle is smaller than the subsurface catchment area, and, therefore, the Pedernales Province receives less groundwater from the rainy Bahoruco area than the Neiva Valle.

Very often, stable environmental isotopes of the water and other water components have been used for the *separation of discharge components*, specially the determination of direct (overland- and inter-flow) and indirect run-off (base-flow) during storm or snowmelt events (section 4.12). Basically, this exercise distinguishes between concentrations (C) and amounts (Q) of the end members precipitation (suffix P) and pre-event subsurface water (suffix SF) and the resulting mix in the surface discharge (suffix r):

$$C_r Q_r = C_p Q_p + C_{SF} Q_{SF}. \quad (4.59)$$

With

$$\begin{aligned} Q_r &= Q_p + Q_{SF} \\ n &= \frac{Q_p}{Q_r} \end{aligned} \quad (4.60)$$

and

$$1 - n = \frac{Q_{SF}}{Q_r} \quad (4.61)$$

eq. 4.59 transforms into

$$nC_p + (1 - n)C_{SF} = C_r = \frac{Q_p}{Q_r}$$

or

$$n = \frac{C_r - C_{SF}}{C_p - C_{SF}}. \quad (4.62)$$



the relative amount of direct discharge. Knowing the total discharge  $Q_r$  at the sampling time, delivers the absolute contribution of  $Q_p$  and  $Q_{SF}$  to the total discharge according to eqs. 4.60 and 4.61.

Tracer-based separations of run-off components have often been performed with  $^2\text{H}$  or  $^{18}\text{O}$  (Sklash et al., 1976; Sklash & Farvolden, 1979; Herrmann & Stichler, 1980) and could also refer to the electric conductivity of waters, because subsurface water acquires its dominant chemical composition quasi instantaneously in carbonate rocks (>5 weight% of  $\text{CaCO}_3$ ), which are wide spread, and electric conductivity refers quasi linearly to total dissolved solids (TDS); TDS is in common groundwater about 0.65 times the electric conductivity. In some cases, also major anions and cations, silicon and DOC have been used to separated discharge components. In all these exercises, it is important to know the origin and content of the end members, producing the mix in surface water.

The stable isotope content of rain varies spatially and temporally; this is especially true for meso- and macro-scale studies and where convective rains dominate. Generally, several bulk rainfall samplers are repeatedly collected during an event, analyzed for the stable water isotopes and combined in a weighted mean local or regional value (eq. 4.53, section 3.1) that is used for the separation of run-off components. Special care has to be taken in forests and densely vegetated catchments, because there, rainfall is subject to interception and evaporation on plant receptors, modifying the composition and amount of rain.

As the variability of stable isotopes in one individual precipitation event and by seasons is significant, often melting snow covers have been used as input signals for the separation of discharge components. The tracer signal of melting snow covers is less variable than the rain input signals (section 3.1). To quantify the influence of snow on run-off and groundwater recharge by stable water isotopes, it is necessary to determine the present isotope input of the snow cover outflow, which corresponds to the amount weighted input. For this purpose, snowmelt lysimeters have often been used to better account for the temporal variability of the isotope input as well as the rain falling on snow pack and infiltrating through it during melt periods (Herrmann et al., 1984).

In discharge component separation, the  $^2\text{H}$  and  $^{18}\text{O}$  application needs sampling; whereas, *electric conductivity* measurements can be applied online; the latter offers a more detailed insight into the discharge process than sampling does. However, it has to be taken into account that

1. The yearly variability of the input concentration in the rains as referred to the yearly mean is different in amount and direction for  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  and the electric conductivity and
2. That the rain input of
  - (i)  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  lies either above, equal or below the yearly mean in subsurface water, and
  - (ii) The electric conductivity of precipitation is the year long always lower than that of subsurface water of all except crystalline rocks.

Thus, any discharge analysis using the electric conductivities imposes lower restrictions for single rain events than applying stable environmental isotopes; but it implies that electric conductivity is governed during the discharge event by chemical constituents of the same ion activity, which is mostly realized.

The electric conductivity does often not well apply for any discharge component separation in silicate rocks because

- There is no instantaneous chemical transformation of rain or snowmelt into a water with a typical subsurface finger print, because of the missing easy soluble minerals in crystalline rocks, and
- Groundwater in crystalline rocks is scarce at all.

Among *major anions*, particularly chloride, nitrate, and sulphate applied in separation exercises, because they are considered as conservative tracers (see also section 5.1.1), derive mainly from atmospheric input or geogenic contributions. During dry periods in semi-arid and arid climates, however, evaporation concentrates these tracers on receptors at the interface atmosphere/lithosphere/pedosphere; hence, the vegetation stand and not the open air precipitation represent the true input signature. Linked to acid rains, however, chemical precipitation and storage of sulphates in the percolation zone create new or future sources of sulphate inputs.

*Major cations* are usually subject to various processes (section 4.4) such as sorption, solution and chemical/microbial transformations, thus constricting their conservative nature.

In natural waters, *silicates* derive primarily from the weathering and subsequent dissolution of silicates; the dominant species is  $H_4SiO_4$ , which dissociates at pH 9.8 into di- and trihydrogen silicate ions. The atmospheric silicate input is supposed to be close to non-measurable, but can account for significant loads, if aeolian transport processes came into the game. The use of dissolved silica in discharge separation studies is based on the finding that the dissolution of silica occurs quickly, reaches a steady-state concentration in soils and sediments within a short period of time and maintains this concentration during the discharge event. Considering these properties and assuming the dissolved silica content in precipitation to be virtually zero, dissolved silica has been used to quantify the fast run-off component.

The carbon fraction of organic matter (TOC – Total Organic Carbon) is subdivided into Particulate Organic Carbon or Matter (POC or POM) and *DOC*, where by definition dissolved substances are those that pass through a 0.45- $\mu$ m filter. In precipitation and groundwater out of porous aquifers DOC is less than 1.5 mg/L and accounts in soil water up to 20–40 mg/L and even more (White, 1985). Freitag (1997) presents a short review of factors governing DOC concentrations in natural waters, which is influenced by natural and anthropogenic sources along or close to the catchment surface and underlies mechanical filtering processes in the percolation zone, especially in its upper part; in fissured rocks, this filtering process is not as pronounced as in porous sediments; although fissures in the rock dilatation zone have lower porosities than unconsolidated rocks, they have larger fissure width than pores. Filtered DOC is preferentially exported to surface waters through interflow (Seiler et al., 2002) and linked to this export many agro-chemical (ammonia,

pesticides, etc.) followed by particle favored transport the propagation paths of DOC (Seiler et al., 2000). Hence, in the scope of discharge, DOC concentrations have often been observed to increase with rising stream discharges during storm events (Fig. 5.4, section 5.1.1).

Discharge separation has a different meaning in unconsolidated and consolidated rocks. In unconsolidated rocks the components groundwater-, inter- and overland-flow can be separated applying appropriate end members of the mixing equation and combinations of discharge analysis. In consolidated rocks with unlimited infiltration capacities, slow matrix-flow (often called diffusive-flow without being diffuse), controlling discharge during base-flow conditions, and conduit-flow after rain events can be determined (Seiler, 1968; White, 1998, Seiler et al, 2000). From such run-off separations in consolidated rocks, a mean a 40% conduit-flow and 60% matrix-flow during discharge events (e.g., Seiler, 1968; Pfaff, 1987) has been reported.

The use of environmental stable isotopes of water in quantifying *Forced River-infiltration* into aquifers is based on a comparison

- Of the damping and phase shift of the stable isotope signal in the river water as compared to the respective response signal in any groundwater well; this is the way to determine flow times along given distances, and
- Of the mean isotope concentration in the river water as compared to the mean in groundwater to determine mixing ratios.

An example for stable isotope exercises to quantify natural and forced river-infiltration into aquifers, results from the river Lech/Germany (Fig. 4.33) and the response in groundwater wells (Fig. 4.34) with and without groundwater extraction. The river Lech belongs to a temperature-driven discharge system (section 3.1) with high  $^{18}\text{O}/^{16}\text{O}$  contents in winter and low contents in late spring because of the snowmelt in the Alps (Fig. 4.33). As compared to the changing river signals,

- Wells close to the river behave similarly, but with a phase shift and damped variations and
- Wells in remote areas from the river refer only to the local recharge (Fig. 4.34 upper curve).

Between these two extremes, all kinds of transition occur.

The quantitative determination of admixed river water to the locally recharged groundwater is based on isotope means of the infiltrating river and of the local groundwater recharge on the input site, and the means of the isotope mix in the studied well. As this calculation has been performed for many observation wells, the percentage of admixed river water to groundwater is represented in Fig. 4.35. From this, it can be seen that in the south of the study area, where no groundwater extraction occurs, the zone influenced by natural river infiltration, is narrow (profiles VI and VII in Fig. 4.35), widens downstream (profiles IV and V in Fig. 4.35) of a river dam and widens further in the area of forced river infiltration (profiles I, II and III in Fig. 4.35).

The evaluation of the mean residence time of water on the flow path from the river to the groundwater-sampling site is not based on averages but on the dynamics of river isotope variations; it can be calculated using eq. 4.47. At low mean residence times (<1 year), the choice of the model has little influence on the result.

If the input and output concentration functions are known, the mean residence time of water ( $MTT_w$ ) can be calculated according to eqs. 4.47; by experience the dispersion expression  $[D/(vx)]$  is mostly in between 0.1 and 0.3. In Table 4.15 some calculated mixing ratios and mean residence times are listed from two observation periods; results are mostly identical, because the exploitation boundary conditions were kept close to constant.

#### 4.4.3 Artificial Tracers

Artificial tracing is applied in the percolation zone to determine groundwater recharge and hydrodynamic dispersion parameters and in rivers to measure discharge.

Flow in the *unsaturated zone* can be determined by hydraulic (section 4.3) and tracer means. For both methods, it is supposed that percolation is vertical down and lateral flow is negligible. Using hydraulic methods, lots of box, compartment, and numerical models are available, which are all based on the equation of the conservation of energy (eq. 3.1) and masses (eq. 4.33); such models are fed with data on

- precipitation and ET,
- the hydraulic functions of soils/sediments,
- water content and
- suction.

This data set for hydraulic evaluation comes from meteorological stations, tensiometers, and TDRs on the experimental site; hydraulic functions are often

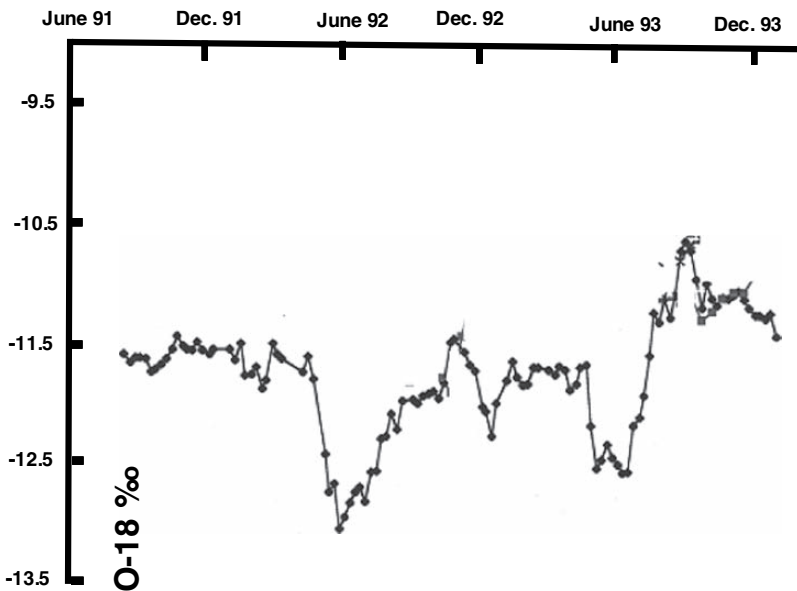


Figure 4.33.  $^{18}\text{O}/^{16}\text{O}$  ratios in the river Lech, Germany, from 2 weeks sampling campaigns. Sampling has been performed on different sides along the river in the study area (Fig. 4.35). Data from P. Trimborn, GSF-Institute of Hydrology, Neuherberg, Germany

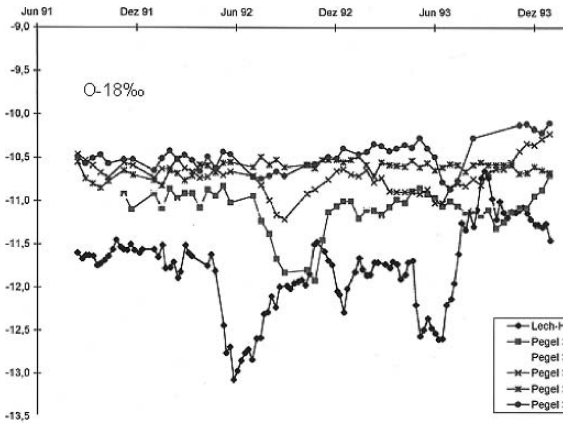


Figure 4.34.  $^{18}\text{O}/^{16}\text{O}$  ratios in the groundwater remote and close to the river Lech, Germany, from 2 weeks sampling. Data from P. Trimborn, GSF-Institute of Hydrology, Neuherberg, Germany

approximated with empirical formulas (Mualem, 1976; eq. 4.30). In contrast, the determination of groundwater recharge with artificial tracers depends on the choice of an appropriate non-reactive tracer, the implantation of suction cups for continuous water sampling and the choice of a representative season to start tracing.

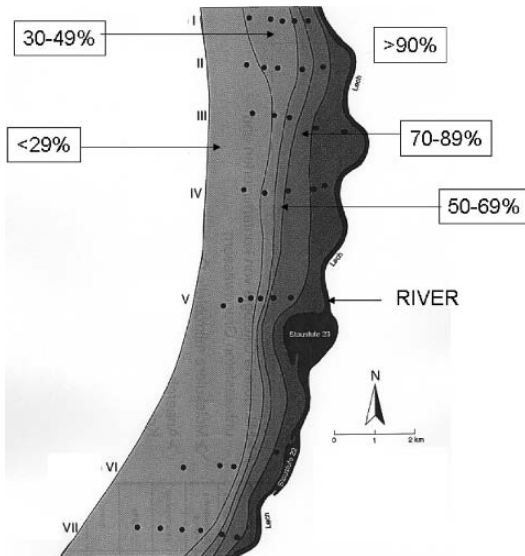


Figure 4.35. Distribution of the relative admixture of river water (%) to groundwater in the study area. Black points show the sampled wells; roman numbers = well row. Data from P. Trimborn, GSF-Institute of Hydrology, Neuherberg, Germany

Table 4.15. Mean-turnover-times (MTT) and admixed river water, calculated from the Lech river input and the groundwater output ratio of  $^{18}\text{O}/^{16}\text{O}$

Sampling row	Well No.	Campaign 1986–1988		Campaign 1991–1994	
		% river water	MTT in days	% river water	MTT in days
<b>II</b>	7004	87	16	86	16
	7029	46	16	54	16
	7026	31	8	37	8
	7023	n.d.	n.d.	41	14
	2020	94	4	94	4
<b>III</b>	2023	86	14	95	12
	2024	45	15	58	15
	2025	24	14	32	14
	2048	0	n.d.	3	n.d.

n.d., not determined.

Soil moisture changes along profiles have also been used to determine flow velocities and groundwater recharge. However, such results are often in disagreement with simultaneous, tracer-based determinations of groundwater recharge, which is mainly attributed to a quick pressure wave displacement (Andersen & Sevel, 1974) apart from the very slow mass transport. Tracer methods measure only mass transport by matrix or preferential-flow and never refer to pressure equilibration.

Tracer experiments in the percolation zone can start

- In temperate climates from the land surface, but should exceed in length the depth range of the effective root zone, which corresponds in crop lands to  $>100$  cm from the land surface and which is an important sector of transformation of the infiltrated water into lateral inter-flow respectively vertical down groundwater recharge;
- In arid (dry-land) areas, they should start beneath the evaporating front (Fig. 4.30) or at  $>30$  cm depth to avoid a fractionation of tracers of the water molecule or a concentration increase of soluble tracers, both by evaporation; thus, evaporation

Table 4.16. Water content variations in a Quaternary loess (2-17, 2-18) and two Tertiary fluvial sediments (gravely sand 9-3, 9-B, medium to coarse grained sand 12-9, 12-R); in 20 cm below surface it expresses seasonal variations, in 130 cm below surface inhomogeneities

Location	Water content (%) in 20 cm below surface				Water content (%) in 130 cm below surface			
	No. of measurements	Mean	Maximum	Minimum	No. of Measurements	Mean	Maximum	Minimum
2-17	899	33	50	19	810	44	46	36
2-18	1098	32	48	22	714	35	40	30
9-3	1140	34	41	21	728	25	28	22
9-B	1267	29	49	22	822	31	32	30
12-9	1147	31	43	12	760	42	44	33
12-R	1353	33	49	18	885	43	44	40

makes tracer balances difficult or may even lead to delayed flow velocities, if the tracer was first enriched close to the soil surface by evaporation and later leached by an efficient infiltration event.

As compared to hydraulic methods, tracer experiments are easy to execute; to evaluate, however, they deliver only average percolation values over a long run of times; as matrix-flow velocities in the unsaturated zone are low (<2 m/year), tracer experiments last about 1 to more than 3 years over a depth range of 2 m in temperate and 1 m in semi-arid/arid areas; these averages on percolation are weighted means with respect to the prevailing land use, plant covers, seasons, and special meteorological conditions. Contrary to tracer experiments, continuous in-situ measurements of water tension and water content provide process information on the influence of daily and seasonal cycles, crop/water interactions and land cultivation upon percolation. As the wide range of fabrics of the unsaturated zone conducts to a respective wide range of water contents and capillary forces,

- Any detailed information from hydraulic methods gives an excellent insight into processes, but needs transfer functions to transform local results to the catchment scale, and
- The averaged information from tracer tests cannot immediately contribute to optimize protection, cultivation, and land use strategies, but is less scale dependent than hydraulic methods are.

Tracers have been applied for percolation studies on surface areas of 20–50m<sup>2</sup> in size; they are supposed to propagate in the unsaturated zone

- Only in  $z$ -direction, whereas any flow in the  $x$ - and  $y$ -direction can be neglected, and
- Propagate as a front more or less homogeneously through the percolation zone.

Both assumptions are not always realistic. Any lateral transport (section 3.5, Figs. 3.12 and 3.15) (Behrens et al., 1980; Seiler & Baker, 1985) may come into the game at very high infiltration amounts like in the case of river-infiltration and then needs a three-dimensional consideration. In many unconsolidated and almost all consolidated sediments/rocks preferential-flow (section 3.4) plays a major role (an average of 20% [fine-grained sediments] to 50% of infiltration [gravels] may contribute to preferential-flow). Figure 4.36 presents the design of a natural lysimeter (section 4.2), which has often been used with three replicate cups per monitoring level.

The non-reactive tracer propagation in the unsaturated zone is described by the dispersion/convection equation

$$\frac{dC}{dt} = D'_L \frac{d^2C}{dz^2} + D'_{Tx} \frac{d^2C}{dx^2} + D'_{Ty} \frac{d^2C}{dy^2} - v_a \frac{dC}{dz} \quad (4.63)$$

in which

$$D' = \lambda D_M + \alpha' v_a \quad (4.64)$$

The first three terms on the right side of eq. 4.63 correspond to dispersion and the fourth term to convection; in the case of piston flow, the dispersion terms can be neglected; hence, only the convection term dominates tracer propagation and the

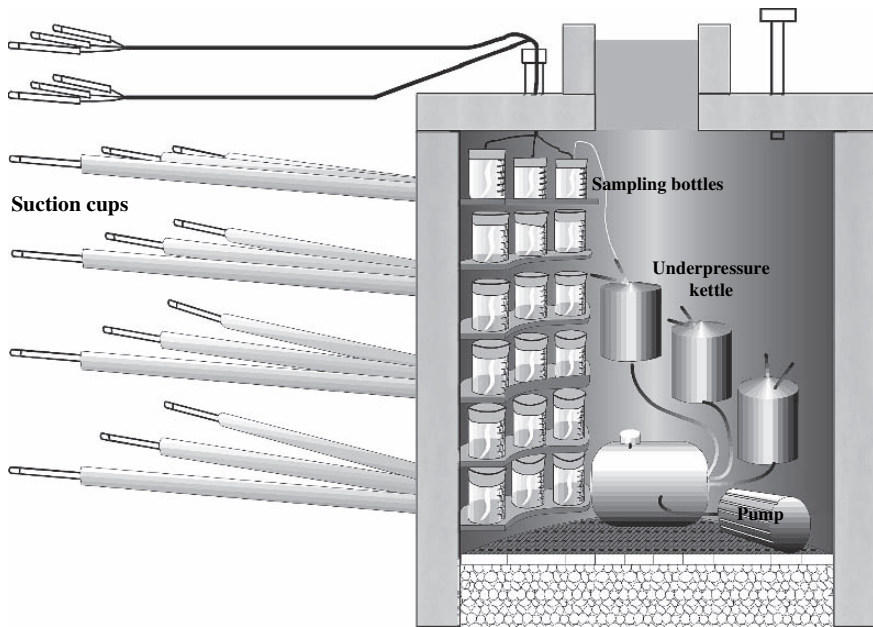


Figure 4.36. Experimental set up to execute tracer experiments in the unsaturated zone and to sample soil solution beneath an agricultural area

geometry of any break through curve of a non-reactive tracer appears unchanged as compared to the geometry of the input signal.

Hydrodynamic dispersion (eq. 4.64) has the two components, molecular diffusion in the pore channels ( $\lambda D_M$ ) and the dispersivity-velocity term ( $\alpha' V_a$ ); as can be seen from eq. 4.64, at low flow velocities, the molecular dispersion and, at high flow velocities, dispersivity dominates the geometry of the response function.

Many laboratory and field experiments on percolation have shown that in the observation scale of centimeters to less than 5 m longitudinal dispersion coefficients ( $D_L$ ) are in the order of  $7 \times 10^{-10} \text{m}^2/\text{s}$  to  $4 \times 10^{-9} \text{m}^2/\text{s}$  or the Dispersivity  $\alpha'$  was in the order of 0.03–0.5 m (Table 4.17). These low dispersion coefficients/dispersivities are close to the diffusion constant of most artificial, non-reactive tracers, which is in the order of  $10^{-8} \text{m}^2/\text{s}$  in water and even lower in water saturated media.

With the propagation time of any non-reactive tracer, percolation velocities are determined and are then transferred into groundwater recharge rates with prevailing mean water contents (eq. 4.33). As this evaluation does not include preferential-flow, results often underestimate recharge rates.

Tracer based *surface discharge* measurements often apply to quantify amounts of run-off in connection with river-bed-infiltration studies. They can be performed with dye tracers under turbulent and laminar flow conditions as well; in contrast to tracer experiments, discharge measurements with current meters can only be performed under steady-state and laminar flow. The use of dye tracers (Käss, 1998)



*Table 4.17.* Dispersivities and dispersion coefficients determined by means of  $^2\text{H}$  tracing of the unsaturated zone

Location	Lithologic/soil unit	Sampling depth in m	$v_a$ in m/year	Dispersivity $\alpha'$ in m	Dispersion coefficient in $10^{-10}$ m <sup>2</sup> /s
2-18	Lu with TU3, Quaternary loess	10	0.09	0.24	6.9
		10	0.8	0.047	12.0
		10	0.31	0.088	8.7
		20	1.10	0.088	30.9
		90	0.60	0.166	31.8
		90	0.67	0.055	11.8
9-3	Ls4-St2 with clay lenses, Tertiary sand	10	0.44	0.140	8.2
		10	0.49	0.058	9.1
		10	0.88	0.104	29.3
		50	1.10	0.097	34.1
		50	16.64	0.137	72.9
		180	1.24	0.173	68.6
12-9	Ls3, Tertiary sand	10	0.34	0.087	9.5
		10	0.78	0.035	8.7
		10	0.73	0.041	9.6
		10	0.62	0.075	14.9
13-16	Ls2-St3, Tertiary sand	10	1.14	0.085	31.0
		10	0.27	0.046	4.0
		20	0.24	0.440	33.8
		90	0.78	0.300	74.9

Results from field experiments.

requires a sufficiently long flow distance to provide a complete mixing of the tracer over the whole cross section of the river and no in- or outflow along this river section; appropriate distances for homogeneous mixing are 50 m to few kilometers in turbulent respectively meandering rivers.

Tracer injection can be instantaneous or continuous, and the discharge evaluation refers to the tracer break through curve (as a response to instantaneous injection), respectively, the break-through front (as a response to continuous injection). To calculate the discharge along the river section, the equation of conservation of masses applies. It delivers in the case of an instantaneous injection a discharge  $Q$  (eq. 4.65) of

$$Q = \frac{M}{\int_0^{\infty} C dt} \quad (4.65)$$

and in the case of a continuous injection (eq. 4.66) of

$$Q = \frac{Q_i C_i}{C_{\text{plateau}}} \quad (4.66)$$

The indices  $i$  refer to the injection point and the index plateau to the tracer plateau at the detection point.

The advantage of this tracing method is that only one measuring point, mostly in the centre of a river, is necessary, and both the continuous tracer input and the tracer output can be performed online with high accuracy. These measurements, however, do not quantitatively apply on long distances of big rivers, because of the mass balance equation, which supposes no losses or gains of water along the flow path; big rivers, however, are important for groundwater/surface-water exchanges and forced groundwater recharge.

#### 4.4.4 Application of Tracers

Basic preconditions to apply artificial tracers have already been reported in section 4.4; here, application refers only to what is the goal and how to approach representative groundwater recharge results.

Most artificial tracing has been performed

- In areas with shallow rooting vegetation, because of the accessibility of the percolation zone,
- On short profile lengths, because of time restrictions in studying low percolation velocities as well as because of the detection limit of tracers,
- With replicates of suction cups, because they do not cover a wide range of stream bundles, and to better control both the representativeness of such tracing results and preferential-flow.

Bromide has often been used instead of  $^3\text{H}$ , because of missing liquid scintillation counting installations or because high  $^3\text{H}$  concentrations would disturb the natural tritium background over a long period of time. Br is scarce in fresh-water but becomes enriched in soil water to several hundred milligrams per liter if the interface atmosphere/lithosphere was exposed over a very long, uninterrupted time to evaporation; under these circumstances, studies in Tunisia and the Jordan rift resulted in bromide background concentrations of several hundred milligrams per liter as compared to humid or irrigated areas, where Br is either not detectable or occurs in concentrations of less than few milligrams per liter.

All tracers other than  $^2\text{H}$ ,  $^{18}\text{O}$ ,  $^3\text{H}$ , or Br should be calibrated against one of the before mentioned tracers, to ensure the non-reactive behavior (Berg et al., 2001).

Tracer experiments in the Scheyern test site (South Germany) have been performed with deuterium;  $^2\text{H}$  contents reached a maximum in the breakthrough curve of about five orders of magnitude (2000‰) above the mean annual deuterium concentration (−60‰) in precipitation. With such high concentrations preferential-flow was still detectable (Fig. 3.8); at deuterium concentrations exceeding only

three to four orders of magnitude the mean annual  $^2\text{H}$  ratio, any recognition of preferential-flow was difficult. This is due to the very small quantities of preferential fluxes during single infiltration events (as an average 20% of infiltration in the study area) and to the high water contents of 25–30vol.% (fine- to medium-grained sediments such as loess and sands). Using fluorescent dyes, much smaller quantities could be applied, because they have a higher detection limit than the stable isotopes of the water molecule, however, they only partly penetrate through the soil, because organic matter sorbs it. As expected, in gravels apply much lower tracer quantities than in loess and sands because of the low natural water content of these sediments.

During tracer experiments, markers should not remain longer than a few hours at the ground surface to avoid fractionation (stable isotopes), enrichment through evaporation (chemical tracers), or any photolytic disintegration (fluorescent dyes). The input of tracers into the percolation zone should meet quasi steady-state hydraulic conditions, which are best verified during the recharge season or by continuous artificial recharge. Therefore, it is recommended to trace during continuous sprinkling or to inject at the base of the humic soil layer or to trace a melting snow cover above an unfrozen soil.

In all climate zones, tracing is favorable in the recharge season but delivers some overestimate of real groundwater recharge. This was

- at any time in arid (dry-land) areas,
- in the mid of the recharge season in semi-arid climates,
- at the end of winter season and during snowmelt in humid climates, and
- close to the end of the melting season in cold climates with open permafrost.

Athavale et al. (1980) and Athavale and Rangarajan (1988) report that tracer-related recharge estimates are reproducible by about 10% and that comparisons of results on groundwater recharge using traditional water balance or numerical modeling or the chloride (section 4.4.2) or groundwater level fluctuations methods (section 4.1.3) were in good agreement with tracer results on groundwater recharge. From humid areas, it is known that tracer-based estimates of groundwater recharge tend to somewhat smaller values than respective hydrograph calculations, because of preferential-flow, which turns into inter-flow (section 3.5) and may account as an average to 20–25% of infiltration in fine- to medium-grained sediments and up to 50% in gravels.

Groundwater recharge studies by tritium tracing have been extensively executed in the Monsoon dominated North of India (Gupta & Sharma, 1984; Sukhija et al., 1996). As related to a yearly average precipitation of 700 mm, these studies led to a groundwater recharge of

- 25 mm/year or 3–5% of precipitation in clay sediments,
- 40 mm/year or 5–7% of precipitation in sandy-loamy sediments, and
- 90 mm/year or 11–6% of precipitation in medium to coarse grained sediments.

Allison and Hughes (1974) determined for the Gambier Plain in Australia (Mediterranean type of climate) in clay rich and sandy to loamy sediments a recharge of 40 mm/year and 140 mm/year respectively. In Transvaal, recharge has

been calculated to 16 and 53 mm/year for loamy and sandy soils, respectively, supposing a piston flow movement of percolation water (Bredekamp et al., 1974). Dincer et al. (1974) estimated with the  $^3\text{H}$ -peak method a recharge of 23 mm/year for the Dahna dunes in Saudi Arabia; this, however, is an astonishing high number as compared with a yearly mean annual precipitation of 60–70 mm. Gvirtzman and Margaritz (1986) found a 19% recharge in the sandy part of the Coastal aquifer of Israel with 600 mm/year of winter rain and 450 mm/year of summer irrigation. All these recharge numbers refer to unconsolidated sediments and disregard any preferential-flow, which may become considerable in shrinkable and coarse grained sediments, but seems to be low in well sorted, loamy and fine- to medium-grained sediments. Sukhija and Shah (1976) found at field sites in North India that the  $^3\text{H}$ -peak displacement method gave 20–40% higher drainage estimates than the  $^3\text{H}$  mass-balance method. Seiler et al. (2002) and Sukhija et al. (2003) have shown that neglected preferential-flow may lead to an estimate of only 80–90% of real groundwater recharge.

To execute tracer-based discharge measurements, non-reactive tracers and tracers with a high detection limit are imperative (section 4.4). In between these tracers halogens and dye tracers proved to be suitable and can be detected on line with conductivity meters or portable fluorimeters.

As dye tracer and current-meter methods deliver only instantaneous results and always refer to steady-state conditions, which hardly prevail during river infiltration over the run of a hydrologic year, environmental tracers opened a new insight into quantities and mean residence times of river infiltration into groundwater (section 4.4.2.3).

#### 4.5. WATER SAMPLING AND SAMPLE CONSERVATION

It is imperative for water sampling to get representative samples from both the collection site and with respect to the sampling goal and to maintain the sample integrity on the way from the field to the laboratory. Water sampling is not representative by nature: It needs a drill with special equipments to sample water or a core. These activities can disturb or average the tracer or chemical information of the sample. It should be further considered that physical or chemical information in water often vary over short distances and with time, hence, include not precisely known scale information. Therefore, fixed-point sampling with fixed sampling tools is preferable to repeated sampling by drilling.

Routine *precipitation sampling* is performed on a daily, weekly, or monthly base with traditional precipitation gauges; however to minimize any contamination of sampled precipitation by dust, particles, and aerosols, wet-only-samplers are preferable. To reduce evaporative fractionation of  $^2\text{H}$  and  $^{18}\text{O}$  in the precipitation gauge, either short-term sampling or any protection of sampled rain against evaporation, both followed by storage of water in well-sealed bottles are recommended. Collected snow should be allowed to melt slowly to avoid evaporation and sublimation. Precipitation sampling must always be associated with a record on

precipitation amounts, to calculate weighted means (eqs. 4.40 and 4.53) of the chemical or isotope tracer input concentration into the hydrologic system.

*Surface water sampling* needs some precaution, which can easily be recognized in the field. According to the vertical and horizontal flow profiles in a straight stream, quasi stagnant water occurs at the river borders and quickly moving water at the water surface in mid river position. Best sampling refers to a flow profile transverse to the river course. Special care applies when sampling takes place downstream of the confluence of a tributary river, because transverse dispersion in streams is very weak; hence, it takes long distances to reach a representative mixing of both waters.

*Water sampling in the unsaturated zone* is faced with small-scale inhomogeneities and a little spherical space increment influenced by an operating suction cup or sampling by coring; therefore, it is emphasized to have samples collected by replicates at the same level. Figure 4.37 demonstrates such differences in the results of a tracer experiment, for which samples were collected with fixed installed suction cups in three replicates at the same level and 0.5 m distant from one another.

In general, water samples from the unsaturated zone may be collected

- Directly by free drainage like in lysimeters, suction cups, or capillary wick samplers or
- Indirectly by extracting water from cores and absorbent materials.

Suction cups and plates mostly are permanently installed in the unsaturated zone and thus favor the record of real parameter variations. The efficiency of suction cups with 20- $\mu\text{m}$  pore size is restricted to under pressures <800 hPa, at smaller pore sizes the air entry point moves to higher values (<3000 hPa), but also filters

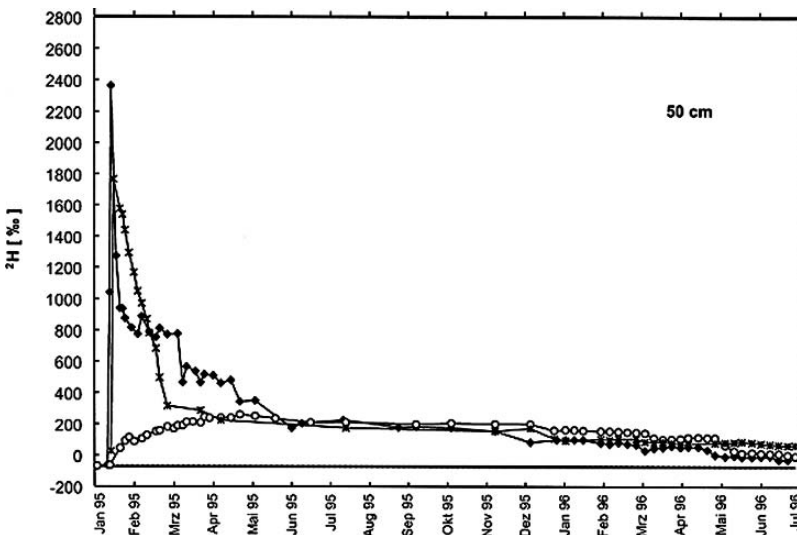


Figure 4.37. Break-through curve of deuterium, sampled at the same depth in replicates at 0.5 m distance

percolation water. In humid areas, suction exceeding 800 hPa prevail during the vegetation period close to the land surface (0–50 cm b.g.s.) and is low during the rest of the year; in dry-lands, it exceeds all over the year till great depth the 800 hPa; therefore, in these seasons or under these dry conditions, water has to be collected by coring or with sorbing materials, followed by an extraction, replacement, or dilution in the laboratory for the analytic purpose.

Suction cups should consist of inert materials such as ceramics or sinter materials, to be not faced with sorption. The pore sizes of suction cups determine the air entry point and together with the cup design (thickness of the wall, inner volume, and tube volume till the collection point) the sensitivity of response to changing quality conditions. Sinter suction cups with 5–20  $\mu\text{m}$  pore sizes are well adapted to sample percolation water in most unconsolidated or decompressed sediments.

Before installing cups in the field, they should become conditioned with water similar to that encountered in the studied percolation zone. This is especially true for any chemical analysis.

The under pressure applied should not differ too much from the prevailing one,

- To avoid degassing of the water, causing disturbance of gas related solute matters such as carbonates in the soil solution and
- Sampling from areas other than the place of the sampling device may occur.

As flow and water content in the unsaturated zone are mostly low, sampling of water for tracer analysis will always cover a long time interval (>1week).

*Sample preservation* needs by

- Temperature control to minimize microbial activities,
- Light protection to avoid photolytic processes, and
- Tide stop cocks and fulfilled bottles to avoid evaporation during transport and storage.

*Storage of collected water* has a significant impact on the analytic result. Plastic containers can allow sometimes an exchange with the surrounding air; glass can release or exchange elements of interest into the water sample. Most useful container materials for water storage are Teflon, glass, stainless steel, and polypropylene. Many others such as silicone, copper tubes, PVC, polyethylene, and so on can exert chemical changes.

*Extraction of water from cores* by dilution aims first to saturate the sediment by a known amount and quality of water to make water easily extractable. This dilution should be combined with a homogenization of the two waters. In the second step, homogenized water is extracted by centrifugation or with suction cups. For the dilution analysis, extreme compositions of waters are used like distilled water for chemical or Antarctic Water for stable isotope analysis. The water content of the sample ( $Q_s$ ) and its natural isotope or chemical composition ( $C_s$ ), the added quantity of water ( $Q_a$ ), and its isotope or chemical composition ( $C_a$ ), and the resulting composition of mixed waters ( $C_m$ ) can easily be determined. From the mass balance equation (4.67)

$$C_s Q_s + C_a Q_a = C_m (Q_s + Q_a) \quad (4.67)$$

Follows:

$$C_s = \frac{C_m(Q_s + Q_a) - C_a Q_a}{Q_s} \quad (4.68)$$

The distillation of water from sediments (Araguas-Araguas et al., 1995; Ingraham & Shachel, 1992) applies only for the isotopes of the water molecule, because they underlie fractionation, whereas all solute matters produce residuals through evaporation; this evaporation must be performed in closed systems and till the point of complete dryness of the sediment. Only under these conditions, isotope fractionation does not show up in the distillate and an uneven distribution of the isotope concentration in the pore water has no more influence on the analytic result.

In some special cases also replacing methods (Ingraham & Shachel, 1992) have been used in applying a wetting liquid that replaces water in the sediment pores. The transition between the two liquids does not go off with a sharp front; the mixing area between both has to be considered in the evaluation of analytic results.

#### 4.6. COMPARISON BETWEEN TRACERS AND CONVENTIONAL TECHNIQUES

The existing methods to determine groundwater recharge are based on

- mass balances,
- turn-over times,
- mixing,
- fluxes,
- hydraulics, and
- the typical outflow characteristics of reservoirs.

Tracer techniques play in all methods an important role.

All these methods have a more or less significant error bare, which is

- High (maximum 25%) at small or local scales, and if too many parameters intervene in determining groundwater recharge, and.
- Low (minimum 10%) at large or catchment scales (>1 km<sup>2</sup>).

Therefore, it is recommended to apply simultaneously different and independent methods to approach the real value of groundwater recharge. This is especially important for climates with exceptional conditions like for arid, semi-arid, and cold climates and to some extent also for mountainous and humid tropical areas, in which different forms of advective respectively often convective rains occur.

Traditional *meteorological water balances* (section 4.1) refer to precipitation and evaporation to calculate total discharge. As groundwater recharge has a long turn-over-time in the percolation and aquifer zone, such water balances do not quantitatively give a direct response to instantaneous meteorological inputs, but reflect averaged, long-term responses. On a long run of time, this methods provides excellent results; this time span is longer for arid than for humid climates and longer for humid tropical (20 years) than for humid temperate climates (10 years), because of

- the mode and areal distribution of precipitation (frontal or convective rains, topography),
- infiltration and interception capacities, which have a seasonal and a pre-event/event related character,
- MTT of run-off components, which may also have a seasonal character, and
- a possible transient discharge.

Applied on short terms, it gives orientations on processes about groundwater transport, recharge and storage if the calculated run-off is compared with the observed event induced change of discharge. Such results, however, are difficult to quantitatively generalize without transfer functions.

The meteorological method often does not allow differentiating between the run-off components overland-flow, inter-flow, and groundwater recharges, except infiltration capacities at the interface atmosphere/lithosphere are unlimited.

Most problematic parameters in water balance studies are

- the determination of the catchment-related effective precipitation under growing vegetation covers or in areas with advective (mountain areas) and convective rains (warm humid climates),
- the seasonal and event related variable water retention and infiltration capacities of interfaces, which distribute precipitation on different flow-path,
- present evapo-transpiration on short-terms,
- the role of dew to precondition interfaces or to directly contribute to discharge, and
- the often missing congruence of the size of surface and subsurface catchments in flat ( $<5 \text{ km}^2$ ) and mountain recharge areas, respectively.

In humid climates, ET is significantly governed by the plant cover and the groundwater table—if too close to the ground surface ( $<2.5 \text{ m b.g.s.}$ )—in semi-arid and arid climates E is the most difficult number to calculate.

Artificial lakes in catchments, which have been constructed for irrigation purposes, for the production of electric energy or for flood control have a significant influence on water balances by means of an always high evaporation and sometimes by a decrease of infiltration capacities because of silting of the storage space.

Discharge analysis by *hydrograph methods* (section 4.1.2) allow a good approach to quantify mean flow paths governing river discharge, but cannot consider subsurface run-off beneath the reference point, for which the hydrograph analysis has been established; this missing subsurface run-off, which also belongs to groundwater recharge, does not play a significant role in catchments exceeding  $100 \text{ km}^2$ , but is important in small catchments ( $<5 \text{ km}^2$ ).

Perched groundwater may lead to an under- or overestimate of groundwater recharge through hydrograph methods, according to a subsurface export or import, respectively, of groundwater from and to neighboring catchments; this, however is only important for small catchments  $<5 \text{ km}^2$ .

To relate the discharge analysis to the respective catchment size, the subsurface catchment area must be known; in catchment areas  $<100 \text{ km}^2$  the extent of surface



and subsurface catchment areas may significantly differ, in larger catchments this difference is mostly not important (Febrillet et al., 1988).

Hydrograph analysis can be falsified, if natural or artificial lakes respectively reservoirs intervene in the discharge formation. For example, lakes in contact with groundwater change the aquifer out-flow characteristic and flatten the overland- and inter-flow response on rain or snowmelt events.

As compared to hydrograph analysis, *discharge separation by environmental tracers* (section 4.4) (e.g.,  $^2\text{H}$ ,  $^{18}\text{O}$ ) leads generally to an overestimate of subsurface contributions to discharge, because inter-flow includes also some pre-event signatures. To better understand and quantify inter-flow, it is recommended to also analyse DOC in river discharge during storm event; it has been shown (Seiler et al., 2002) that DOC in fine to medium grained, unconsolidated sediments as well as in crystalline rocks is a very good marker of inter-flow, because DOC is mechanically filtered and thus stored within the effective root zone and, therefore, reaches river discharge mostly through inter-flow (section 3.5). Hence, run-off separation by environmental isotopes should be combined with DOC-,  $\text{SiO}_2$ -, hydrograph-methods to better approach groundwater contributions to surface run-off.

Often, the discharge separation method can be replaced by continuous registrations of the electric conductivity of river water, to study special discharge processes, if this measurement has been calibrated through isotope analysis. The isotope discharge separations delivers instantaneous information, which are important to better understand bulk processes, but does not provide short- or long-term process information, which are more suitable for management strategies and became available by continuous measurements of the electric conductivity of river discharge.

The hydrograph and isotope analysis of discharge events apply well in humid, cold, and semi-arid climates, but do not well apply in arid (dry-land) areas, because of preferential rivulet/Wadi/Oued discharge, which is sporadic and contributes along the surface flow path and through ponds to groundwater recharge, if infiltration capacities are not too much reduced by organic/inorganic crust formations or silting of ponds and thus favouring evaporation.

The determination of groundwater recharge through the analysis of *fluctuations of groundwater levels* (section 4.1.3) requires that

- The observation point is representative for the regional groundwater flow field; for example, that it is not influenced by local hydraulic sinks or sources,
- In case of low groundwater thickness morphology at the aquifer base does not guide groundwater flow, and
- The design of the observation point is representative.

To apply this approach, the storage coefficient for instantaneous wetting and long-term drying conditions must be known, which differs mostly from effective porosity, because it appears that gas may be entrapped in the zone of rising water tables and porosities follow a hysteretic behavior during wetting and drying phases; this has a significant influence on the magnitude of groundwater level changes and thus on calculated groundwater recharge.

Using effective porosities, groundwater recharge is mostly overestimated; using storage coefficient for instantaneous wetting, it should be considered that it is not constant all the time.

This method does not consider changes in groundwater flow, hence, underestimates groundwater recharge to some extent. It delivers short- and long-term information on groundwater recharge, if referring to long-term mean groundwater table fluctuations. The error bare in this method may become rather high (maximum 25%).

As far as the hydraulic intrinsic (transmissivity, storage coefficient) and boundary parameters (water table, base and lateral borders) of aquifers are well known, groundwater recharge can be determined applying *numerical models* in an inverse manner and using a best fit procedure between calculated and measured water tables. If all parameters are known except the input, groundwater recharge as the driving agent of groundwater flow can be calculated. This method delivers bulk information on recharge in a catchment; as most of the large-scale methods, it does not differentiate between the many REV's in a catchment and their weighting function, contributing to bulk recharge. This should be considered in applying groundwater recharge data from numerical modeling to develop local groundwater management concepts.

The *environmental chloride method* (section 4.4.2.1) to determine groundwater recharge from chlorides in groundwater as compared to chloride in precipitation applies well on both small and large scales, if

- the Cl-input function in precipitation is well known,
- no other sources of chloride input than through precipitation exists, and
- overland-flow can reliably be subtracted from precipitation.

Unfortunately, in most climate zones, the input function is often not well known.

Inter-flow communicates with stored water in the infiltration and effective root zone and thus may dilute the chloride concentration in stored soil water. This interference may lead to a little overestimate of groundwater recharge.

The determination of *groundwater recharge using MTT* (section 4.4.2.2) is not well known, although quite suitable. It requires a good knowledge of the thickness of the groundwater recharge zone of concern and a good approach to MTT. This good approach was optimal to apply for the determination of present groundwater recharge in the time of bomb tritium in precipitation; today, it becomes difficult, because the tritium input function approached at the end of 1980 the natural tritium production rates, which is constant over the run of years.

In principle, this method also applies for old groundwater, if MTT can be attributed to a well-defined aquifer thickness.

*Environmental tritium* (section 4.4.2.2) was a suitable tracer during 1964 and the end of the last century and has been successfully applied in all climate zones to determine groundwater recharge quantitatively and to show that it presently also occurs in water scarce areas; the latter application is still useful today. Results on groundwater recharge in arid (dry-land) areas must be carefully interpreted, because it originates from sporadic and local rains, which may penetrate to some depth of the

percolation zone, but could later rise upward by capillary forces to the evaporating surface and hence, do not reach groundwater. Therefore, a repeated sampling in intervals of several years was necessarily here, to overcome this problem. In arid (dry-land) zones this method and the chloride profile method can be considered as the only reliable methods to determine groundwater recharge. Because of the quasi constant, present tritium input, this method does no more apply quantitatively, but qualitatively it can be used to delineate the active groundwater recharge zone and hence, to estimate recharge through MTTs.

*Artificial tracing* (section 4.4.3) has often been used to determine dispersion parameters, flow velocities, and groundwater recharge. It always refers to a scale smaller than or close to the REV; hence, any transfer of such results to the REV or an even larger scale needs respective care. Best tracers are those of the water molecule ( $^2\text{H}$ ,  $^3\text{H}$ ,  $^{18}\text{O}$ ), because they are really non-reactive and do not change the ion balance in the percolation zone, however, require analytic tools, which are not everywhere available; in this case, the use of bromide is recommended, because it occurred in low concentrations in soils, except in non irrigated areas of arid and semi-arid zones, behaves non-reactive and experiences only little plant uptake.

Appropriate tracing allows differentiating between matrix- and preferential-flow and often shows that even matrix-flow is composed—as expected—by different matrix-flow paths, respectively, is not homogeneous. Matrix-flow contributes 100% to groundwater recharge; preferential-flow contributes in hilly terrains in parts, in flat areas also totally to groundwater recharge; thus evaluating results on matrix-flow in terms of groundwater recharge may result in an underestimate of it.

How representative groundwater recharge can be determined by tracing the water molecule also depends from the season of tracer application; best application follows the low evaporation season, to avoid stable isotope losses by fractionation or an enrichment of chemical tracers, both by evaporation, which falsifies the tracer mass balance and may conduct to a seemingly low percolation velocities; the low evaporation season, however, has a maximum in groundwater recharge.

Often, *soil hydraulic methods* have been applied to determine fluxes and transport through the unsaturated zone applying the hydraulic laws of filter flow (energy law) in combination with the mass conservation law. These methods base on suction and water content measurements and approach the hydraulic functions of the unsaturated zone either using empirical formulas or measurements on the laboratory scale; both ways of approaching the hydraulic functions provide primarily a significant error bare, which can be reduced by a best numerical fit of fluxes in the percolation zone; this procedure, however, results in good local but often not reliable REV approximations.

*Lysimeter studies* have been applied manifold to calculate ET and groundwater recharge. Comparing lysimeter with regional results on groundwater recharge results very often in higher recharge rates by lysimeters than with other methods; lysimeters suppress lateral-flow and overland-flow as well and add both components to groundwater recharge; finally often sediment fabrics of filled as well as digged lysimeters are not too representative to transfer lysimeter results to the catchment scale; digging three lysimeters from the same place and observing these undisturbed lysimeters

over the run of 10 years showed that results are hardly comparable. However, data series from lysimeters give an excellent qualitative overview on the influence of fabrics of sediments and individual meteorological parameters on percolation and offer the unique opportunity to execute process oriented, chemical and microbial studies.

All above-mentioned methods finally refer to long-term groundwater recharge, only few are suitable for short runs of time (<0.5 years). Contrary, most small scale approaches are suitable to elucidate quantitatively and qualitatively the interference of short-term meteorological variations, but the transformation function to the REV as well as to the catchment scale is often unknown.

Meteorological data on precipitation and basic parameters to calculate evapo-transpiration are determined locally with a precision lower than 5% each, and some parameters have a significant areal variability like reflected solar radiation (see below), rain distribution and intensities.

The precision of groundwater recharge determination with the mentioned methods is minimum 10% and maximum 25%; the more parameters coming into the game, the less representative is the output with respect to time and space and the larger becomes the error bare.

In humid temperate climates, measurements of discharge and precipitation generally cover at least 70 years; with such data sets, mean evapo-transpiration can be determined through the water balance as far as the catchment areas are extended (>5 km<sup>2</sup>) and the surface and subsurface catchment areas have the same size.

In humid tropical climates, the meteorological and hydrologic data sets are very variable and cover often too short time intervals to neglect in water balance studies the changing storage and consumption of water in the subsurface.

The determination of the hydraulic parameters of aquifers have an error in the range of a factor of 2–5 and hydraulic gradients in arid and semi-arid zones often express a transient behavior, because of an extended system and a very low present recharge (Seiler et al., 2006).

## CHAPTER 5

### RECHARGE UNDER DIFFERENT CLIMATE REGIMES

From low to high latitudes, four general climate zones exist:

- The humid tropical,
- The warm semi-arid and arid,
- The humid temperate, and
- The cold climate zone.

This general scheme is modified by the plant cover, land/water partitioning, ocean currents and topographic features (section 2.2.2). Such climate zones, however, are responsible for the different contribution of precipitation to run-off generation and the groundwater recharge.

Humid tropical climates follow more or less a 2,000-km-wide belt north and south of the equator (Fig. 5.1), which borders arid (dry-land) climate zones with semi-arid areas as a transition. This belt covers about 20% of the continental surface and is mostly built up of crystalline rocks, which decay to fine grained silt and clay weathering products. The humid tropical climate zone did not undergo cold-warm climate changes during the last 50 million years; hence, both chemical and physical weathering prevailed and contributed to a thick weathering cover (Fig. 5.1); here, boundary conditions are not very favorable for infiltration.

In contrast, the humid temperate climate belt, which borders the arid (dry-land) zone again with a semi-arid transition, was influenced by the Cenozoic and specially in the north hemisphere by Pleistocene glaciations with expanding and shrinking glaciers, ice shields, and permafrost conditions. In this climate zone, sedimentary and crystalline rocks and physical weathering dominated, whereas chemical weathering was weak; hence, together with significant glacial erosion and accumulation of coarse grained sediments thin weathering covers resulted and favorable infiltration conditions in unconsolidated and consolidated rocks exist.

In the cold climate zone, chemical weathering is close to zero, but physical weathering is quite strong. This provides favorable fabric conditions for infiltration in both unconsolidated and consolidated sediments/rocks; however, small precipitation amounts and permafrost conditions often reduce the favorable boundary conditions for groundwater recharge.

Rock/sediment weathering is strongest close to the landscape, interfering there with the decay of organic matter at the infiltration interface and resulting in soil

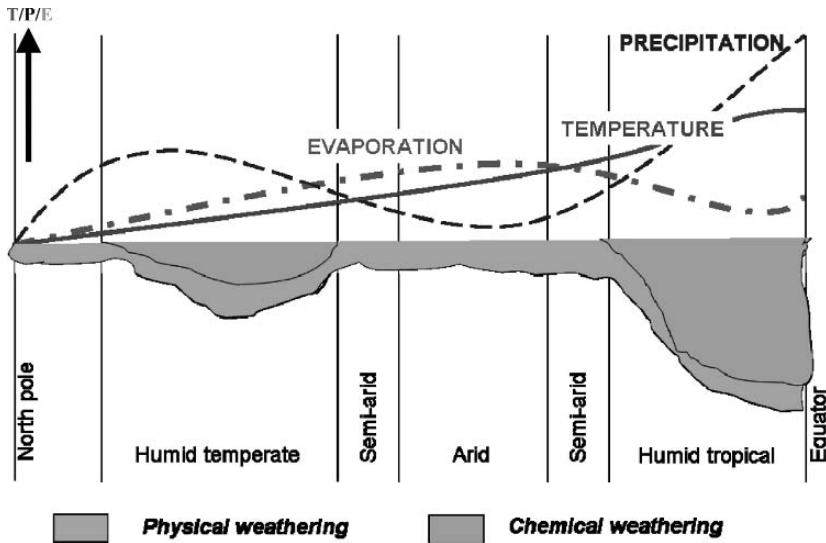


Figure 5.1. Generalized climate and weathering zones between the equator and the pole

formation. Weathering processes disintegrate rock and sediment fabrics (physical weathering), producing new, stable minerals (chemical weathering), bind water in clay minerals (chapter 2), which returns through metamorphic processes as juvenile water to the water cycle and makes nutrients available for plants. All these processes have an individual kinetic, are catalyzed by microbial activities, governed by the run-off generation during rain events, and develop individually under different climate conditions.

From a rock point of view, infiltration capacities are much better in humid temperate than in humid tropical climates; from a climate point of view, they are again better in humid temperate climates, because in humid temperate areas, convective rains are scarce, frontal and advective weather conditions prevail and no monsoon or large cyclones occur. Therefore, the high precipitation amounts in the tropics, exceeding several thousand millimeters, do not contribute as much to groundwater recharge than the many hundred millimeters of precipitation in humid temperate climates.

Groundwater recharge receives in both humid temperate and tropical climate zones

- A first chemical impact through the precipitation, which contains sea spray, aerosols, dust, heavy metals, N and S species, and  $\text{CO}_2$ ,
- A second by enrichment and metabolic processes at the interface atmosphere/biosphere/lithosphere,
- A third finger print by the chemical species resulting from decay processes within the soil zone, and
- Its final and most important chemical characteristic by water rock interactions.

The chemical charges and physical/chemical/microbial reactions along the pathway precipitation, infiltration, and percolation produce the chemical quality of the groundwater recharge.

- In cold and arid climates, the soil zone plays a minor role for the chemical quality of groundwater recharge,
- In arid (dry-land) climates, however, the interface atmosphere/lithosphere is outstanding for the quality of percolation water, because infiltration is mostly no areal, but follows overland flow and ponding, and the quality of groundwater recharge depends mostly upon leaching of accumulated salts at the land surface as well as along the infiltration lines (river bed infiltration) and points (ponds).

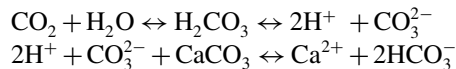
This natural bulk scenario on groundwater quality changed with the industrial age, because of additional gas, aerosol, and dust emissions into the atmosphere ( $\text{SO}_x$ ,  $\text{NO}_x$ ,  $\text{NH}_3$ , and heavy metals), as well as solid, liquid waste releases and the intensified land use (agriculture with and without irrigation, urbanization, mining, and traffic).

In a first approximation, the chemical quality of groundwater recharge and groundwater in humid and semi-arid climates can be characterized according to the most abundant host rock outcrops as crystalline, carbonate, and sulfate waters (Table 5.1); these groundwater quality types undergo, independent from the host rock, changes

- To less mineralized groundwater in cold climates, because of the missing or the too thin soil cover,
- To high-mineralized or high-pH waters in arid (dry-land) climates, because of evaporation exceeding present precipitation and thus favoring the accumulation of chemical residuals.

Additionally and still in general terms, there are kinetically quick and slow processes in weathering or water rock interactions, differentiating groundwater qualities according to the mean residence times (section 2.4). Therefore, shallow groundwater (Table 5.1), which gives easy access to groundwater use, but also to pollution, differs in quality regularly from deep groundwater, which often contains ion exchange evidences, more trace elements, and chemical species from a chemical reducing environment (F, J, As, Fe,  $\text{H}_2\text{S}$ ), has higher temperatures and less anthropogenic contaminants than shallow groundwater does.

For carbonate solution, acids are necessary. The ubiquitous  $\text{CO}_2$  in the atmosphere and pedosphere produces in a first step carbon acid, which dissolve in a second step carbonates from the rock matrix and keep the dissolve equilibrium:



$\text{CO}_2$  is easy available from soils in lowlands of humid areas; however, it is scarce in all cold areas of high latitudes or altitudes and in arid (dry-land) areas, because of a missing or very thin soil cover, hence, cannot sufficiently charge infiltration water with  $\text{CO}_2$ ; atmospheric  $\text{CO}_2$  is too small in quantity to start a significant carbonate

Table 5.1. Groundwater types in the active groundwater recharge zone, characterized by averaged main anion and cation concentrations and bulk parameters

	Crystalline water			Carbonate water			Sulfate water		
	mg/L	meq/L	meq%	mg/L	meq/L	Meq%	mg/L	meq/L	meq%
Na	3.5	0.15	14.0	5.5	0.24	3.0	26.6	1.15	4.1
K	2.5	0.06	5.9	2.5	0.06	0.8	10.6	0.27	1.0
Mg	4.5	0.37	34.1	25.0	2.06	25.4	95.7	7.88	27.8
Ca	10.0	0.50	46.0	115	5.74	70.8	381	18.99	67.1
Cl	6.0	0.17	17.4	12.5	0.35	4.3	23.2	0.65	2.3
NO <sub>3</sub>	5.0	0.08	8.3	10.0	0.16	2.0	20.0	0.32	1.1
SO <sub>4</sub>	15.0	0.31	32.1	47.5	0.99	12.0	938	19.51	68.4
HCO <sub>3</sub>	25.0	0.41	42.2	410	6.72	81.7	490	8.03	28.2
EC at 25°C	100 μS/cm			665 μS/cm			2060 μS/cm		
pH	5.4			7.3			6.7		
Free CO <sub>2</sub>	3.5 mg/L			35 mg/L			50 mg/L		
Ionic strength	2.5 mmol/L			12.6 mmol/L			51.6 mmol/L		

solution process. Thus in humid areas, percolation and groundwater out of high altitudes (>1,300 m a.s.l.) have in carbonate rocks a hardness of 1.5–2.5 mval/L as compared with 6–8 mval/L in low altitude carbonate rocks.

In silicate rocks, calcium comes from slowly weathering plagioclases, pyroxenes, amphibolites, and sulfur from sulfide oxidation, mostly pyrite. As pyrite is often a “dirty” mineral, pyrite oxidation may also liberate arsenic, antimony, cooper, lead, cadmium, and others in concentrations exceeding permissible standards; but pyrite oxidation may also produces storage minerals such as iron sulfates (Jarosite etc.) as well as iron and aluminum oxihydrates, which coat grains and sorb and co-precipitate organic contaminants and many heavy metals and metalloids. There is, however, a debate about the stability of storage minerals under changing pH- and Eh-conditions.

The following examples on groundwater recharge in different climate zones refer basically to the shallow groundwater recharge zone, through which most of the present groundwater recharge is turned over, whereas deep groundwater is less involved in the present recharge mechanisms.

## 5.1. HUMID CLIMATES

In humid temperate climates, the weathering cover above outcropping rocks/sediments is thin (decimeters to few meters, Fig. 5.1) and often less than 10,000 years old, whereas in humid tropical climates, this weathering cover is very thick (many decameters till 100 m), because it developed over millions of years. Hence, in general, infiltration capacities are higher in humid temperate than in humid tropical climates.



Present evapotranspiration (ET) in humid temperate climates is in the ranges of 350–650 mm/year and in humid warm climates between 700 and 1,100 mm/year, potential evaporation is much higher and may exceed 3,500 mm/year. As an average, precipitation in both climates is higher than actual ET, thus generating run-off. However, in both climate zones also potential excess ET over precipitation is known during the run of a limited number of months a year. This can lead to the fact that no run-off results from the water balance calculation for these months but can be observed in nature; here, run-off depends on precipitation intensities and the preconditioned infiltration interface.

Groundwater recharge studies in humid areas have to differentiate between consolidated and unconsolidated rocks (Fig. 2.7). Unconsolidated rocks receive their groundwater recharge directly from the infiltration interface; in contrast, consolidated rocks without weathering cover have very low infiltration capacities, hence, produce primarily overland flow; an exception are soluble rocks (karst), in which overland flow can penetrate through sink holes to the groundwater table, provided the karst is well developed. In contrast to unconsolidated rocks, any weathering cover over consolidated rocks enables to collect infiltration in the so-called epizone, from where the infiltrate can be distributed to different subsurface flow paths. The weathering zone upon consolidated rocks results primarily from the physical processes of rock dilatation as rocks approach by the land surface erosion as well as from repeated frost/thaw influences during permafrost times.

The distribution process of infiltrates to groundwater recharge or inter-flow is governed by the ability of the non-weathered rocks to store and conduct groundwater over long distances.

- Clays and crystalline rocks have very low yields either because of too narrow pores that result in groundwater movement close to molecular diffusion or because of too high flow velocities and simultaneously a missing storage capacity, as in the case of crystalline rocks or very advanced karstified rocks in the Mediterranean, China, or the Caribbean.
- In contrast, fluvial Quaternary gravels deposited in the foreland (sander) of or upon or within glaciers (Kames, Eskers) develop very high groundwater yields; these sediments have high porosities, low natural water contents, and high hydraulic conductivities.
- Favorable safe yields have biporous fissured media such as reef carbonates, chalk rocks, and sandstones; they combine a huge volume of small pores with a well-developed fissure system, draining, and recharging the narrow pores, thus combining the advantages and disadvantages of the two before-mentioned rock groups.

In the humid warm climate of *Africa*, old crystalline rocks play a crucial role for groundwater resources, because they have very low storage capacities and hydraulic conductivities. Locally, delta sediments of river systems can play a role for the formation of abundant groundwater resources.

In *Central and South America*, volcanic rocks and their resedimented weathering products in the tectonically active Andean zone are principle water resources with

considerable yield; in the low lands of South America, the Amazon, and Parana, sedimentary basin extends with more than 3,000,000 km<sup>2</sup> each, containing important groundwater resources in sandstones. In the Caribbean Latin America, karst rocks with high groundwater recharge, but low groundwater retention capacities dominate, making the groundwater resources on the small islands very vulnerable to salt water intrusions.

In tropical *India*, crystalline and volcanic rocks are basic groundwater reservoirs, which are often used as artificial stores of excess rain during monsoon times; they have limited storage capacities. In contrast, in the Punjab of India and Pakistan, unconsolidated delta sediments host huge volumes of groundwater for water supply.

In the north part of the humid temperate climate of *America and Europe*, crystalline rocks dominate (Scandinavia, Canada, North UK), which are covered with sediments of glacial origin; crystalline rocks have a low yield, but Quaternary Kames and Esker gravels contain important groundwater resources, which, however, are only of local importance.

In the central part of the north hemisphere sedimentary rocks, especially Mesozoic carbonates and sandstones, Tertiary and Quaternary unconsolidated rocks dominate with a thin weathering cover. These areas are prone to an optimal infiltration of precipitation. However, in west-east direction, continental effects intervene, reducing the precipitation quantities with the distance from the coast in North America and Eurasia as well as in north-south direction the transition from the humid temperate to a semi-arid/arid climate occurs in the south USA and in South Europe.

In *China's* coastal areas, the unconsolidated rocks receive sufficient groundwater recharge through river bed infiltration and local precipitation. These coastal areas, however, have a narrow extent considering 1.2 billion of people, are often interrupted by outcrops of the mostly crystalline basement and suffer from high contamination inputs from agriculture, industry, urban areas, and traffic.

Groundwater recharge studies in humid areas have to take four essential steps:

1. Calculation of long-term averages and variabilities of precipitation and evapotranspiration,
2. Analysis of existing run-off data to complete, specify and quantify the meteorological water balance,
3. To define the scale for which these results on groundwater recharge are representative, and
4. Developing an appropriate conceptual model on discharge and run-off mechanisms in the area of concern, to contribute to the development of management and protection strategies through mathematical modeling.

In special cases of land use, also detailed short-term water balance studies are of interest to optimize irrigation schemes; this, however, will not be discussed here.

The following example is from the Molasse Basin in South Germany. The investigated and all other catchment areas in the Molasse basin are hilly and build up of Tertiary sands and gravels and covered on east dipping hill slopes often by

Quaternary loesses. The study area is without direct contact to the regional groundwater, but drained by many creeks, with many local springs and an extended perched groundwater occurrence, which makes the determination of surface as compared with subsurface groundwater crucial.

The area was equipped (Fig. 5.2) with many natural lysimeters to trace percolation water and to continuously observe the quality of percolation water as a function of the season and crop (Seiler et al., 2000). Many multi-level wells have been drilled along the general groundwater flow direction (well I to well V in Fig. 5.2) to sample groundwater twice a year and to analyze it chemically and isotopically. All springs and creeks have been monitored by means of water quantities and qualities and two meteorological stations monitored the precipitation and radiation input to this catchment.

The catchment size was about 1 km<sup>2</sup> and for comparative reasons five neighboring catchments (larger than 1 km<sup>2</sup> and smaller than 40 km<sup>2</sup>) have been monitored too, although not as intensive as the central catchment, to control the transferability of local results to the area. Thus, the studied scales reached from square meters in natural lysimeters to maximum 40 km<sup>2</sup>. Each catchment was about 50% covered by forests and 50% was agriculturally used: pasture land was the exception.

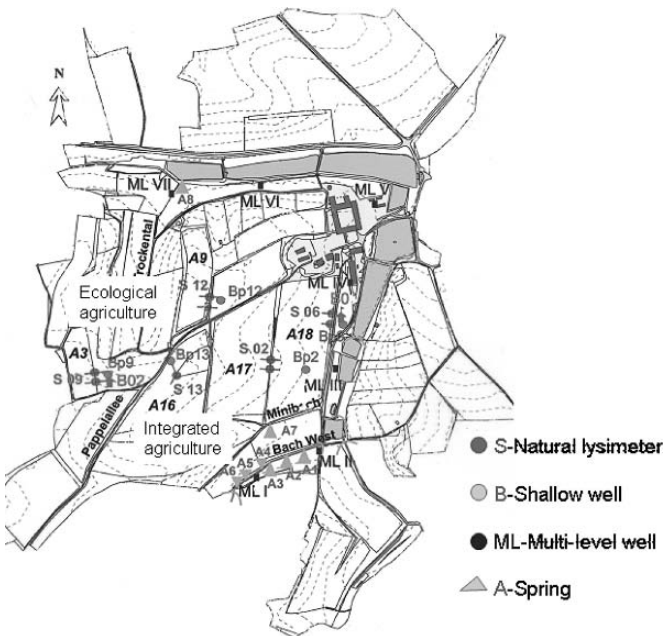


Figure 5.2. The study area in the Molasse basin in South Germany and the installations to study the water balance

The study area itself and the environmental catchments had already been investigated before the beginning of the systematic study; hence, a good first conceptual model was already available at the beginning of the 10 years lasting studies (1992–2001).

### 5.1.1 Conceptual Models

The conceptual model of groundwater recharge describes the mechanisms, which come into the game during discharge events and describes the intrinsic and boundary data set and its variations in time and space, directing discharge and thus enables to proceed to a mathematical model. After the validation and calibration of such a mathematical model, it can be used to develop management and protection strategies and to make any prediction on the behavior of the discharge and transport capacities of run-off components during storm events.

On top of the *unconsolidated rocks* (Fig. 2.7) of the Molasse basin exists a decompression zone, in which fabrics parallel morphology and thus differ from fabrics of the underlying sediments; this decompression zone developed because of

- Sediment expansion as a consequence of erosion (transition from a three-dimensional into an one-dimensional overburden stress situation) or tectonic movements,
- Chemical weathering in connection with infiltration and percolation fronts,
- Past permafrost and present winter impacts, producing changes of sediment fabrics by freezing–melting cycles and mass movements,
- Bio- and human activities in the root respectively cultivation zone.

The decompression zone has in hilly terrains an important influence on the generation of discharge components. In the study area applies a conceptual discharge model based on two or three run-off components, (overland-), inter-flow, and groundwater recharge according to Fig. 4.2 and sections 3.3–3.5; overland-flow only develops, when infiltration capacities of the land surface are limited. In contrast, in flat areas with decompressed unconsolidated rocks, any rain in excess of present infiltration contributes to water ponding and enhanced ET and thus delays and reduces the amount of groundwater recharge.

In catchments with a water table and capillary fringe below the local valley, natural vegetation often indicates high water contents along the foot hill areas by mosses, shave-grasses, or dark soil colors, all missing in mid- and uphill areas, where low water contents prevail. In the study area, Time Domain Reflectivity (TDR) measurements of soil water contents along hill slope transect quantified this observation, which is interpreted in terms of infiltration water, which transformed into lateral or inter-flow (section 3.5), moved slowly in the subsurface parallel to the hill slope and finally accumulated in the foot hill area.

In recent years, much attention has been given to recognize inter-flow, and many methods have been developed to quantify it (sections 3.5 and 4.1.2). Among the quantitative methods to determine inter-flow, (dissolved organic carbon DOC) applied successfully in the study area (Seiler et al., 2000). DOC originates under

natural conditions primarily from the disintegration of the humic substances of the soil cover and to a small extent from metabolism of soil organisms or from fossil organics (wood, hydrocarbons) imbedded in sediments. Within the effective root zone (<1 m) DOC concentrations (Fig. 5.3) are high (>>4 mg/L); in contrast, groundwater DOC concentrations are low (<1.5 mg/L), because DOC is forming aggregates, which are mostly mechanically filtered at the base of the decompression zone of unconsolidated sediments and moves with inter-flow to the surface discharge. Only in evenly grained medium to coarse sediments such as dune sands DOC filtering in the effective root zone does not play a significant role.

In the study area, DOC concentrations or DOC freights regularly increase in surface run-off during storm events (Fig. 5.4), and with DOC, many sorbing agrochemicals have been co-transported by direct run-off to the surface discharge, thus producing contamination pulses to lakes and rivers; such particle fixed agrochemicals are, for example, ammonia, heavy metals, pesticides, and phosphates. Figure 5.5 shows how the intensity of this DOC export increases in the study area with the rain amount.

The  $SO_4^{2-}$ ,  $NO_3^-$ ,  $Cl^-$ , and DOC concentrations in surface run-off, analyzed frequently over a period of 8 years (Fig. 5.6), shows that chlorides and sulfates behave similar, but different from nitrate and DOC. Sulfate and chloride occur in the three discharge components in about the same partitioning as the three run-off components; this coincidence is attributed to a non-reactive transport of sulfate and chloride with overland-flow, infiltration, inter-flow, and percolation water. In contrast to  $Cl^-$  and  $SO_4^{2-}$ , DOC dominates—as expected—in the inter-flow run-off component, because it turns within the decompression zone from vertical down to lateral and because of mechanical filtering moves preferentially with lateral or inter-flow. Nitrate, unexpectedly, behaves intermediate as compared with DOC on

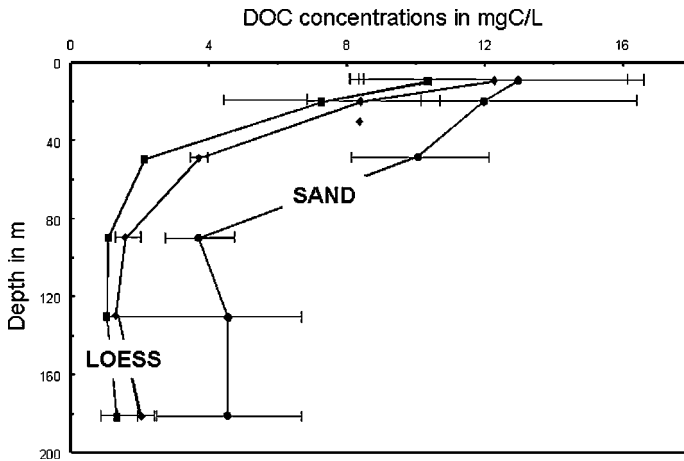


Figure 5.3. DOC concentrations in the effective root zone of loess and sand soil/sediments. Points and beams: Averages of 1 year and the standard deviation

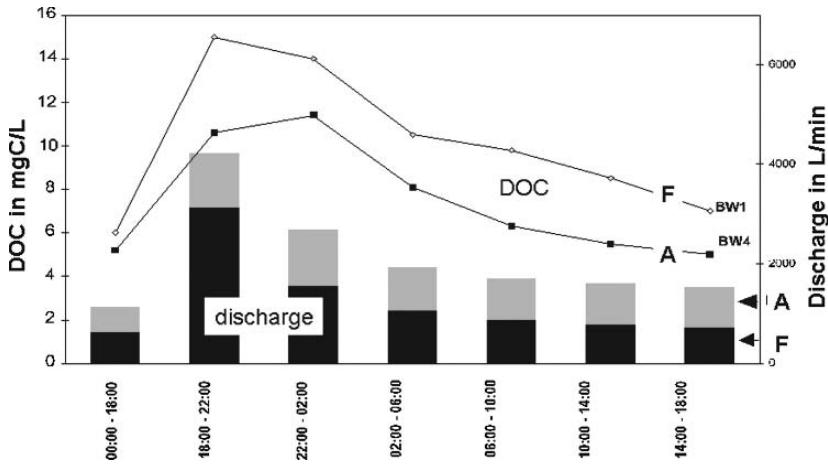


Figure 5.4. DOC in surface discharge during a discharge event in Tertiary sediments of the Molasse basin in south Germany (Scheyern area); F = 100% forest area, 0.45 km<sup>2</sup> in size A = 95% agricultural area and 5% forest area, together 0.74 km<sup>2</sup> in size

the one hand and to the non-reactive chloride and sulfate on the other (fig. 5.6); this is interpreted in terms of ammonia, which is sorbed on DOC, flushed out with DOC from the effective root zone and which oxidizes along the lateral flow path to nitrate. Similar co-transport observations are known from pesticides such as atrazine, which have been observed in other areas to regularly increase with storm events in the surface run-off of rivers (Fig. 5.7); this atrazine export is strongest during the month of application (May, June), decreases to low concentrations thereafter, and can be observed in all run-off events the year around (Fig. 5.7). Evidently, inter-flow protects groundwater to some extent from sorbing pollutants, which were stored together with organic matter in the decompression zone.

The stable isotope signature of percolation and groundwater reflects the stable isotope composition of precipitation so long as the infiltration interface is medium to coarse grained. However, when percolation takes place through fine grained sediments (fine sand, silt, and clay), often a little evaporation impact appears in the stable isotope content. This evaporation impact mostly dates back to the bare soil conditions after harvesting in the late summer/early fall, when transpiration turns close to zero and evaporation dominates. Later, this evaporated residual soil water mixes with the winter infiltrate and thus shifts the stable isotope concentration in percolation and groundwater to the left of the local meteoric water line (LMWL) (Fig. 4.29). Any interception evaporation is not known to show up in the stable isotope content of groundwater recharge.

To develop a conceptual model for *consolidated rocks*, some singularities have to be taken into account. Consolidated rocks are always overlain by a decompression zone, often called epizone; the contrast of hydraulic conductivities between the decompressed and compressed zone is always much stronger in consolidated rocks than in unconsolidated sediments. This epizone (Fig. 2.7) stores infiltrated

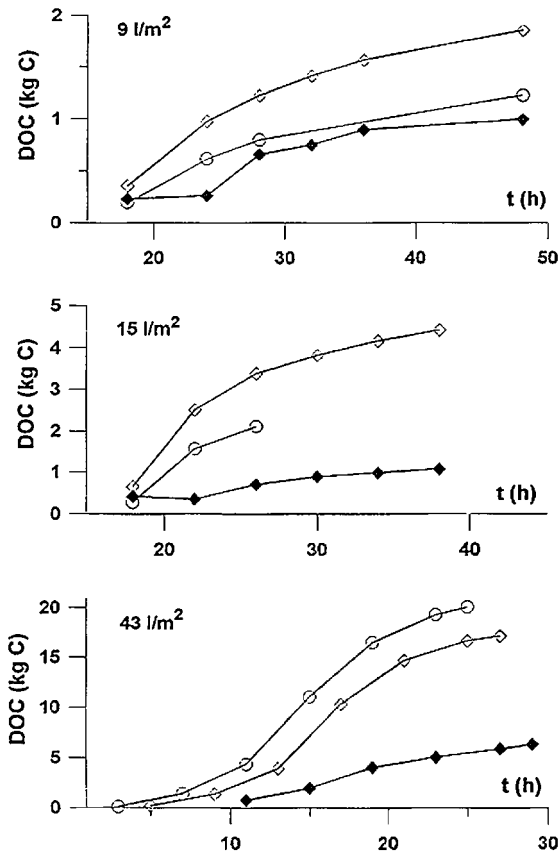


Figure 5.5. DOC concentrations in surface discharge during low and high rain amounts, shown for catchments with different vegetation covers (circles = mixed forest and agro-land, open rhomb = forest, black rhomb = grassland)

water, thus forming intermittent, perched groundwater, and facilitates infiltrates to reaches fissures directly or retarded on the one hand and it produces on the other hand lateral flow in hilly terrains. Depending on the age of the landscape, these decompressed and weathered zones may reach meters (humid temperate zones) to several decameters in thickness (humid tropical zones). This decompression zone contributes in silicate rocks much more to inter-flow respectively to overland-flow than in unconsolidated rocks, so reducing groundwater recharge.

It is peculiar to consolidated rocks that infiltration distributes much more on inter-flow, widened fissures or solution channels than on the rock matrix. Flow in the rock matrix is slow and experiences natural attenuation, all other flow components impact instantaneously surface discharge; unfortunately, inter-flow and flow in wide fissures (channels) can usually not be distinguished by means of river discharge measurements or isotope or chemical analysis, hence, representing a health risk for all kind of water supply out of consolidated rocks, which is difficult to assess in advance.

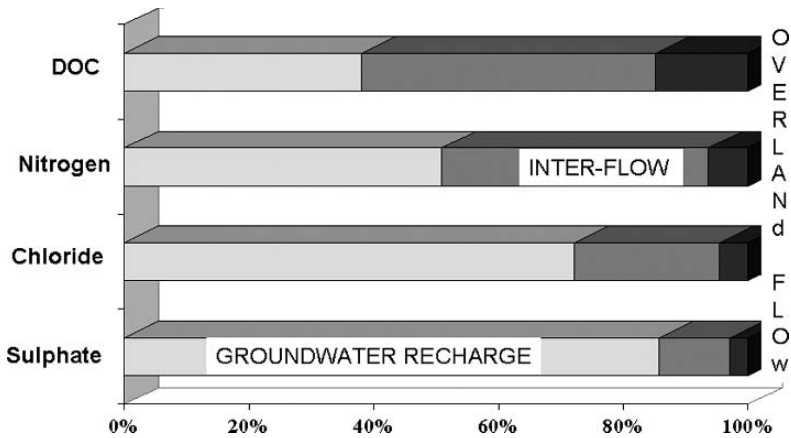


Figure 5.6. DOC and other chemical components discharging during storm events

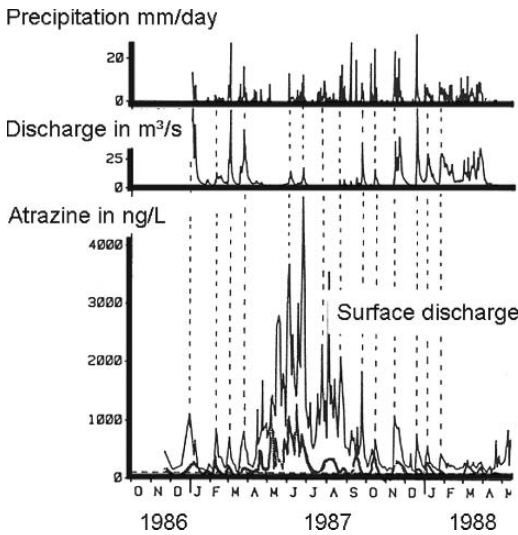


Figure 5.7. Atrazine in surface discharge of two rivers as a function of rain events

### 5.1.2 Water Balance and Separation of Discharge Components

In humid temperate climates, the traditional meteorological water balance applies to:

$$P = D + ET + \Delta S.$$

For time series of 5–10 years,  $\Delta S$  can be neglected, and the Haude (1954, 1955, 1959) approach to calculate actual ET proved to be well established (section 4.1.1) for many of Central Europe, Asian, and Mediterranean areas.



In 0.5–40 km<sup>2</sup> neighboring catchments of the Molasse Basin, the run-off was calculated for the period 1994–2001 to

$$855 = D + 623 \pm 0$$

or

$$D = 232 \text{ mm/year.}$$

Traditional hydrograph analysis (section 4.1.2) resulted for the period 1994–2001 in 75% indirect ( $D_G$ ) and 25% direct discharge ( $D_{I+O}$ ), which corresponds to a base-flow contribution of

$$D_G = 174 \text{ mm/year and}$$

an inter-flow/overland-flow contribution of

$$D_{I+O} = 58 \text{ mm/year.}$$

Applying the discharge component separation using continuous electric conductivity measurements, DOC analysis during storm events and selected analysis with the stable water isotopes (Fig. 4.5) resulted conformably in 5% of overland-flow ( $D_O$ ) and 95% of groundwater and inter-flow ( $D_{G+I}$ ), which corresponds to

$$\begin{aligned} D_O &= 12 \text{ mm/year and} \\ D_{G+I} &= 220 \text{ mm/year.} \end{aligned}$$

From these numbers, inter-flow has been calculated to amount

$$D_{G+I} - D_G = D_I = 46 \text{ mm/year.}$$

These are averaged numbers, which refer to a catchment size of close to 1 km<sup>2</sup> and, therefore, have to be checked for variations according to the amount, duration, and intensity of the rain input as well as for scale effects.

- Variations in overland-flow are expected to exist, but are hardly perceivable, because of the small amount of it.
- In individual discharge analysis, inter-flow showed significant variations (0–60%) according to vegetation and non-vegetation seasons, vegetation development, kind of crops, soil hydraulic, and meteorological conditions.
  - During a very dry summer season, rain events of 40 mm/day did not produce any response in river discharge; in normal years, river responses occur already at >4 mm/day of rain;
  - Under very wet conditions and high rain intensities inter-flow may rise to 50 mm/day,

- During winter, run-off events in the Molasse Basin lasted longer than during summer (Fig. 4.4), because winter inter-flow has a longer MTT than summer inter-flow according to soil compaction and the missing plant, animal, and farming activities.

To check these calculations of traditional water balance and discharge analysis, groundwater recharge has also been determined by tracing matrix-fluxes in the percolation zone. Matrix percolation velocities amount in Loess to 0.65 m/year and in Tertiary gravels and sands to 1.15 m/year (mean values of nine tracing experiments). Both flux values refer to tracing during the snowmelt season and represent an average over the tracer observation time of 2–3years.

From these flux data, groundwater recharge was calculated, using eq. 4.33 and referring to measured water contents of 25vol% in Quaternary loess and 15vol% in Tertiary gravels and sands:

$$\begin{array}{ll} \text{Quaternary loess} & R' = 163 \text{ mm/year and} \\ \text{Tertiary gravel and sand} & R' = 173 \text{ mm/year.} \end{array}$$

Comparing groundwater recharge calculations, based on tracer experiments on plots (20 × 20 m) with the combined traditional water balance and hydrograph method (about 1 km<sup>2</sup>), it comes out that scale effects do not play a significant role.

Water balance studies in six neighboring catchment areas, extending over 9–40 km<sup>2</sup> in size, showed that with the same geologic, vegetation, land use, and meteorological boundary conditions, the same partitioning of run-off components came out. From these studies resulted a mean

- Precipitation of 816 mm/year,
- Total discharge of 193 mm/year, and
- Groundwater recharge of 179 mm/year.

As compared to the small size catchments, groundwater recharge does not differ in the different scales, but mean direct run-off was significantly lower (14 mm/year or 7% of surface discharge); evidently, small differences in the amount of precipitation do not change groundwater recharge (indirect discharge), but direct run-off, which was in good agreement with percolation modeling (section 4.3).

The average chloride concentration in precipitation amounts to 1.2 mg/L; beneath the effective root zone chloride was 9 mg/L. Reducing the precipitation of the study area (855 m/year) by direct discharge (58 mm/year) and applying the chloride balance method (section 4.4.2), results in

$$R' = \frac{1.2}{9}(855 - 58) = 106 \text{ mm/year,}$$

which is far from reality; apparently, in the study area with intensive farming chloride concentrations in groundwater recharge do not only refer to chlorides in rain, enriched by evaporation, but also refer to chlorides in chemical and organic fertilisers, which are applied excessively.

## 5.2. SEMI-ARID CLIMATE

Semi-arid regions are those characterized by a rainfall of more than about 250 mm/year, but with a ratio of  $P/ET < 0.5$ . Without the uneven distribution of precipitation the year around and the occasional heavy rainfall during the wet season, no excess water for either run-off or groundwater recharge would be available. One must distinguish between the Mediterranean semi-arid regions, where the rainy season occurs during the cold winter months, and the semi-arid areas in North America or in the Brazilian Northeast, where rains occur primarily during warm months.

The former have an advantage with respect to the availability of water for recharge, because the water consumption during the wet season is relatively restrained. At higher elevations where part of the precipitation is in the form of snow, the rapid meltdown in spring provides a further opportunity for recharge to occur. The payoff is in the parched appearance of the summer landscape, where only deep-rooted trees can survive the dry summer. The latter evidently thrive on the infiltrated waters into the deep soil layers, the residues of the winter percolation flux, which also keeps the soil salinity buildup in bounds. In contrast, in the region with the warm season rainfall, the abundant periodical vegetation consumes most of the moisture, leaving little to recharge and also resulting in the buildup of soil salinity. Evidently, the monthly ratio of  $P/ET$  is of greater concern than the year round average, with antecedent soil moisture and rainfall intensity and persistence also of great importance.

Taking the eastern Mediterranean lands as an example, regions with annual rain amounts of 500–1000 mm/a usually show little direct surface run-off (i.e., between 2 and 5%), whereas recharge was estimated to account for up to 35% of the annual precipitation (Goldschmidt & Jacobs, 1958). The present number evidently depends on the surface morphology and structure as well as the land-use pattern. Recharge is strongly correlated with the saturation deficit in the soil, and for the region investigated by these authors, they established a threshold value of 360 mm of cumulative rain amounts that is necessary to make up for the moisture deficit in the soil incurred by the evapotranspiration during the rainless period. Under such conditions, recharge (and also flushing of the soil of accumulated salinity) favors sites with a relatively thin soil layer above the rock exposures. In valley terrains with deep soil and a rich vegetation cover, all of the soil moisture may be used up locally, except during an exceptionally rainy season. This region, moreover, is characterized by large annual fluctuations as a result of the up to 50% variability of the precipitation amounts and their distribution during the rainy season, so that large fluctuations in the annual recharge are the rule.

The irrigation water input in these climate regions is another factor that needs to be considered in the water budget. Conflicting effects of the irrigated agriculture come into play: On the one hand, the substitution of a rather dense plant cover for the sparse natural vegetation further decreases the  $P/ET$  ratio during the rainy season and potentially results in the accumulation of soil salinity, further acerbated by the irrigation's water salinity. On the other hand, the application of the irrigation water

during the rainless period prevents the water deficiency in the soil column during the dry period and enables a deep percolation already of the early rainfall. Also, when applied in excess, the irrigation water may provide an additional percolation flux, alas accompanied by polluting chemicals. The special case of the Australian experience is to be noted, however, where the substitution of fodder crops for the natural bush vegetation (characterized by deep roots) presently increased the availability of drainage water with the catastrophic flushing of the accumulated soil salinity into ground and surface waters—the so-called secondary salinity effect (Kenneth-Smith et al., 1994; Leany et al., 1999).

The Mediterranean region is characterized by sandy and calcareous sediments, which have a relatively high infiltration capacity. Some ponding in surface depressions or local overflow reservoirs may occur during strong intensity downpours, which exceed the infiltration capacity. This effect is accentuated in areas characterized by high clay content, in which case one encounters a large variability of the run-off/infiltration relationship, which makes the assessment of the recharge potential very difficult. In detailed studies of the semi-arid Southern High Plain of Texas and New Mexico, it was shown that recharge estimates based on classical and tracer methodologies differed by an order of magnitude; an important reason for such discrepancies was blamed on the important role of macropore recharge (preferential-flow) from surface wetlands and ephemeral playa lakes, in distinction to the matrix-flow under these conditions (Wood & Osterkamp, 1987; Wood & Nativ, 1994; Wood & Sanford, 1995).

From the geo-chemical point of view, the dominant process is the increase in the salinity deposited by the precipitation and surface fallout, because of the low P/ET ratio, which indeed is being used in the case of chloride as a measure of the ET component in the water balance (Eriksson & Khunakasse, 1969). In an extreme case, the buildup of salinity results in secondary precipitation of the less soluble portion of the soil water salinity. Owing to the relatively sparse vegetation in this climate zone, the plant-mediated calcification of the natural percolating waters is relatively minor; on the contrary, the widespread practice of irrigated agriculture expresses itself in the nitrification of the residual flux and more extreme modification of the chemical character of the groundwater recharge flux.

The stable isotope signature of the recharge process under conditions where the surface waters do not play a major role in the formation of groundwater sources (with notable exceptions to be discussed below) can be expected to follow that of the rainfall rather closely, with a bias in favor of the heavy rains during the peak of the rain season. The isotope enrichment because of evaporative losses of water from the surface wetness before infiltration has been estimated by Gat and Tzur (1967) to be rather small, amounting typically in the Israeli coastal plain to no more than 1‰ in  $\delta^{18}\text{O}$ . Larger differences between precipitation and groundwater isotope composition are being attributed either to recharge from lakes or other surface waters such as storage reservoirs or possibly by return flux of irrigation waters from sprinkler applications, where in an experimental plot an enrichment of up to 3‰ in  $\delta^{18}\text{O}$  between the water supply and the drainage waters were recorded.

In all these cases where open surface waters are exposed, the isotope enrichment of the  $\delta^2\text{H}$  is about four to five times as large as that of the  $\delta^{18}\text{O}$ , commensurate with the expected slope of the evaporation line (Fig. 4.29) in  $\delta$ -space.

The water loss by evapo-transpiration from within the soil column, which is such a dominant factor in the water balance in this region, also has a relatively minor effect on the isotopic composition to be compared with the dominant role it plays in the salinity balance. The reason is that transpired waters are taken up essentially non-fractionated by the root system. Thus, only a shift of the isotope composition by selection can take place. Similarly, the late rainfall in the season that infiltrates only to the top of the soil column will be completely lost during the following dry period. However, partial evaporation of soil water in-between rain events may impart an evaporative signature onto the percolation flux when the residual waters are then flushed down by a subsequent rain event. As described before, this is a nonlinear effect where little effect is recorded both when very little or most of the water is evaporated during this process (Gat, 1998). In any case, the isotope enrichment from within the restricted space of the soil column follows a lower slope in  $\delta$ -space than that of the open surface process, as described by Barnes and Allison (1988). The comparison of both the salinity buildup and the change in isotope composition relative to the Meteoric Water Line provides the possibility to distinguish between the different components of the evapo-transpiration flux.

### 5.3. ARID CLIMATES

Groundwater recharge occurs in arid (dry-land) areas most commonly through infiltration of surface run-off into Wadi alluvials, Sabkhas and karst terrains. In contrast to this line or point recharge, in volcanic or coarse grained unconsolidated rocks with low field capacities (e.g., dune sands and gravels) also areal infiltration takes place with deep and rapid penetration of the infiltrate into the subsurface, thus protecting the infiltrate from re-evaporation in arid climates.

Present recharge occurs in almost all arid (dry-land) areas and is documented by the appearance of tritium in deep parts of the vadose zone (>1 m) and in very shallow groundwater. Recent tritium results from fresh and salty waters in the Badain Jaran Shamo (part of the Gobi) (Table 5.2) clearly show that, even in this hyper arid area groundwater is recharged albeit very little according to the chloride water balance (0.5–1.5 mm/year).

Forty years after the end of the atmospheric nuclear weapon test, however, it is difficult to use the instrument of tritium profiling in the vadose zone for determining groundwater recharge (section 4.4.2.2) and from  $^3\text{H}$  close to the water table a quantification of groundwater recharge is hardly possible. In the past, the tritium-profiling instrument was often applied and delivered together with the chloride-balancing method interesting results on groundwater recharge for arid areas (sections 4.4.2.1 and 4.4.2.2, Fig. 4.22).

Infiltration in arid (dry-land) zones, however, is linked not only to favorable geologic conditions but also to the intensities of rains as can be learned from

Table 5.2. Stable isotopes and tritium in groundwater of the Badain Jaran Shamo (Gobi desert)

Place	Date of sampling	$\delta^{18}\text{O}\text{‰}$	$\delta^2\text{H}\text{‰}$	$d\text{‰}$	$^3\text{H TU}$	$\Delta^3\text{H}$
Fresh and salt waters without tritium						
SGJL (S)	25.09.2002	-1.12	4.1	13.0	0.8	0.7
ZEGT (S)	26.09.2002	-2.13	-40.8	-23.8	0.7	0.7
LT (DW)	27.09.2002	-2.62	-46.0	-25.1	1.1	<1.1
Fresh and salt waters with tritium						
SGJL (DW)	26.09.2002	-5.39	-61.7	-18.6	2.9	0.7
NRT (S)	25.09.2002	-5.21	-62.2	-20.5	11.4	0.9
LT (S)	27.09.2002	9.85	2.7	-76.1	1.6	0.7
LT (DW)	27.09.2002	8.00	-2.0	-66.0	4.7	0.7

S = spring, DW = dug well.

stable isotopes and the chemical composition of waters. Heavy rainfalls, which are mostly isotopically depleted, flush surface salinity away and contribute little to infiltration, as can be seen from the isotope and salinity indicators in groundwater; low rainfall intensities either re-evaporate before or along the interface atmosphere–lithosphere, hence, are also not very efficient to groundwater recharge; intermediate rainfall events contribute first to overland-flow and after adequate wetting of the infiltration interface also to groundwater recharge; here it is supposed that specially preferential-flow conducts infiltrates to depth, in which re-evaporation of water by capillary rise can be excluded. Thus, the unpredictable nature of rainfall events and the flush response or re-evaporative response of arid and semi-arid catchments makes estimates of groundwater recharge painful.

These limitations in mind, many recharge studies just state if recharge takes place at all or determine unproductive water losses instead of the groundwater recharge for management purposes. Therefore, groundwater exploitation in arid (dry-land) areas is often close to the availability of rechargeable groundwater or over-exploits, respectively mines, groundwater resources.

Traditional water balances, evaporation measurements or lysimeter studies in arid (dry-land) areas will not significantly contribute to the knowledge of groundwater recharge, because of the missing representativeness of the results for large areas (scale effects) and logistics

The rain recharge to the groundwater reservoir entails a sequence of transport steps from the surface to the groundwater table. Surface water infiltrates the vadose zone, wherein some water is retained by the surface of and the contact point between particles through attractive (capillary) forces; the excess drains downward through pores under the influence of gravity and capillarity, to eventually reach the groundwater surface, provided the infiltration escapes transpiration or direct evaporation from within the subsurface close to the landscape.

The recharge regime of the arid (dry-land) and the humid zone differs most significantly:

- In humid zones, overland-flow diminishes the water amounts available for recharge and the larger this amount the lower the groundwater yield.
- By contrast, in the arid zone, where evapo-transpiration losses locally exceed the rain amount, the confluence of waters by means of overland-flow onto infiltration appears to be a pre-requisite for the occurrence of groundwater recharge (Schoeller, 1959; Gat, 1984).

In the desert, long rain spells are a rarity (Sharon, 1972) and intervals between rain events long enough for drying up the top soil to be the rule. The top soil in the arid (dry-land) environment is bone dry, with a pronounced moisture deficit because of water loss by evaporation. The depth to which evaporation is effective depends on the openness of the pore structure and the time elapsed since last wetting; in sand dunes of arid areas, it can descend to a few meters, and in fine grained materials (less than medium grained sand), it is typically confined to the top 20–30 cm, so long as shrinking cracks do not deepen the desiccation depth. Transpiration further adds to the moisture deficit at depth if there are deep rooting plants in the system.

The moisture deficit in the unsaturated zone depends on

- The field capacity of the soil/sediment and
  - The percent deficiency in this water content because of evapo-transpiration losses.
- Given such data, it is evident that the water deficiency in sands might reach the equivalent of 40 mm of water, whereas in silt materials, the moisture deficiency could well approach 150 mm. The disparity is even more pronounced if one considers the top 10 cm of a sediment column. If now rain occurs and water infiltration, then a semi-quantitative formulation of the recharge flux (eq. 5.1) is

$$\begin{aligned} R' &= P_r - D_O - \Delta S \\ P_r &= \text{direct precipitation.} \end{aligned} \quad (5.1)$$

Under conditions of field capacity,

$$S = \int (\theta_{fc}) dz \quad (5.2)$$

The water deficit ( $\Delta S$  becomes

$$\Delta S = \int (\theta - \theta_{fc}) dz = \int_0^i (EP + TP) dt \quad (5.3)$$

Evidently the condition for occurrence of recharge by the direct infiltration of rain is  $P_r - D_O > \Delta S$ , and this condition cannot be satisfied in the desert environment, where a typical rain shower rarely exceeds 20 or 30 mm and desiccation time is very long. Isotope evidence indicates that major aquifers in the arid zone are not recharged by direct infiltration. If so, what is the recharge mechanism that overcomes the problem of the large water deficiency in the top soil relative to the amount of precipitation? Evidently, the recharge depends on the reversal of the role

of the overland-flow term in the balance equation. Whereas in the humid regime the discharge usually detracts from the recharge flux ( $R$ ), it appears that a positive term ( $+R$ ) is a prerequisite for groundwater recharge under aridity (Schoeller, 1959).

The focus of groundwater recharge problem thus shifts in the arid environment from the desert sediment generally to the mechanism and efficiency of run-off inception, on the one hand, and to the sediment at particular infiltration sites on the other.

The mechanisms whereby groundwater recharge occurs through overland-flow would not be effective were it not for the occurrence of discharge in the desert following even relatively small rain amounts of a few millimeters only. The foremost factor responsible for this phenomenon is the absence of a continuous vegetation cover, which in turn results in a deficiency of soil and the denudation of rock exposures. A secondary factor is the prevalence of an impermeable surface cover on the sun baked eolian sediments. The fact that desert precipitation often occurs in the form of relatively heavy showers although of short duration is a contributing factor to the efficiency of flood inception.

The desert flood is a very different phenomenon from humid zone's direct run-off, being more a skin process. The flood in arid (dry-land) zones is engendered under extreme dry conditions on bare rock exposures, boulders, and so on on surfaces ponded by the rain drops to form an impermeable pavement.

Two related numerical indices can be used to describe the recharge potential of the overland-flow process:

- These are the length scale from rain to the infiltration site and
- The areal reduction achieved by the discharge process, namely the ratio of the area of the impounded waters to the total rain-out area.

This latter index defines the maximum possible water yield of the process. The present water yield is evidently less than the maximum possible because of both the inefficiency of discharge inception and the losses from the discharge by evaporation or by some infiltration. Unlike in the humid zone, where the discharge continually swells by drainage from the saturated zone, in the arid (dry-land) zone the water balance along the flood path is negative, once rain has stopped (Gat, 1980). The simplest case to consider is that of a rock strewn area. In this case, the characteristic length scale is that of the impermeable surface elements, typically of dimension of 10–100 cm. Along the edges of the rock, the accumulated discharge drains to the ground, forming a more favorable environment for plant growth. Manipulation of this discharge was indeed used by ancients to enhance water availability for crops.

Enhanced factors of the water depth ( $E_f$ ) at the site of infiltration can be estimated from geometrical considerations, as shown schematically in Fig. 5.8. In domain A,  $E_f$  is given by eq. 5.4

$$\text{For } P > P_o \quad E_f = 1 + \left(1 - \frac{P_o}{P}\right) \frac{r}{2d} \quad (5.4)$$



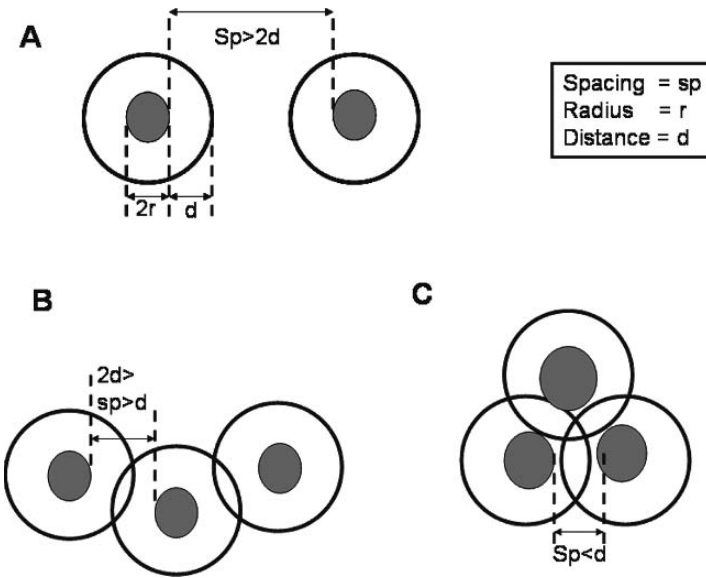


Figure 5.8. Schematic representation of the areas wetted by discharge in a rock-strewn field. A = widely dispersed impermeable elements without, B = with some and C = with maximum overlap

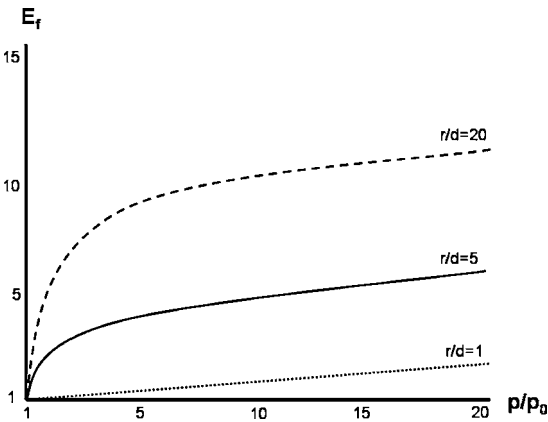


Figure 5.9. The water depth enhancement effect for widely dispersed surface elements as a function of rainfall depth. Results are given for  $d = 10$  cm

Where  $r$  is the radius of the impermeable surface element and  $d$  is the width of the area between two elements and  $P_0$  is the rain retained on the surface. Figure 5.9 gives values of  $E_r$  for a range of  $r/d$ .

Whenever the spacing between the length scales (radius) of the impermeable surface elements is of the order of  $2d$  or less, the water depth can be further

enhanced in the area of overlap by the synergistic effect of two rocks or more. In the range of overlap, when the spacing ranges between  $d$  and  $2d$  (domain B in Fig. 5.8), the additional enhancement in the affected zone is given in Fig. 5.9 and is a function of the size of the surface element. At still closer spacing (domain C in Fig. 5.8), the fraction of area ( $A$ ) covered by the impermeable surface is very high; the enhancement factor is expressed by

$$E_f = \frac{\left(1 - \frac{AP_0}{P}\right)}{(1 - A)} \tag{5.5}$$

As  $A$  in eq. 5.5 becomes 1, the water depth reaches quite high values as shown in Fig. 5.10. The details surface morphology will then determine whether ponding occurs, giving a chance for local infiltration, or whether larger scale discharge will initiate as from an inclined surface.

A convenient yardstick for  $E_f$  was found to be the accumulation of rain-born fall-out isotopes, such as  $^{90}\text{Sr}$  in the desert sediments (Gilat & Gat, 1960).

A subtle point has to be considered, namely the so-called ‘‘oasis effect.’’ In the area of water confluence and given a sufficient depth of sediment, perennial plants can grow. Their deep reaching roots extract water throughout the dry season in amounts far exceeding the water loss by direct evaporation and affecting the subsurface to great depth. As a result, the water deficiency is increased considerable. Local groundwater recharge will thus occur primarily only in areas of shallow depth or on cracked and fissured rock exposure.

Large-scale overland-flow, beyond the dimension of the impermeable surface elements, requires favorable morphology such as sloping surfaces. Yet this mechanism of discharge enhancement does not seem to be as effective as one could imagine. Yair et al. (1980) have shown that much of the hillside run-off,

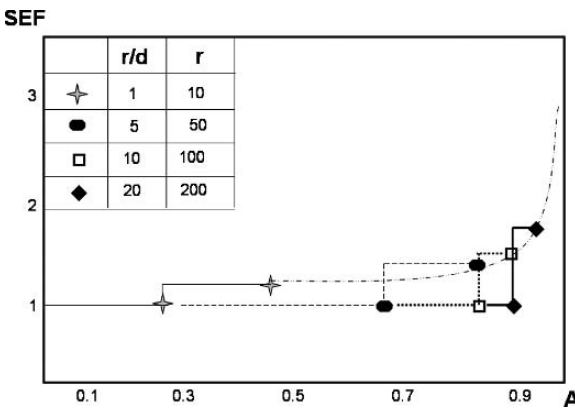


Figure 5.10. The enhancement of water depth as a function of the spacing of the impermeable surface elements

which gravitates downhill, infiltrates into the foot area of the hill, and does not significantly contribute to stream-flow in the Wadi.

Isotope studies on groundwater pockets, which are recharged locally in mountain areas, where large-scale flooding is not yet effective and discharge from hillsides shows that there is little selection between rainfall events in initiating this local discharge, as is evident from the fact that the isotope composition of discharge is about equal to that of the total rain event (Fig. 5.11). In contrast to this situation, the isotope data from the big regional flood-flows show that these are characterized by much depleted isotope values relative to the mean composition of the rain event and, unlike the discharge discussed above, engendered under rather special circumstances, namely very intensive showers. It is thus evident that they account only for a rather minute fraction of the desert rainfall. Even so, one finds immense water quantities along the flow path and the site of infiltration the conditions are for a short time akin to the recharge from a lake or river bed (saturated conditions).

The isotope signature of different recharge pathways (Fig. 5.12) enables one to assess their contribution to recharge of the desert groundwater bodies. The isotope signature imprinted by the recharge path is the result of processes of selection and fractionation between isotopes before infiltration (Gat & Tzur, 1967), and of changes, which occur within the unsaturated zone.

The primary selection between rainfall events is based on discrimination against small showers of less than 1 mm, which are re-evaporated and evidently ineffective in either recharge or discharge. As a rule, small showers are enriched in the heavy isotope species as a result of evaporation from falling droplets as is the case in the Negev (Levin et al., 1980). Discrimination against these rains of less than 1 or 2 mm results in a slight shift of the isotope composition.

Many cases of rainfall in the Negev show a typical V-shaped evolution of the isotope composition with the progress of the shower, the more depleted values, often by more than  $-2\%$  relative to the mean oxygen isotope composition of the total rain event, being associated with the most intense portion of the rain (Levin et al., 1980). As is evident from the discharge collected on an instrumented hillside (Yair et al., 1978) and from the large-scale run-off collection, the former represent the average and the latter selects only the most intensive portion of the rain, which is depleted in the heavy isotopes. The sojourn of water near the surface in such an arid environment results in further enrichment of the isotopes in the residual surface water in proportion to the amount of water lost by evaporation. As the enrichment of  $^2\text{H}$  and  $^{18}\text{O}$  has a characteristic relative enrichment, this imprint can readily be discerned.

Evaporation from within the soil/sediment also results in the enrichment of isotopes if it occurs directly by vapor diffusion, less so, if it occurs through the intermediary of transpiring plants. As shown by Allison et al. (1983), the isotope enrichment then proceeds along an evaporation line of lower slope than the water loss occurs from a water surface directly exposed to the turbulent atmosphere.

Taking the Negev as a model—as described by Issar et al. (1983)—desert groundwater recharges from local isolated pockets of water, occurring mostly along the

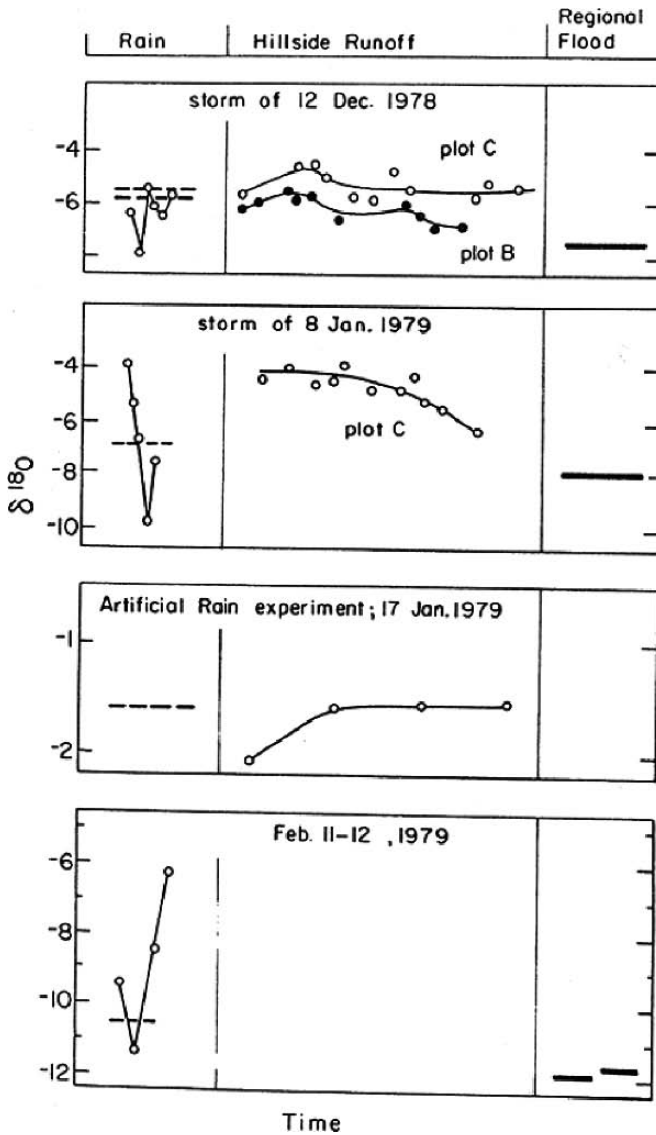


Figure 5.11. The isotope composition of run-off and rain initiated by a number of desert showers and one case of artificial sprinkling

floor of the dry river beds, at the foot hills of mountains or in local depressions. This aquifer recharge is of local character and gives rise to various springs of usually good water. Large-scale, regional aquifers in sandstone formations are either found deep under the surface and contain palaeo-water, recharged millennia ago, or

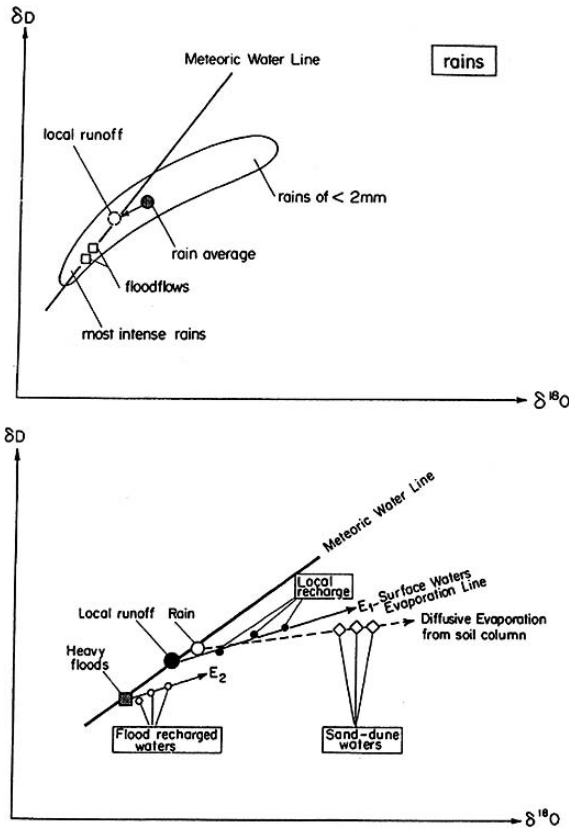


Figure 5.12. Isotope relationship between the mean desert showers and discharge

are situated in the marginal areas of the drainage systems and associated with the discharge of large Wadis.

The isotope composition of the groundwater from the Negev and Sinai deserts (Levin et al., 1980) suggests that the large aquifers, situated at the mouth of the large Wadis are flood recharged and characterized by depleted isotope values with little or no indication of subsequent enrichment. This fits the fact of rapid water flow and large water excess at the point of infiltration.

Smaller, local aquifer pockets in the hill region of the Negev are evidently recharged from local run-off (with isotope composition close to that of the mean rainfall) with some further isotope evaporative enrichment of the order of 1–2‰ in  $\delta^{18}O$ . In most cases, water derived from fractured crystalline terrain are even more enriched, up to 5‰, signifying a longer sojourn near the surface. Small events along the Wadi floor show quite varied isotope composition, often quite enriched in the heavy isotopes, indicating the contribution of locally small flows, which have lost much of their water by evaporation.

The extremely enriched sand dune water, which are encountered in the form of saline seepages from the base of sand dunes (Gat & Levy, 1978), have not been located in any of the aquifer bodies of the Negev and evidently do not constitute a regional important recharge pathway.

#### 5.4. COLD CLIMATES

Cold climates are characterized by mean annual air temperatures close to or beneath the freezing point of water, thus, producing permafrost conditions. Two types of permafrost typical occur:

- Wet permafrost with a partial melting of the subsurface ice during the summer season and
- Dry permafrost without thawing throughout the year.

Permafrost typically occurs in high altitudes of mountain areas and high latitudes; hence, wide areas of the Himalaya and some Alpine areas as well as North Canada, Iceland, Spitzbergen, and Siberia have presently permafrost conditions. During the last glacial age, Central and North Europe and North USA were also covered by permafrost and some of the present permafrost areas are reminders of former glacial conditions.

In some areas of the north hemisphere, permafrost reaches down to several 100 m below ground, in many mountainous areas present permafrost protects from rock avalanches and favors water ponding at the ground surface for stock farming during the warm season as well; as a consequence, an increase of mean air temperature may trigger rock slides and rock avalanches and many summer lakes in high altitudes will disappear.

All permafrost areas start with wet and may end in an advanced status with dry permafrost conditions, which typically occur today under cold ice shields (Greenland, Antarctica).

Permafrost conditions, however, do not automatically mean that all recharge pathways are blocked all over the year or during special seasons, because two basic kinds of subsurface ice formation exist. Either the formation of

- Ground ice or
- Ice pillows

both depending from the capillarity of porous or fissured sediments/rocks. As a rule, in fine grained sediments, the formation of ground ice dominates more than in coarse grained sediments.

The formation of ice pillows favors capillary driven flow toward ice crystallization centers, hence, dries the sediment adjacent of the ice pillow and thus conducts to sediment shrinking, which triggers the formation of ice wedges. Such ice wedges typically occur at mean annual temperatures of 0 to  $-3^{\circ}\text{C}$  and are missing at lower mean annual temperatures. These ice wedges may reach several meters deep from the ground and act as preferential percolation path ways. Therefore, it is not surprising that Michel and Fritz (1978) found tritium in groundwater beneath permafrost.

In the cold climates, the recharge/run-off relationship is dominated by the freezing and melting of the subsurface/percolation water. As melting proceeds slowly from the surface down into the frozen soil layers, the majority of the melt waters is either consumed by plants in wet permafrost areas (Sugimoto et al., 2002) or channeled by preferential subsurface flow path or contributes to surface run-off. Indeed, palaeowater records, especially  $^{14}\text{C}$ -isochrones of many European areas with permafrost conditions during glacial periods have been interpreted in terms of reduced groundwater recharge (Beyerle et al., 1998). This interpretation, however, may be ambiguous, because most of these examples have been reported from areas, in which rivers receive regional groundwater discharge. As natural tracing of groundwater does not parallel the potential field (section 4.4), but follows parallel to stream lines, the isochrone field will always narrow beneath receiving rivers by geometric reasons. Further on, in areas of receiving streams narrow isochrone fields depend significantly from sampling depths and locations, hence, making any quantitative interpretation on quantities of groundwater recharge difficult. Therefore, any narrow isochrone field under receiving rivers cannot automatically be a proof of any reduced groundwater recharge; other arguments and data have to support it.

The stable isotope signature of the melt waters is quite complex and varied and cannot be unambiguously identified. Whereas, the isotope composition of snowfall is very depleted in the heavy isotopes and often also characterized by a higher  $d$ -excess value than the precipitation in these areas (Fig. 4.27), as described by Jouzel and Merlivat (1984), the melt-water composition at times is much changed as it is that of the residual snow pack following partial melting. Indeed changes in the isotopic composition occur within a snow pack because of vapor transport and re-equilibration (Moser & Stichler, 1970; Friedman et al., 1991).

Direct sublimation is believed to occur without any change in the isotope composition. The difference in the isotope composition between the melt water and the original precipitation, which has been widely noticed and described in the literature (Arnason, 1981), is being blamed on a number of competing processes during meltdown:

- Runoff of partially melted snow,
- Evaporation from the wet snow surface with subsequent refreezing of the residual water,
- Diffusion of isotopically depleted vapor (in equilibrium with the snow) through the air-space in the snow pack.

On the basis of the isotope fractionation factors for the phase transitions between ice/liquid and vapor (Majoube, 1971), the first process would result in run-off, depleted in the heavy isotopes, leaving the residual solid phase enriched in the heavy isotopes of hydrogen and oxygen, respectively. The partial evaporation of the melt waters as well as the third process is expected to result in an enrichment of the isotopes in the residual snow; so that the complete melting of the residual snow is then expected to result in a seemingly evaporated isotope composition. Fortuitously, the relative change in the two isotopes is very close for both the first (solid/liquid) and the second (evaporation of surface waters at  $0^\circ\text{C}$ ) process, yielding a trend

line with slope between 5.5 and 6 in  $\delta$ -space. For the third process that involves diffusion of water vapor through stagnant air, the slope is even lower, just as for evaporation from within the soil.

Evidently, the rate of heating up and the geometry of the system are important parameters to consider the stable isotope composition of melt water; thus, the almost complete melting and run-off at the edge of the snow accumulation will show these effects to a lesser degree.

The same processes as for stable isotopes have to be considered for chloride. As all these processes are not yet well quantitatively understood, any determination of groundwater recharge in cold climates is even more difficult than in arid (dry-land) areas; but it is for sure that groundwater recharge presently occurred in these climates according to the type of permafrost.



## CHAPTER 6

### MAN'S IMPACT ON THE GROUNDWATER RECHARGE

The water cycle is being constantly and slowly modified since ever by atmospheric, erosion, land cover, and tectonic changes; these changes have been accelerated since activities and growth of mankind (Fig. 6.1) passed a certain threshold number in about the year 1850.

A general definition of man's impact on groundwater recharge is impossible, because it includes transient, direct, and indirect impacts on factors influencing infiltration, storage, and discharge properties of the subsurface in a since ever changing climate, geologic and biologic environment. Finally, man-made changes express under different climates, geological, social, and economic conditions in various ways.

Climate on earth shifted about 4,000,000,000 years B.P. from a reducing to an oxidizing atmosphere, and since that time oscillated from wet to hot, hot to dry, and warm to cold, thus, producing various geological periods with ice ages on the one and under strong evaporation conditions with salt precipitation on the other extreme. Such major shifts are basically caused by

- Plate-tectonics and orogenesis, influencing the atmosphere, ocean/land partitioning, topography, and thus, the extent of the heat and water vapor exchange on the earth surface, and
- The interaction of the biosphere with the atmosphere and hydrosphere.

These changes had triggering, reinforcing, and feed-back effects and modified the functioning of both the interface atmosphere/hydrosphere and atmosphere/biosphere/lithosphere, which both govern vaporization and recharge processes.

Man's influence on the hydrological cycle in general and the groundwater cycle in particular starts at its dawn and changed very much when mankind turned in Neolithic time from hunting to farming activities, which resulted

- First in a change of the plant cover (deforestation, crops, and bare areas). As can be seen from Table 3.1, agricultural crops consume much more water than forest trees do, to produce 1 kg of dry mass;
- Later in an enhanced increase of transpiration and infiltration by introducing irrigation;
- By urbanization, which changed the radiation balance and the infiltration capacities of the subsurface, and

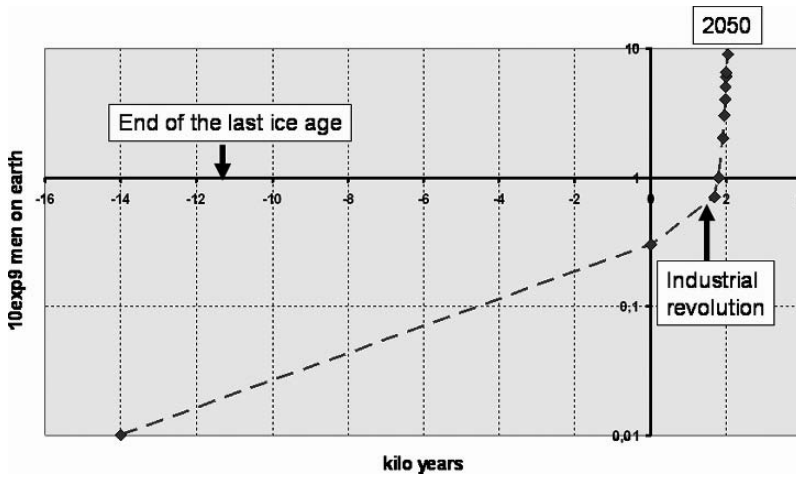


Figure 6.1. Development of mankind by numbers over the the last 14,000 years

- Finally by changing the chemical composition of the earth's atmosphere by emissions.

The early activities of civilization modified only the local climate. However, the intensification of food and energy production, of industrialization as well as urbanization developed to a global concern in changing infiltration, run-off, evaporation, and the water quality. Combustion of fossil fuels and the reduction of forest areas (to provide farm land) increased in the atmosphere the greenhouse gasses  $\text{CO}_2$  from 290 to 350 ppm;  $\text{CH}_4$  from rice cultivation and meat production increased emissions into the atmosphere from 0.95 to 1.65 ppm and  $\text{N}_2\text{O}$  emissions from advanced agricultural areas are in the range of 3 kg/(ha year). To assess these numbers, it should be kept in mind that the greenhouse effect of methane is many times stronger than the one of  $\text{CO}_2$ .

The redistribution of the incoming precipitation between the surface storage, the re-evaporation losses, the infiltration flux, and the surface run-off is determined on the one hand by the geo-morphological structure of the surface layers, the plant cover, and, in general, the eco-hydrological feedback processes. On the other hand, it depends on the temporal and spatial characteristics of the precipitation input as well as on the distinction between liquid and solid precipitation.

Even under undisturbed "natural" conditions, there is a marked seasonal effect in the response of the recharge flux to a given water input, which depends on the seasonal change of the ecological surface structure, the antecedent moisture content of the surface layer, and most extreme, the presence of a snow or ice cover. Among the most prominent factors responsible for these changing responses, one can enumerate

- The shedding of leaves in deciduous forests;
- Forest fires and other 'natural disasters';

- The resurgence of grasses during the rainy season;
- Surface ponding and flooding following extreme precipitation events; and
- Snowmelt.

With the increasing density of human population and intensification of agricultural and industrial activities, one can distinguish between a number of far-reaching effects on the local and regional water balance. This results

- From the major land use changes with important repercussions on the distribution of the precipitation input into the fluxes of evaporation, run-off, and recharge.
- The regulation or damming of the river courses and drainage of wetlands, including flood-control measures.
- The use of additional water resources, whether from local groundwater or interception of surface waters to imported water for urban uses or irrigated agriculture.

Any change in the plant cover evidently affects the hydrological relationships throughout the interface zone: the degree of canopy interception (associated with a relatively large evaporative water loss), the soil water balance (both the direct evaporation loss and the transpiration component from deep layers), the surface structure, and especially changes because of plowing on the one hand and compaction on the other, which affect the infiltration capacity. An example from the arid (dry-land) zone are sand-dune areas, where the recharge flux depends on impervious algal mats that enable the confluence of rain from a large area unto preferred infiltration sites (Danin et al., 1989; Yair, 1990). The free grazing of goats on such sites destroys these impervious layers by the churning-up of the surface by the animals, with the result that the incoming rain only wets the surface sand layers and is then lost to evaporation.

Deforestation and afforestation are the best-known cases of far-reaching effects on the water and energy balance of the interface biosphere/atmosphere. Under humid conditions, for example, the Brazilian rain forest, the most noticeable local effect of the deforestation is that of increased surface run-off resulting in soil erosion and land deterioration. Under less humid conditions, on the other hand, afforestation shields the exposed soils and may at times presently enhance infiltration and unproductive loss of water, as well as providing a more favorable micro-climate.

## 6.1. LAND USE CHANGE: AGRICULTURE

Any cultivated field in place of the natural vegetation changes the potential groundwater recharge flux at times with consequences, which of course differ appreciably in different climate zones and settings. A number of opposing effects have to be considered, among them the changed evapo-transpiration rate of the agricultural crop when compared with the natural vegetation (Tables 4.2 and 4.3). This in some cases increases the availability of water for recharge, because of the combination of the reduction of surface run-off by plowing of the soil surface layer, reduction of the water loss by canopy interception as well as the fact that it covers the area only periodically from seeding until harvest time. An extreme example is the Australian experience under semi-arid conditions, resulting from the replacement

of the native Mallee vegetation by grasses for fodder, which caused an increased flushing of the accumulated salinity in the unsaturated zone into the adjacent aquifers and rivers, accompanied by severe environmental damages (the secondary salinity effect) (Allison et al., 1990 ). On the other hand, especially under a Mediterranean climate, the evapo-transpiration rate of the crops grown during the rainy season often exceeds that of the sparse native vegetation resulting in a reduction of the groundwater recharge flux and the buildup of higher salinity in the soil moisture.

Food production of a growing world population (Fig. 6.1) depends from agriculture practice in dry and humid areas of the globe. To increase crop yields and crop quality, three activities have been developed:

- The use of heavy machines,
- The application of fertilizers, pesticides, and herbicides, and
- The use of irrigation systems.

With the beginning of the Neolithic revolution, mankind turned from hunting to agriculture and realized very early that the fertility of forest-land, transformed into agro-land, declined within a short run of time; therefore, early farmers transformed one forest plot after the other into agro-land and tried to govern water availability (section 4.2) for an optimal plant growth. In the mid of the 19th century Libby and at the beginning of the 20th century Haber-Bosch made fertilizers available, which increased crops yields two to three times during the second half of the 20th century; however, fertilizers in excess and applied under non-favorable weather conditions reach run-off and contribute to some eutrophication of lakes and ocean shelf areas or sometimes to a deterioration of the groundwater quality as far as they did not disintegrate into other chemical species, such as gases. Some of these gases, however, reach the atmosphere as trace gases ( $N_2O$  or  $CH_4$ ) and there contribute to degrade the ozone layer respectively to enhance the green house effect.

Pesticides based first on heavy metals, which sorb at the prevailing soil pHs well on clay minerals and organic matter; however, in the long run of time they harmed soil organisms, contributed to soil compaction and thus also to a reduction of infiltration or finally groundwater recharge. In the second half of the 20th century, these heavy metal pesticides have been replaced by organics, which were supposed to sorb and disintegrate short after application, but long enough to efficiently fight against plant diseases and the competitive growth between crop plants and weed. Short after application, pesticides and herbicides appeared in small concentrations in surface and groundwater (Fig. 5.7, section 5.1.2). As the metabolic chains and the health impact of many chain species of the many pesticides and herbicides are not yet well understood, their role for food and water quality is still difficult to assess.

The introduction of machines in agriculture was a big step forward to intensive agriculture, but the high weight of the machines compacted the unconsolidated weathering cover of rocks/sediments to an extent that erosion, respectively, overland-flow increased and infiltration decreased. Hence, the cultivation tools reduced groundwater recharge; one counter-measure was deep ploughing.

Especially in drylands, agriculture cannot achieve adequate crop yields without irrigation systems, and in wet areas, irrigation is often applied to gain more crops a year and to enhance crop quality. As an average of the 20th century, the water demand of agriculture covered about 75%, of industry about 16%, of the private sector about 7%, and of other users about 2%. As can be seen from Table 1.1, these numbers changed with the run of time, according to a changing technology. As a rule, the growth of 1 t of dry matter needs about 2,000 m<sup>3</sup> of water, and many plants in dry-lands are originally from temperate climates.

Dry-lands (Petrov, 1976) comprise about 37% of the continental surface and about 50% of the nations on earth are totally or in parts affected by the constraints of aridity; basically for these areas, irrigation has been developed as an important tool for the production of food and natural raw materials. Today about 17% of the world's croplands are irrigated (about 240 mio. hectares) and 75% of these areas are located in developing countries. From 1960 to 1970, the yearly growth rate of irrigation areas was about 2–4% and since then dropped to a present growth of less than 1%. Today all these irrigation areas produce about one-third of the food demand in the world.

The water inputs because of irrigation add up to the natural infiltration. This results not only in additional effluents from the irrigated fields, but may, moreover, also increase the water excesses during the beginning phases of the rainy season because of a reduced moisture deficit in the soil compared with the natural precipitation cycle. This potentially beneficial excess that can increase the natural recharge rate has to be balanced, however, against the increased demand for evapotranspiration of the dense plant cover in the irrigated field compared with the undisturbed natural situation resulting in salinity buildup. Some harmful cases of water logging in irrigated fields are also on record (Seiler, 2000) as well as the rise of the water table under such fields (Tanwar, 1979).

There are different irrigation systems in use:

- Flood irrigation,
- Furrow irrigation,
- Sprinkling irrigation, and
- Drip irrigation,

which are all connected through a sophisticated channel system with a water source such as groundwater wells, rivers, a dam, desalination, or waste water treatment plants. Flood and furrow irrigation lose much excess water. In contrast, sprinkling irrigation favors fungi infections of plant leaves; the sprinkling process is the most wasteful in this respect because partial evaporation from the droplets is added to the transpiration loss of the plants. On the basis of the enrichment of the heavy isotopes during the sprinkling process (by 2‰ in  $\delta^{18}\text{O}$ ) at the Gilath experimental field in southern Israel, reported by Gat and Tzur (1967), an average loss of more than 10% of the sprinkled water can be estimated. The drip-irrigation efficiency in terms of the overall water balance is optimal (Table 6.1). Only drip irrigation offers an optimal water use for plants; it could be supported by capillary barriers (sand beds; section 3.5), to break upward capillary rise of water from the unsaturated zone to

*Table 6.1.* A comparison between furrow and drip irrigation applied in Egypt for different crops (Springuel, 2003)

Crop	Furrow irrigation (m <sup>3</sup> /ha)	Drip irrigation (m <sup>3</sup> /ha)
Sunflower	2,380	1,980
Wheat	1,850	–
Corn	1,790	950
Bean	1,240	810
Tomatoes	1,190	950
Grapes	500	380
Citrus	790	400

the evaporating interface; such capillary barriers do not only reduce unproductive water consumption by evaporation, but reduce simultaneously soil salinization. A comparison of the efficiency of two irrigation systems is shown in Table 6.1.

Crop growth is optimal at about 60–80% of water content at field capacity. In contrast, at water contents below 30–40% of field capacity, crop yield reduces as much as it did if water contents exceeded 80% of field capacity; in the first case, plants miss water for transpiration, and in the second case, plant roots miss sufficient air for respiration; in both cases, crop yields decline. Thus, there exists a small soil water window for optimal crop yields, which could be controlled combining TDR measurements with irrigation practice. Such a control, however, depends not only from the crop but also from the plant development during the vegetation period. For example, water deficits in May/June, June/August, or July/September can significantly reduce the crop yield of summer grains, potatoes respectively sugar-beets.

The most common setting of an irrigated field is such that the water excesses drain vertical down through the soil, thus adding to the natural groundwater recharge flux. When this groundwater is used again to supply irrigation waters, a closed loop can be established leading to a successive buildup of the natural salinity in each cycle because of the evapo-transpiration loss, as exemplified in the coastal plain of Israel. The severity of the problem will depend on the water efficiency of the agricultural application, in terms of percentage of the applied water lost to evapo-transpiration (Eriksson & Khunakasse, 1969) and of the distribution of the effluent flux in time and space.

Irrigation increases primarily evapo-transpiration, but to some degree also infiltration through irrigation return water. The amount of return water is estimated to average 0–20% according to the type of sediment, in which irrigation is applied. In addition, irrigation canals, distributing water from a central source to the fields, produce often significant water losses, because they are not lined – like in the Punjab – or often not well maintained. Isotope studies in Pakistan (Sajjad et al., 1985) showed that most of the groundwater logging is due to water losses from the distribution canals, which are unlined and end mostly blind. This situation in the

Punjab, however, cannot be meliorated by counter-measures, because the irrigation areas belong to a very flat delta area, where it is difficult to construct an appropriate gravity drainage system. Therefore, in some areas, water levels, reaching the ground surface, must be drawn down by the installation and management of groundwater wells.

When the source of the irrigation water is from outside the region, the local groundwater balance in terms of water quantity may presently be improved because an additional recharge flux is activated; the issue, however, is then the compatibility of the extraneous waters with the local situation in terms of topography and of water quality. In areas with flat topography like in delta areas, the additional recharge flux highers the groundwater table, which may come up to the evaporating front (Fig. 4.30), hence, increase soil salinization.

As the cleanup or desalination of the diffuse recharge flux is usually not a viable option, the pretreatment of the applied irrigation water may be the recommended procedure in those cases where relatively saline waters are used as a source of water. To circumvent this procedure, the import of clean waters or even desalinated ones, though apparently more expensive than the locally available ones, may be the preferred option on the long run.

In all cases, the drainage waters out of irrigation fields contain relatively high concentrations of fertilizers and pesticides; these concentrations are beyond the natural attenuation capacity of the soil and aquifer. Therefore, any situation where the effluent flux can be channeled into treatment facilities before recharge or export is to be preferred. In such a case, the requirement on the quality at the input can also be relaxed. Controlled greenhouse agriculture meets this criterion to the highest degree.

In the case of effluents, discharging to surface waters, two opposing factors have to be considered. The diluting potential of fast river flows and the remediation potential of bank overflow areas and wetlands in relation to some of the pollutants in the agricultural effluents can be considered a mitigating factor. On the other hand, the eutrophication of the downstream aquatic systems because of the export of nutrients is a serious problem in many cases, severely curtailing the use of these waters, as exemplified in Lake Tiberias of the Jordan River system. Whenever the effluents from the fields drain through identifiable feeder channels, their remedial treatment can be accomplished relatively easily. Following dissemination in the larger stream any treatment presents a much more costly operation.

Irrigation without sufficient drainage creates salinization of soils, soil mechanical and hygienic problems, and a rise of groundwater levels, often called groundwater logging. On a long run of time, chemical residuals accumulate by evaporation in soils and thus contribute on the one hand to salinization and on the other hand to a reduction of crop yields. As a consequence, irrigated soils, which are not well naturally drained, must be flushed from time to time with irrigation water, to leach accumulated salts. Systematic studies on percolation of irrigation water in the Punjab (Sajjad et al., 1985) and the Jordan valley showed that clay, silt,

and fine grains sands contribute very little to percolation vertical down, because capillary forces keep water against gravity: hence, plant water availability is high, but air availability for plant roots is low; in contrast, coarse grained sands and all gravels have very good water retention and downward drainage capacities and thus, contribute little to soil salinization.

Fine-grained soils/sediments need under-drainage to optimize the air/water partitioning in the effective root zone. Under-drainage of fields applies to facilitate downward movement of water in the effective root zone. To do so, permeable earth ware or plastic pipes are laid in line at depth of 1–1.2 m b.g.s.. Only in heavy soils, this drainage must be supported by moling and sub-soiling; moling consists in forming unlined channels at the surface and sub-soiling refers to deep ploughing. Both these supporting activities have an efficiency of considerably less than a decade.

Before the construction of an irrigation system in Pakistan at the end of the 19th century, the average Punjab groundwater table was about 30–40 m below the ground surface, only along the few rivers it was close to the surface (Fig. 6.2). At the end of the 20th century, this groundwater table logged to depth close to the ground surface, as it did in many other areas of the world too. When groundwater tables approach 2–0 m below ground, actual evaporation turns to potential and thus accelerates salinization of soils. As in drylands groundwater used for irrigation is often old and carries lots of sodium, this salinization makes soils and sediments impermeable for plant roots.

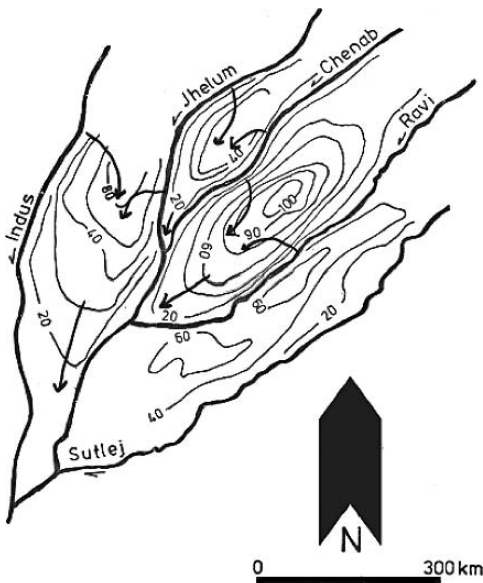


Figure 6.2. Depth to the groundwater table in the Punjab before irrigation times. Numbers in feet. Arrows = groundwater flow direction



Flood irrigation costs in developed countries are in normal years at about 250–300 €/ha and may rise in dry years to more than 500 €/ha. Using more efficient irrigation systems, such as drip irrigation, increased these cost significantly; therefore, only rich countries apply it.

Any reduction of irrigation water in drylands can be achieved by an appropriate selection of crop sequences, cultivation of dry resistant seeds like millet and Sorghum and finally through a very shallow ploughing (Ellmer et al., 2001). All these agriculture activities, such as ploughing, the application of fertilizers, pesticides, herbicides, and irrigation can be enhanced in view of crop yield and quality and a decrease of undesired environmental impacts, such as the reduction of groundwater recharge or any deterioration of water or air quality, if these tools apply in an appropriate time, quantity, and intensity. Thus, the global nutrient production could increase by 70%, although the arable land will increase only by 20% and the yearly number of crops by 10% (FAO, 2001). A supporting measure can be greenhouse agriculture, which controls the nutrient and pesticide supply best, and can save the environment from pollution. However, water practices developed for temperate climates may not apply in arid area for environmental, economic, and cultural reasons.

## 6.2. LAND USE CHANGES: URBAN AREAS

At the beginning of the 21th century, about 50% of the world population lived in big- or mega-cities, imposing special challenges for drinking water supply and liquid and solid waste management. Most big- or mega-cities must import their major water supply from catchments beyond the urban limits, leading to challenges to manage a surplus of water in a small catchment without losing control on floods and groundwater levels, which may result in soil mechanical, soil erosion, hill slope and hygienic problems.

Urbanization changes groundwater recharge significantly, introducing new recharge mechanisms and modifying existing ones. Common factors to most urban areas are an impermeabilization of the infiltration interface and a compaction of the percolation area by constructions and pavements as well as leakages from water distribution and waste water collector systems. These effects vary as a function of the scale of settlement, its location in relation to the hydrologic pathways and the climatic and social settings. Furthermore, the design and operation of the hydrological infrastructure (water supply, drainage and run-off systems, effluent control, and treatment) are of great importance.

The effect of urbanization on the water resources results from the following changes of the environment and its hydrologic patterns:

- Micro-climate changes, including increase in precipitation intensity because of the “heat island” effect;
- Blocking of soil surfaces by impervious layers;
- Release of water intentionally or inadvertently to local recharge or run-off with a time distribution different from the natural pattern;

- Release of pollutants.

On the one hand, corrections of river courses accelerate discharge velocities and volumes and keep in flood periods flood plains free of inundations; thus, it improved settling activities as well as agricultural activities in mostly fertile flood plains. On the other hand,

- The increase of flow velocities enhanced erosion, which led to a deepening of the discharge altitude and in extreme situations to an emptying of alluvial aquifers,
- With increased flow velocities and erosion, river-infiltration reduced, and thus reduced natural water availability in aquifers, and
- Inundations disseminated nutrients in the flood area, which have now to be replaced by chemical fertilizers; the Nile valley is a famous example for it.

Urban areas have a significant influence on the formation of precipitation. Studies in Europe and North America reveal an urban maximum of precipitation as compared with the urban surroundings; this is attributed to the relative warmth of towns, the great concentrations of gas and particulate pollutions and mechanical effects on air motion. They all favor convective precipitation, increase the number of condensation nuclei, and change the physical boundary conditions to keep water vapor in the air.

There are four basic processes, dominating run-off in cities:

- Building activities disturb the natural infiltration capacity by dewatering and compaction of the infiltration pathways,
- The introduction of impervious surfaces increase the run-off speed and reduce evaporation,
- The introduction of an improved drainage system, which is constant over the seasons, increases or decreases groundwater recharge,
- Run-off from impervious surfaces begins immediately after storm events as compared with run-off in open areas, thus, changing the time distribution of run-off.

Impermeabilization of land surfaces reduce both infiltration and evaporation, hence, increase and accelerate surface run-off. Storm water management, however, can compensate the losses of groundwater recharge by appropriate infiltration techniques. Infiltration in urban areas is often focused to the margins of impermeable areas; hence, groundwater recharge may become higher than for natural vegetation (van de Ven, 1990). A study in Long Island (USA) showed (Ku et al., 1992) that an impermeabilization of 20–30% of the area leads to

- An increase of groundwater recharge by 12% through infiltration in pavement margins and infiltration plots and
- A loss of groundwater recharge by 10% through routing the drainage to the sea.

The city of Niamey in West Africa has some 70% of unpaved area; however, this area compacted to a degree that infiltration capacities reduced (Bouvier, 1990). Quantifying this groundwater recharge, however, is difficult.

In many big- or mega-cities, it can be observed that beneath the residential areas of the rich, groundwater recharge is significantly higher than else where, because of the excess application of irrigation of amenity areas.

Water distribution and waste water collector systems of urban areas (Seiler & Alvarado, 1998) can significantly increase groundwater recharge. Water losses of 5% seem to be quite normal, but in some towns of the world, these losses amount to 60% and cause groundwater logging, if water is imported from distant catchments to towns; contrary, losses from the collector system may impact groundwater quality (Seiler, 2000).

The general climate setting is one important factor to consider, because of the different relationships between the surface and the subsurface run-off in response to the precipitation input for different climates. Under humid conditions, where in any event groundwater recharge is not limited by the availability of water but rather by the infiltration capacity, the run-off from the urban area can change the locality of recharge but usually affects the overall balance of the aquifer only marginally. Under semi-arid climates, where the surface run-off is normally only a minor factor in the water balance and the recharge rate is determined by the competition between the evapo-transpiration losses from the soil layers and the percolation rate, the prevention of the natural infiltration by the impervious surfaces detracts from the recharge to any underlying aquifers and a decline of the water table, possibly accompanied by encroachment of saline waters.

The situation is quite different in the arid drylands where, as described above, some degree of surface run-off is a necessary condition for the occurrence of recharge. In this case, the higher yield of run-off for any given precipitation event can be a positive factor in the quantity of the recharge flux, provided the run-off is properly channeled onto a suitable infiltration site. However, the possible polluting effect of these surface waters, if not treated properly, requires attention.

### **6.3. GLOBAL CHANGES AND THE WATER CYCLE**

The climate system on earth was always changing, which, however, evolved mostly slowly, and was always followed by a long readjustment time of subsurface hydraulic system; this becomes evident from dry-lands, where water discharges from the geologic time occur till today, although significant groundwater recharge does presently not occur. As compared to these slow, natural changes, a growing number of humans accelerated these changes, because of food and energy production.

Present global changes refer to two basic human activities, which have a climate implication; men's activities

- change the land surface, which is an important receptor and transformer of solar energy, heat, and run-off from precipitation, and
- influence the chemical composition of the atmosphere, which is in between others responsible for the filtering of solar energy and storage of heat.

Although men's activities exist since many hundred thousand years, a growing population number and activity shifted global changes from a local to a global scale of concern as other bio-populations also did in the geologic past.

The atmosphere and the interface atmosphere/hydrosphere/biosphere/lithosphere belong to a dynamic system with an inflow, reflection, and transformation of solar

energy and precipitation. This system governs the water cycle and becomes modified by the distribution of land and ocean masses, by topography factors, a changing vegetation cover, by polar ice, as well as atmospheric water vapor and clouds. All interactions and feed backs in this coupled system are complex and not yet adequate quantitatively understood.

Any change in the heat production, storage, and distribution mechanisms will change the water cycle on a regional or global scale and affect all sectors of our life, such as food security, human and ecosystem life and health. Historically and of local dimension, such changes are known from the migration of nations according to their socio-economic resistance, the soil fertility, and the degree of climate changes.

In recent times, only few issues have produced so much scientific and political attention and controversy discussions as the increase of greenhouse gases (mainly CO<sub>2</sub> and CH<sub>4</sub>) and its consequences for life and health. CO<sub>2</sub> emissions date mainly from energy generation and hydrocarbon processing, CH<sub>4</sub> from the intensification of agriculture.

From the beginning of the industrial age till the end of the 20th century, the average temperature has increased by about 0.6°C and the average sea level has logged by about 0.1–0.2 m; in the same period of time, rainfall increased in the North of the north-hemisphere, but decreased in the tropics and subtropics of Africa and Southeast Asia. These just noticeable changes increased from 1960 to 2000 about three times the economic losses by natural disasters. Such disasters were

- diseases and plagues,
- floods and draughts,
- hill slope stability.

According to the output of GMCs, the present assessment of climate prediction for the end of the 21st century furnishes a temperature increase of minimum 1.4°C to maximum 5.8°C as compared with the beginning of the industrial period with the consequence of

- increasing EP, TP, and precipitation, resulting in a wetter world,
- higher precipitation variabilities and intensities,
- shift of peak stream flow in mountain areas from the spring to the winter season,
- increased melting and calving of polar ice and reduction of the volume of mountain glaciers,
- an Arctic Sea, which will partly or completely be ice free during the summer period,
- a further mean sea level rise from 1990 to 2100 of 0.1–0.9 m, which exceeds the already observed rate in the 20th century by 2.2–4.4 times, hence, damaging coastal areas and moving the salt-/fresh-water interface landwards,
- a reduction of the permafrost in Siberia by about 0.5 m and in the high mountains with the consequence of the disappearance of some lakes in permafrost regions, more rock slides and avalanches in mountain areas,
- a further decrease of precipitation in South Africa, Australia, the Near East and Central America,

- seasonal changes of precipitation amounts in North America and Western Europe,
- changes of the precipitation intensities.

Even with a drastic reduction of greenhouse gas emissions, the present climate trend will continue beyond the 21st century, because of a delayed response time of global ocean and ice shield systems. So, all such changes will trigger a significant transient behavior not only at the output but also at the input site, as it is well known from desertification processes and the change of hydro-geologic systems from an exorheic to endorheic discharge system.

Global warming will have major impacts on the magnitude and mean residence times of surface and subsurface run-off. However, completely unknown but of outstanding importance is the missing knowledge, if mankind moved under natural conditions from an interglacial to the next or to the end of the Cenozoic glaciations; it is well known that the last interglacial age (150–80 ka B.P.) had a significant warmer climate in Central Europe than present. As this discussion lacks any degree of accuracy in our prediction and is faced with a transient behavior of natural systems, it is still difficult to really assess the magnitude of impact of greenhouse emissions for the future availability of water resources, especially for groundwater recharge.

Comparing globally the predicted changes with the present water availability (Table 2.2) would result in no serious problems for Americas and Australia, because the present high availability of water per capita and year exceed  $10,000 \text{ m}^3$  (Table 2.2) as compared with the minimum or maximum total water demand of  $1,000\text{--}1,500 \text{ m}^3/(\text{capita and year})$ . On the contrary, in some areas of South Europe, North Africa, and the Near East, water scarcity will raise serious problems.

From a plant physiologic point of view, on the one hand, elevated  $\text{CO}_2$  concentrations decreased the stomata resistance of leaves, hence, transpiration; this effect expresses stronger in herbs than trees. On the other hand, high  $\text{CO}_2$  contents will also stimulate the growth of leaves and larger leaves could compensate the reduced stomata water losses of small leaves.

Not only  $\text{CO}_2$  but also ozone influences the continental water cycle; abundant ozone reduces plant growth, hence, also transpiration. This ozone is produced by combustion processes.

Another aspect of global climate changes refers to the snow/rain ratio. Snow is a more important external water reservoir than dams and artificial lakes; it shifts discharges from winter to spring/summer time by delay, does not suffer from significant evaporation or sublimation losses, and is on a long run of time not submitted to any geometric reservoir change by sedimentation. These properties of snow covers offer, for example, to some areas of the Near East, South Iran, the Punjab, Central Europe, Western America, and many inner Asian areas a seasonally better equilibrated discharge (section 3.1) and more intensive groundwater recharge than rain produced alone, hence, favors access for domestic and irrigation water use. Any temperature increase will decrease the snow/rain ratio as compared with present, will speed up snowmelt and discharge of melt water, and, thus, mostly increase erosion and, if stored in surface reservoirs, unproductive evaporation losses.

All these factors produce a change of groundwater recharge and oblige to construct new and higher dams to replace the natural by an artificial retardation of surface discharge.

In unconsolidated rocks with overland-, inter-flow and groundwater recharge, a reduction of rain, however, may reduce overland- and inter-flow, but increase groundwater recharge (section 3.5); however, if this reduction of rain parallels an increase of the rain intensities, groundwater recharge may also reduce.

From these few examples comes out that an assessment of the impact of the present global change on the continental water cycle and groundwater recharge is still difficult. As a consequence, only future sceneries can be elaborated, which may be far from realistic. Therefore, and being aware that global changes will occur, hydrology has to develop concepts of flexibility on water management and on how the natural water cycle becomes influenced by means of water imports/exports, including the desalination of ocean water. This flexibility requires from hydro-geologists more precise data on the amount and fate of groundwater recharge. Water managers, who often seem to be mainly interested in assessing short-term risks to reducing vulnerability, should be encouraged to take climate variability and change more serious. And adaptation to climate change, in parallel with mitigation, should be included in national development plans under integrated water resources management (IWRM). IWRM itself is all about managing for variability and change, including climate impacts.

## BIBLIOGRAPHY

- ABDULLAEV, I.: Environmental impacts of large scale irrigation: examples from the Aral Sea. In: GAT, J.R. & NETHANYAHU, S. (Eds.): *Water and Environment: Resolving Conflicts in the Development of Drylands*, Conference Proceedings, CWST-Ben-Gurion University of the Negev, 2000, 68–69, Beer Sheba.
- ABOU ZAKHEM, B. & HAFEZ, R.: General hydroisotopic study of direct infiltration and evaporation process through the unsaturated zone in Damascus Oasis, Syrian Arab Republic. In: *Isotope Based Assessment of Groundwater Renewal in Water Scarce Regions*, IAEA-TECHDOC-1246, 2001, 131–170, (IAEA) Vienna.
- ADAR, E.M., GEV, I., LIPP, J., YAKIR, D., GAT, J.R. & COHEN, Y.: Utilization of oxygen-18 and deuterium in stem flow for the identification of transpiration sources: soil water versus groundwater in sand dune terrain. *IAHS-Public.* 232, 1995, 329–339.
- ADAR, E.M., NEUMANN, S.P. & WOOLHISER, D.A.: Estimation of spatial recharge distribution using environmental isotopes and hydrochemical data. *J. Hydrol.* 97, 1988, 251–302.
- ADMUNDSON, R. & WANG, Y.: Relationship between the oxygen isotopic composition of soil CO<sub>2</sub> and water. In: *On Isotopes in Water Resources Management* Vol. 1, 1995, 315–332, (IAEA) Vienna.
- AEBY, P., FORRER, J., STEINMEIER, C. & FLÜHLER, H.: Image analysis for determination of dye tracer concentrations in sand columns. *Soil Sci. Soc. Am. J.* 61, 1997, 33–35.
- AIREY, P.L., CALF, G.E., HARTLEY, P.E., ROMAN, D. & SPRAGG, W.T.: Use of environmental isotopes and artificial tracers to study recharge to groundwater in the Burdekin Delta, Queensland. In: *Isotope Techniques in Groundwater Hydrology* Vol. I, 1974, 115–126, (IAEA) Vienna.
- ALBRECHT, F.: Die Methoden zur Bestimmung der Verdunstung der natürlichen Erdoberfläche. *Arch. Meteor., Geophys., Bioklim.* B2, 1951, 1–38.
- ALLEN, R.G., PEREIRA, L.S., RAES, D. & SMITH, M.: Crop evaporation. Guidelines for computing crop water requirements. FAO irrigation and drainage paper 56, 1998, 300 p.
- ALLISON, G.B.: The relationship between <sup>18</sup>O and <sup>2</sup>H in water sand columns undergoing evaporation. *J. Hydrol.* 55, 1982, 49–72.
- ALLISON, G.B.: A review of some of the physical, chemical and isotopic techniques available for estimating groundwater recharge. In: SIMMERS, I. (Ed.): *Estimation of natural groundwater recharge*, 1988, 49–72, (Reidel) Dordrecht, Boston.
- ALLISON, G.B. & BARNES, C.J.: Estimation of evaporation from non-vegetated surfaces using natural deuterium. *Nature* 301, 1983, 143.
- ALLISON, G.B., BARNES, C.J. & HUGES, M.W.: The distribution of deuterium and oxygen-18 in dry soil (II. Experimental). *J. Hydrol.* 64, 1983, 377–397.

- ALLISON, G.B., BARNES, D.J. & HUGHES, M.W.: Towards understanding of stable isotope profiles in field soils. In: *Recent Investigations in the Zone of Aeration*. Vol. 1, 1984, 293–301, (Dpt. Hydrogeology and Hydrochemistry of the University) Munich.
- ALLISON, G.B., BARNES, C.J., HUGHES, M.W. & LEANEY, F.W.J.: Effect of climate and vegetation on oxygen-18 and deuterium profiles in soils. *Isotope Hydrology*, 1984, 105–123, (IAEA) Vienna.
- ALLISON, G.B., COLIN-KACZALA, C., FILLY, A. & FONTES, J.-C.: Measurement of isotopic equilibrium between water, water vapor and soil CO<sub>2</sub> in arid zone soils. *J. Hydrol.* 95, 1987, 131–141.
- ALLISON, G.B., COOK, P.G., BARNETT, S.R., WALKER, G.R., JOLLY, I.D. & HUGHES, M.W.: Land clearance and river salinisation in the Western Murray basin, Australia. *J. Hydrol.* 119, 1990, 1–20.
- ALLISON, G., FONTES, J.-C. & SONNTAG, C.: Conclusions and recommendations on the usefulness of studies of the isotopes <sup>18</sup>O, <sup>2</sup>H and <sup>3</sup>H in water in the unsaturated zone. In: *On Stable and Radioactive Isotopes in the Study of the Unsaturated Soil Zone*, 1985, 179–183, (IAEA) Vienna.
- ALLISON, G.B., GEE, G.W. & TYLER, S.W.: Vadose-zone techniques for estimating groundwater recharge in arid and semi-arid regions. *Soil Sci. Soc. Am. J.* 58, 1994, 6–14.
- ALLISON, G.B. & HUGHES, M.W.: Environmental tritium in the unsaturated zone: Estimation of recharge to an unconfined aquifer. In: *Isotope Techniques in Groundwater Hydrology*, Vol. I, 1974, 57–72, (IAEA) Vienna.
- ALLISON, G.B. & HUGHES, M.W.: The use of environmental tritium to estimate recharge to a South-Australian aquifer. *J. Hydrol.* 26, 1975, 245–254.
- ALLISON, G.B. & HUGHES, M.W.: The use of environmental chloride and tritium to estimate total recharge to an unconfined aquifer. *Aust. J. Soil Res.* 16, 1978, 181–195.
- ALLISON, G.B. & HUGHES, M.W.: The use of natural tracers as indicators of soil water movement in a temperate semi-arid region. *J. Hydrol.* 60, 1983, 157–173.
- ALLISON, G.B. & PECK, A.J.: Hydraulic scaling theory in recharge estimation. In: SHARMA, M.L. (Ed.): *Groundwater Recharge*, 1989, 57–66, (Balkema) Rotterdam, Boston.
- ALLISON, G.B., STONE, W.J. & HUGHES, M.W.: Recharge in Karst and dune elements of a semi-arid landscape as indicated by natural isotopes and chloride. *J. Hydrol.* 76, 1985, 1–26.
- AL-SAGABY, I. & MOALLIM, M.: Use of isotopes to study groundwater recharge through sand dunes in A Qasim Area, Saudi Arabia. In: *Isotope Field Applications for Groundwater Studies in the Middle East*, 1996, 11–32, (IAEA) Vienna.
- AL-SAGABY, A. & MOALLIM, M.A. Isotope based assessment of groundwater renewal and related anthropogenic effects in water scarce regions: Sand dune study in Qasim area, Saudi Arabia. In: *Isotope Based Assessment of Groundwater Renewal in Water Scarce Regions*, IAEA-TECHDOC-1246, 2001, 221–230, (IAEA) Vienna.
- ALVARADO, J., SEILER, K.-P. & TRIMBORN, P.: Investigación hidro-geológica, isotópica e hidroquímica de la cuenca del Lago de Valencia, Venezuela. *On Isotopes in Water Resources Management*, Vol. 2, 1996, 281–299, (IAEA) Vienna.
- AMBACH, W., ELSÄSSER, M., MOSER, H., RAUERT, W., STICHLER, W. & TRIMBORN, P.: Variationen des Gehalts an Deuterium, Sauerstoff-18 und Tritium während einzelner Niederschläge. *Wetter und Leben* 27, 1975, 186–192.
- AMRO, H., KILANI, S., JAWAWDEH, J., ABD ELDIN, I. & RAYAN, M.: Isotope based assessment of groundwater recharge and pollution in water scarce areas: a case study in



- Jordan. In: *Isotope Based Assessment of Groundwater Renewal in Water Scarce Regions*, IAEA-TECHDOC-1246, 2001, 171–220, (IAEA) Vienna.
- ANDERSEN, L.J. & SEVEL, T.: Six years' environmental tritium profiles in the unsaturated and saturated zones, Grønhøj, Denmark. In: *Isotope Techniques in Groundwater Hydrology*, Vol. I, 1974, 3–20, (IAEA) Vienna.
- ANDRES, G. & EGGER, R.: A new tritium interface method for determining the recharge rate of deep groundwater in the Bavarian Molasse Basin. *J. Hydrol.* 82, 1985, 27–38.
- ANDREWS, J.E., BRIMBLECOMBE, P., JICKELLS, T.D. & LISS P.S.: *An Introduction to Environmental Chemistry*. 1966, (Blackwell Science Ltd) London.
- ARANYOSSY, J.F., FILLY, A., TANDIA, A.A., LOUVAT, D., OUSMANE, B., JOSEPH, A. & FONTES, J.-C.: Estimation des flux d'évaporation diffuse sous couvert sableux en climat hyper aride (erg de Bilma, Niger). Proc. of a symposium, 1991, 309–324, (IAEA) Vienna.
- ARNASON, B.: Ice and snow hydrology. In: *Stable Isotope Hydrology: Deuterium and Oxygen-18 in the Water Cycle*. Technical Report Series No. 210, 1981, 143–176, (IAEA) Vienna.
- ARRAGUAS-ARRAGUAS, L., ROZANSKI, K., GONFIANTINI, R. & LOUVAT, D.: Isotope effects accompanying vacuum extraction of soil water for stable isotope analyses. *J. Hydrol.* 168, 1995, 159–171.
- ATAKAN, Y., ROETER, W., MÜNNICH, K.-O. & MATTHESS, G.: The Sandhausen shallow-groundwater tritium experiment. In: *Isotope Techniques in Groundwater Hydrology*, Vol. I, 1974, 21–43, (IAEA) Vienna.
- ATHAVALE, R.N., MURTI, C.S. & CHAND, R.: Estimation of recharge to the phreatic aquifers of the lower Maner Basin, India, by using the tritium injection method. *J. Hydrol.* 45, 1980, 198–202.
- ATHAVALE, R.N. & RANGARAJAN, R.: Natural recharge measurements in the hard-rock regions of semi-arid India using tritium injection: a review. In: SIMMERS, I. (Ed.): *Estimation of Natural Groundwater Recharge*, 1988, 175–194, (Reidel) Dordrecht, Boston.
- BAHADUR, J., SAXENA, R.K. & MOOKERJEE, P.: Soil moisture movement and ground water recharge by tritium tracer tagging technique. *Proc. Indian Acad. Sci., Sect. A.*, 1977, 85.
- BAJSAROWICZ, J. & WELTON, J.: Surface water-groundwater conditions in the Senegal River basin near Matam, Senegal. In: *The Hydrology of Areas of Low Precipitation*, Proceedings of the Canberra Symposium, *IAHS Public.* 128, 1979, 235–248.
- BAKER, R.S. & HILLEL, D.: Observations of fingering behaviour during infiltration into layered soils. In: GISH, T.J., SHIRMOHAMMADI, A. (Eds.): *Preferential-Flow*. *Am. Soc. Agricult. Engineers*, 1991, 87–99.
- BAKER, D., KLOTZ, D. & SEILER, K.-P.: Dispersion and movement of water in the unsaturated zone of sands and gravels. In: *Stable and Radioactive Isotopes in the Study of the Unsaturated Soil Zone*, (IAEA)-TECDOC-357, 1985, 7–35, (IAEA) Vienna.
- BALDISON, R., SEILER, K.-P. & TRIMBORN, P.: Investigaciones isotópicas ambientales, químicas e hidrogeológicas en la cuenca del Lago Atitlán, Guatemala. Estudios de hidrología isotópica en America Latina, IAEA-TECDOC-835, 1995, 225–236, (IAEA) Vienna.
- BARNES, C.J. & ALLISON, G.B.: The distribution of deuterium and oxygen-18 in dry soils (1. Theory). *J. Hydrol.*, 60, 1983, 141–156.

- BARNES, C.J. & ALLISON, G.B.: The distribution of deuterium and oxygen-18 in dry soils, 3. Theory of Non-isothermal Water Movement. *J. Hydrol.* 74, 1984, 119–135.
- BARNES, C.J. & ALLISON, G.B.: Tracing of water movement in the unsaturated zone using stable isotopes of hydrogen and oxygen. *J. Hydrol.* 100, 1988, 143–176.
- BARNES, C.J., JACOBSON, G. & SMITH, C.D.: The distributed recharge mechanism in the Australian arid zone. *Soil Sci. Soc. Am. J.* 58, 1994, 31–40.
- BARNES, C.J. & WALKER, G.R.: The distribution of deuterium and oxygen-18 during unsteady evaporation from a dry soil. *J. Hydrol.* 112, 1989, 55–67.
- BARNETT, S.R.: The effect of land clearance in the Mallee region on River Murray salinity and land salinisation. *J. Aust. Geology. Geophys.* 1, 1989, 205–208.
- BARRETT, S.R., HISCOCK, K.M., PEDLEY, S., LERNER, D.N., TELLAM, J.H. & FRENCH, M.J.: Marker species for identifying urban groundwater recharge sources. The Nottingham case study. *Water Res.* 33, 1999, 3083–3097.
- BARRY, R.G.: Evaporation and transpiration. In: R.J. CHORLEY (Ed.): *Introduction to Physical Hydrology*, 1969, 82–98, (Methuen) London.
- BAUMGARTNER, A. & REICHEL, E.: *The World Water Balance*. 179 pp., 1975, (Elsevier) Amsterdam.
- BECHER, H.H.: Problems in estimating water and solute movement into, within and through soil with macropores. In: *Recent Investigations in the Zone of Aeration*. Vol. 1, 1984, 241–250, (Dpt. Hydrogeology and Hydrochemistry of the University) Munich.
- BEEKMAN, H.E., GIESKE, A. & SELAOLLO, E.T.: Groundwater recharge studies in Botswana 1987–1999. *Botswana J. of Earth Sciences* 3, 1996, 1–17.
- BEHRENS, H., SEILER, K.-P. & NEUMAIER, F.: Geländeversuche mit Fluoreszenz-Tracern zur Wasserbewegung im wasserungesättigten Lockergestein in den Tälern der Bayerischen Alpen. *Z.d.t. geol. Ges.* 131, 1980, 129–138.
- BELMANS, C., WESSELING, J.G. & FEDDES, R.A.: Simulation model of the water balance of a cropped soil: SWATRE. *J. Hydrol.* 63, 1983, 271–286.
- BENECKE, P.: Investigations into the behaviour of precipitation water in soils by means of <sup>131</sup>I. In: *Isotope and Radiation Techniques in Soil Physics and Irrigation Studies*, 1967, 227–239, (IAEA) Vienna.
- BENECKE, P. & GERKE, H.: Messung und Simulation des Wasserflusses in der ungesättigten Bodenzone. In: *Proc. Symp. on Recent Investigations in the Zone of Aeration*. Vol. 1, 1984, 167–179, (Dpt. Hydrogeology and Hydrochemistry of the University) Munich.
- BENECKE, P. & LORCH, S.: Untersuchung der Versickerung von Niederschlägen mittels <sup>131</sup>I in einer tonig-schluffigen, gedrähten Seemarsch. *Geol. Jb.* 81, 1964, 601.
- BENTLEY, H.W., PHILLIPS, F.M., DAVIS, S.N., GIFFORD, S., ELMORE, D., TUBBS, L. & GOVE, H.E.: The Thermonuclear <sup>36</sup>Cl Pulse in Natural Water. *Nature* 300, 1982, 737–740.
- BERG, W., CENCUR CURK, B., FANK J., FEICHTINGER, F., NÜTZMANN, G., PAPESCH, W., RAJNER, V., RANK, D., SCHNEIDER, S., SEILER, K.-P., STEINER, K.-H., STENITZER, E., STICHLER, W., TRHEK, B., VARGAY, Z., VESELIH, M. & ZOJER, H.: Tracers in the Unsaturated Zone. *Beiträge zur Hydrogeologie* 52, 2001, 7–102.
- BEVEN, K.: On subsurface storm flow: an analysis of response times. *Hydrol. Sci. J.* 4, 1982, 505–521.
- BEVEN, K. & GERMAN, P.: Macropores and water flow in soils. *Water Resources Res.* 18, 1982, 1311–1325.
- BEVEN, K., HENDERSON, D.E. & REEVES, A.D.: Dispersion parameters for undisturbed partially saturated soil. *J. Hydrol.* 143, 1993, 19–43.

- BEYERLE, U., PURTSCHERT, R., AESCHBACH-HERTIG, W., IMBODEN, D.M., LOOSLI, H.H., WIELER, R. & KIPFER, R.: Climate and groundwater recharge during the last glaciation in an ice-covered region. *Science* 282, 1998, 731–734.
- BIGGAR, J.W. & NIELSEN, D.R.: Spatial variability of the leaching characteristics of a field soil. *Water Resources Res.* 12, 1976, 78–84.
- BIGGAR, J.W., NIELSEN, D.R. & MACINTYRE, J.L.: Measurement of water and nitrogen fluxes in soil profiles planted with maize. In: Proc. Symp. on *Isotope Ratios as Pollutant Source and Behaviour Indicators*, 1975, 417–428, (IAEA) Vienna.
- BLASCH, K., FERRE, P.A., HOFFMAN, J., POOL, D., BAILEY, M. & CORDOVA, J.: Processes controlling recharge beneath ephemeral streams in southern Arizona. In: Hogan, J.F., Phillips, F.M. & Scanlon, B.R. (Eds.): *Groundwater Recharge in a Desert Environment: The Southwestern United States*, AGU series on Water Science and Applications 9, 2004, 69–76.
- BLASCHKE, A.P., DEAK, J., JAYAWARDENA, D., LIEBE, P., PAPESCH, W., RAJNER, V., RANK, D., RETTINGER, J., STEINER, K.-H. & VARGAY, Z.: Markierungsversuche und Modellrechnungen in der Lysimeterstation Kecksemet (1996–1999). *Forschungsbericht Inst. f. Hydraulik, Gewässerkunde und Wasserwirtschaft* 17, 2000, 89 p. Wien.
- BLEEKER, W., DANSGAARD, W. & LABLANS, W.N.: Some remarks on the simultaneous measurements of particulate contaminants including radioactivity and isotopic composition of precipitation. *Tellus* 18, 1966, 773–785.
- BLÖSCHL, G. & SIVAPALAN, M.: Scale issues in hydrological modeling: A review. *Hydrol. Processes* 9, 1995, 251–290.
- BLUME, H.P., MÜNNICH, K.O. & ZIMMERMANN, U.: Das Verhalten des Wassers in einer Löss-Parabraunerde unter Laubwald. *Z. Pflanzenernähr. Düng. Bodenk.* 112, 1966, 156.
- BLUME, H.P., ZIMMERMANN, U. & MÜNNICH, K.O.: Tritium tagging of soil moisture: The water balance of forest soils. In: *Isotope and Radiation Techniques in Soil Physics and Irrigation Studies*, 1967, 315–332, (IAEA) Vienna.
- BOLIN, B.: On the use of tritium as a tracer for water in nature. In: Proc. 2nd UN Conference on the Peaceful Uses of Atomic Energy, Geneva 18, 1958, 336–344.
- BOERS, T.: Rain water harvesting in arid and semiarid zones. PhD thesis, 1994, Agricultural University, Wageningen.
- BONFILS, P., CHARREAU, C. & MARA, M.: Etudes lysimétriques au Sénégal. *Bull Agron.* 19, 1963, 29–62.
- BOUVIER, C.: Concerning experimental measurements of infiltration for runoff modeling of urban watersheds in western Africa. *IAHS Public.* 198, 1990, 43–49.
- BOUWER, H.: Theory of percolation from open channels. In: CHOW, V.T. (Ed.): *Advances in Hydroscience*, (Academic Press) New York, 1969.
- BOUWER, H.: Artificial recharge of groundwater. Hydrology and engineering. *Hydrogeol. J.* 10, 2002, 121–142.
- BOWMAN, R.S.: Evaluation of some new tracers for soil water studies. *Soil. Sci. Soc. Am. J.* 48, 1984, 987–993.
- BREDEHOEFT, J.D. & PINDER, G.F.: Digital analysis of areal flow in multiaquifer groundwater systems: A quasi-three-dimensional model. *Water Resources Res.* 6, 1970, 883–888.

- BREDENKAMP, D.B., SCHUTTE, J.M. & DUTOIT, G.J.: Recharge of a dolomitic aquifer as determined from tritium profiles. In: *Isotope Techniques in Groundwater Hydrology*, Vol. I, 1974, 73–95, (IAEA) Vienna.
- BRICOUT, J., FONTES, J.-C., LETOLLE, R., MARIOTTI, A. & MERLIVAT, L.: Essai de caractérisation de certaines substances organiques et minérales par leur composition en isotopes stables. In: *Isotope Ratios as pollutant source and behaviour indicators*, 1975, 359–372, (IAEA) Vienna.
- BROADBENT, F.E.: Field measurements of n-utilization efficiency and nitrate movement in soils using  $^{15}\text{N}$ -depleted fertilizer. In: *Isotope Ratios as pollutant source and behaviour indicators*, 1975, 373–382, (IAEA) Vienna.
- BROZA, M.: Dew, fog and hygroscopic food as a source of water for desert arthropods. *J. Arid Environ.* 2, 1979, 43–49.
- BUNZL, K., BACHHUBER, H. & SCHIMMACK, W.: Distribution coefficients of  $^{137}\text{Cs}$ ,  $^{85}\text{Sr}$ ,  $^{141}\text{Ce}$ ,  $^{103}\text{Ru}$ ,  $^{131}\text{I}$  and  $^{95m}\text{Tc}$  in the various horizons of cultivated soils in Germany. In: *Recent Investigations in the Zone of Aeration*. Vol. 2, 1984, 567–577, (Dpt. Hydrogeology and Hydrochemistry, University) Munich.
- BUSENBERG, E. & PLUMMER, L.N.: Use of chlorofluorocarbon ( $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$ ) as hydrologic tracers and age dating tools: The alluvium and terrace system on Central Oklahoma. *Water Resources Res.* 28, 1992, 2257–2283.
- BUTLER, M.J. & VERHAGEN, B.Th.: Isotope studies of a thick unsaturated zone in a semi-arid area of southern Africa. In: *Isotope Based Assessment of Groundwater Renewal in Water Scarce Regions*, IAEA-TECHDOC-1246, 2001, 45–70, (IAEA) Vienna.
- BUTTERS, G.L. & JURY, W.A.: Field scale transport of bromide in an unsaturated soil. 2. Dispersion modeling. *Water Resources Res.* 25, 1989, 1583–1589.
- CABRERA, G. & IROUME, A.: A finite element model applied to stream-aquifer relations during floods. In: The Hydrology of areas of Low Precipitation, Proceedings of the Canberra Symposium, Dec. *IAHS Public.* 128, 1979, 267–278.
- CAMPBELL, G.S.: *Soil Physics with Basic Transport Models for Soil-Plant Systems*. 150 p., 1985, (Elsevier) New York.
- CARLIN, F., MAGRI, G., CERVELLATI, A. & GONFIANTINI, R.: Use of environmental isotopes to investigate the interconnections between the Reno River and groundwater (Northern Italy). In: *Isotope Ratios as Pollutant Source and Behaviour Indicators*, 1975, 179–194, (IAEA) Vienna.
- CARREIRA, P.M., MONGE SOARES, A.M., MARQUES DE SILVA, M.A., ARAGUAS-ARAGUAS, L. & ROZANSKI, K.: Application of environmental isotope methods in assessing groundwater dynamics of an intensely exploited coastal aquifer in Portugal. In: *Isotopes in Water Resources Management*, 1995, (IAEA) Vienna.
- CASSEL, D.K. & NIELSEN, D.R.: Field capacity and available water capacity. In: KLUTE, A. (Ed.): *Methods of Solid Analysis, Vol. 1, Physical and Mineralogical Methods*, 1986, 901–926.
- CHANDRASHEKHAR, H. & NAGANNA, C.: Evaluation of groundwater resources of the Chikkahagari basin, Karnataka, India. In: The Hydrology of areas of Low Precipitation, Proceedings of the Canberra Symposium, *IAHS Public.* 128, 1979, 279–286.
- CHARNEY, J., STONE, P.H. & QUIRK, W.J.: Drought in the Sahara, a bio-geophysical feedback mechanism. *Science* 187, 1975, 434–435.
- CHARREAU, C. & JACQUINOT, L.: Etude, au moyen de l'eau tritiée, de la circulation de l'eau dans un sol sableux du Sénégal. In: *Isotope and Radiation Techniques in Soil Physics and Irrigation Studies*, 1967, 301–314, (IAEA) Vienna.

- CHILTON, P.J., STUART, M.E. & DARLING, W.G.: Use of stable isotopes in the investigation of the effects of wastewater reuse on groundwater in Mexico. In: *Application of Isotope Techniques to Investigate Groundwater Pollution*, 1998, 209–225, (IAEA) Vienna.
- CHILTON, P.J., STUART, M.E., ESCOLERO, O., MARKS, R.J., GONZALEZ, A. & MILNE, C.J.: Groundwater recharge and pollutant transport beneath wastewater irrigation: the case of León, Mexico. In: ROBINS N.S. (Ed.): *Groundwater Pollution, Aquifer Recharge and Vulnerability*. Geological Society of London, Special Publication 130, 1998, 153–168.
- CHRIST, A. & HOFMANN, T.: Particle bound transport of contaminants in the unsaturated zone linked to recycled material. In: SEILER, K.-P. & WOHNLICH, S. (Eds.): *New Approaches Characterizing Groundwater Flow*, 2001, 31–35, (Balkema) Lisse, Abingden, Exten, Tokyo.
- CLARK, I. & FRITZ, P.: *Environmental Isotopes in Hydrogeology*. 1997 (CRC Press/Lewis Publishers) Boca Raton.
- CLARK, J.F., DAVISSON, M.L., HUDSON, G.B. & MacFARLANE, P.A.: Noble gasses, stable isotopes and radiocarbon as tracers of flow in the Dakota aquifer, Colorado and Kansas. *J. Hydrol.* 211, 1998, 151–167.
- CLASSEN, H. & HALM, D.R.: Estimates of evapo-transpiration or effective moisture in Rocky Mountains watersheds from chloride ion concentrations in stream base-flow. *Water Resources Res.* 32, 1996, 363–372.
- COATS, K. & SMITH, B.: Dead-end pore volume and dispersion in porous media. *Soc. Petr. Eng. J.* 4, 1964, 73–84.
- CONRAD, G., MARCE, A. & OLIVE, P.: Mise en évidence, par le tritium, de la recharge actuelle des nappes libres de la zone aride sharienne (Algérie). *J. Hydrol.* 27, 1975, 207–224.
- COOK, P.G., EDMUNDS, W.M. & GAYE, C.: Estimating palaeorecharge and palaeoclimate from unsaturated zone profiles. *Water Resources Res.* 28, 1992, 2721–2731.
- COOK, P.G., HATTON, T.J., PIDSLEY, D., HERCZEG, A.L., HELD, A., O'GRADY, A. & EAMUS, D.: Water balance of the tropical woodland ecosystem, northern Australia: A combination of micro-meteorological, soil physical and groundwater chemical approaches. *J. Hydrol.* 210, 1998, 161–177.
- COOK, P.G., JOLLY, I.D., LEANEY, F.W., WALKER, G.R., ALLAN, G.L., FIFIELD, L.K. & ALLISON, G.B.: Unsaturated zone tritium and chlorine 36 profiles from southern Australia: their use as tracers of soil water movement. *Water Resources Res.* 30, 1994, 1709–1719.
- COOK, P.G., SOLOMON, D.K. & PLUMMER, L.N.: Chlorofluorocarbons as tracers of groundwater transport processes in a shallow, silty aquifer. *Water Resources Res.* 31, 1995, 425–434.
- COOK, P.G. & WALKER, G.R.: Evaluation of the use of  $^3\text{H}$  and  $^{36}\text{Cl}$  to estimate groundwater recharge in arid and semi-arid environments. In: *Proc. Symp. on Isotopes in Water Resources Management*, 1995, 397–403, (IAEA) Vienna.
- COOK, P.G., WALKER, G.R. & JOLLY, I.D.: Spatial variability of groundwater recharge in semi-arid regions. *J. Hydrol.* 111, 1989, 195–212.
- COREY, J.C. & FENIMORE, J.W.: Tracing groundwater with chloride ions and tritium through acid kaolinitic soil. *Int. J. Appl. Radiat. Isotope* 19, 1968, 741.
- COREY, J.C. & HORTON, J.H.: Movement of water tagged with  $^3\text{H}$  and  $^{18}\text{O}$  through acidic kaolinitic soil. *Soil Sci. Soc. Am. Proc.* 32, 1968, 471.

- COREY, J.C., KIRKHAM, D. & NIELSEN, D.R.: The movement of chloride and nitrate through certain Iowa soils. *Iowa Acad. Sci. Proc.* 74, 1967, 130.
- COREY, J.C. & NIELSEN, D.R.: Some factors influencing the interpretation of soil-solute-water interactions. In: *Soil-Moisture and Irrigation Studies II*, 1973, 87–110, (IAEA) Vienna.
- CRAIG, H.: Isotopic variations in meteoric waters. *Science* 133, 1961, 1702–1708.
- CRAIG, H. & GORDON, L.I.: Deuterium and Oxygen-18 variations in the ocean and marine atmosphere. In: E. TONGIORGI (Ed.), *Stable Isotopes in Oceanographic Studies and Paleo-Temperatures*, Lab. Geolog. Nucl., Pisa, 1965, 9–130.
- CRESSWELL, R., WISCHUSEN, J., JOCOBSON, G. & FIFIELD, K.: Assessment of recharge to groundwater systems in the arid southwestern part of the Northern Territory, Australia, using chlorine-36. *Hydrogeol. J.* 7, 1999, 393–404.
- DACHLER, R.: *Grundwasserströmung*. 1933. (Springer) Vienna.
- DANIN, A., BAR-OR, Y., DOR, J. & YISRAELI, T.: The role of cyanobacteria in stabilisation of sand dunes in southern Israel. *Ecologia Mediterranea* 15, 1989, 55–64.
- DANSGAARD, W.: Stable isotopes in precipitation. *Tellus* 16, 1964, 436–438.
- DATTA, P.S., DEDAI, B.I. & GUPTA, S.K.: Comparative study of groundwater recharge rates in parts of Indo-Genetic and Sabarmati alluvial plains. *Mausam* 30, 1979, 29–33.
- DATTA, P.S., DEDAI, B.I. & GUPTA, S.K.: Hydro-geological investigations in Sabarmati basin. I. Groundwater recharge estimation using tritium tagging method. *Proc. Indian Natl. Sci. Acad.*, Part A, 46, 1980, 84–98.
- DATTA, P.S., GOEL, P.S., RAMA, P.A.S. & SENGAL, S.P.: Groundwater recharge in Western Uttar Pradesh. *Proc. Indian Acad. Sci.* 78 Ser A, 1973, 11–12.
- DATTA, P.S., GUPTA, S.K. & SHARMA, S.C.: A conceptual model of water transport through unsaturated soil zone. *Mausam*, 31, 1980, 9–18.
- DAVID, M.B. & VANCE, G.F.: Chemical character and origin of organic acids in streams and percolation lakes of central Maine. *Biogeochem.* 12, 1991, 17–41.
- DAVISSON, M.L. & CRISS, R.E.: Stable isotope and groundwater flow dynamics of agricultural irrigation recharge into groundwater resources of the Central Valley, California. *Symp. on Isotopes in Water Resources Management*, 1995, 405–418, (IAEA) Vienna.
- De SMEDT, F., WAUTERS, F. & SEVILLA, J.: Study of tracer movement through unsaturated sand. *J. Hydrol.* 85, 1986, 169–181.
- De SMEDT, F. & WIERENGA, P.J.: A generalised solution for solute flow in soils with mobile and immobile water. *Water Resources Res.* 15, 1979, 1137–1141.
- DEÁK, J.: Use of environmental isotopes to investigate the connection between surface and subsurface waters in the Nagykunság Region, Hungary. In: *Isotope Techniques in Groundwater Hydrology*, Vol. I, 1974, 157–167, (IAEA) Vienna.
- DEAK, J., FORIZS, I., DESEO, E. & HERTELENDI, E.: Origin of groundwater and dissolved ammonium in SE Hungary: Evaluation by environmental isotopes. Tracers in Hydrology ( Proc. of the Yokohama Symp.) *IAHS Public* 215, 1993, 117–124.
- DELCORE, M.R.: Detrminacion del promedio anual de la recarga a base de la profundidad del tritio termuclear en la zona saturada. *IAEA-TECDOC-502*, 1989, 451–456, Vienna.
- DELCORE, M.R. & LARSON, G.L.: Application of the tritium interface method for determining recharge rates to unconfined drift aquifers. II. Non-homogeneous case. *J. Hydrol.* 91, 1987, 73–81.
- DELWICHE, C.C. & STEYN, P.L.: Nitrogen isotope fractionation in soils and microbial reactions. *Environ. Sci. Technol.* 4, 1970, 920–935.

- DEMUTH, N. & HILTPOLD, A.: Fast-Flow. Eine Übersicht über den heutigen Wissensstand. *Z. Pflanzenern. Bodenk.* 156, 1993, 479–484.
- DETTINGER, M.D.: Reconnaissance estimates of natural recharge to desert basins in Nevada, USA, by using chloride balance calculations. *J. Hydrol.* 106, 1989, 55–78.
- DHARMASIRI, J.K. & DHARMAWARDENA, K.G.: Recharge measurements using tritium tracer at different sites in Sri Lanka. In: *Interam. Symp. on Isotope Hydrology*, 1980, 303–314, Bogota.
- DILLON, P.J.: Calibration and validation of a model of groundwater recharge from an ephemeral stream. In: SHARMA, M.L. (Ed.), *Groundwater Recharge*, 1989, 119–137, (Balkema) Rotterdam, Boston.
- DINCER, T.: Use of environmental isotopes in arid-zone hydrology. In: *Arid-zone Hydrology: Investigations with Isotope Techniques*, 1980, 23–30, (IAEA) Vienna.
- DINCER, T., AL-MUGRIN, A. & ZIMMERMANN, U.: Study of the infiltration and recharge through the sand dunes in arid zones with special reference to the stable isotopes and thermonuclear tritium. *J. Hydrol.* 23, 1974, 79–109.
- DINCER, T., NOORY, M., JAVED, A.R.K., NUTI, S. & TONGIORGIE, E.: Study of groundwater recharge and movement in shallow and deep aquifers in Saudi Arabia with stable isotopes and salinity data. In: *Isotope Techniques in Groundwater Hydrology*, 1974, 363–378, (IAEA) Vienna.
- DROST, W. & NEUMAIER, F.: Application of single borehole methods in groundwater research. *Proc. Isotope Techniques in Groundwater Hydrology*, 1974, 241–254, (IAEA) Vienna.
- DUFFY, Ch.J.: Semi-discrete dynamical model for mountain-front recharge and water balance estimation, Rio Grande of southern Colorado and New Mexico. In: HOGAN, J.F., PHILLIPS, F.M. & SCANLON, B.R. (Eds.): *Groundwater Recharge in a Desert Environment: the Southwestern United States*, AGU series on Water Science and Applications 9, 2004, 255–272.
- DYCK, S.: *Angewandte Hydrologie. Wasserhaushalt der Flussgebiete*. 2. edition, 1980, 544 p., (Ernst) Berlin, München.
- EASTOE, Ch.J., GU, A. & LONG, A.: The origin, ages and flow paths of groundwater in Tucson Basin: Results of a study of multiple isotope systems. In: HOGAN, J.F., PHILLIPS, F.M. & SCANLON, B.R. (Eds.): *Groundwater Recharge in a Desert Environment: The Southwestern United States*, AGU series on Water Science and Applications 9, 2004, 217–234.
- EDMUNDS, W.M.: Investigation of the unsaturated zone in semi-arid regions using isotopic and chemical methods and applications to water resource problems. In: *Isotope Based Assessment of Groundwater Renewal in Water Scarce Regions*, IAEA-TECHDOC-1246, 2001, 7–22, (IAEA) Vienna.
- EDMUNDS, W.M.: Mechanisms, timing and quantities of recharge to groundwater in semi-arid and tropical regions. In: *Isotope Techniques In Water Resource Investigations In Arid And Semi-Arid Regions*, 2001, 77–88, (IAEA) Vienna.
- EDMUNDS, W.M., DARLING, W.G. & KINNIBURGH, D.G.: Solute profile techniques for recharge estimation in semi-arid and arid terrain. In: I. SIMMERS (Ed.): *Estimation of Natural Groundwater Recharge*, 1988, 139–157, (Reidel) Dordrecht, Boston.
- EDMUNDS, W.M. & GAYE, C.B.: Estimating the spatial variability of groundwater recharge in the Sahel using chloride. *J. Hydrol.* 156, 1994, 47–59.

- EDMUNDS, W.M., GAYE, C.B. & FONTES, J.-C.: A record of climatic and environmental change contained in interstitial waters from the unsaturated zone of northern Senegal. In: *Isotope Techniques in Water Resources Development*, 1992, 533–549, (IAEA) Vienna.
- EDMUNDS, W.M. & VERHAGEN, B.Th.: Isotope based assessment of groundwater renewal: An international study of the unsaturated zone. In: SILILO, O. (Ed.): *Groundwater: Past Achievements and Future Challenges*, 2000, 487–492, (Balkema) Lisse, Abingden, Exten, Tokyo.
- EDMUNDS, W.M. & WALTON, N.R.G.: A geochemical and isotopic approach to recharge evaluation in semi-, arid zones past and present. In: *Application of Isotopic techniques in Arid Zone Hydrology*, 1980, 47–68, (IAEA) Vienna.
- EDMUNDS, W.M. & WRIGHT, E.P.: Groundwater recharge and paleoclimate in the Sirte and Kufra basins Libya. *J. Hydrol.* 40, 1979, 215–241.
- EDWARDS, A.P.: Isotope effects in Relation to the interpretation of  $^{15}\text{N}/^{14}\text{N}$  ratios in tracer studies. In: *On Isotope Ratios As Pollutant Source And Behaviour Indicators*, 1975, 455–468, (IAEA) Vienna.
- EGGER, R.: Das Grundwasser in der Oberen Suesswassermolasse im Raum München und Augsburg. PhD thesis, 1978, 110 p., Univ. Munich.
- EHHALT, D.: Deuterium and tritium content of hailstones: additional information on their growth. *Trans. Amer. Geophys. Union* 48, 1967, 106.
- EICHINGER, L., MERKEL, B., NEMETH, G., SALVAMOSER, J. & STICHLER, W.: Seepage velocity determinations in unsaturated quaternary gravel A comparison of various methods. In: *On Recent Investigations in the Zone of Aeration*, Vol. 1, 1984, 303–313, (Dpt. Hydrogeology and Hydrochemistry of the University) Munich.
- EICHINGER, L. & SCHULZ, H.D.: Bestimmung der Sickertrate in einem Sander Norddeutschlands durch Messungen der Umweltisotopen- und Chlorid-Konzentrationen des Sickerwassers. In: *On Recent Investigations in the Zone of Aeration*, Vol. 1, 1984, 155–165, (Dpt. Hydrogeology and Hydrochemistry of the University) Munich.
- EICHLER, R.: Über den Isotopengehalt des Wasserstoffs in Niederschlag, Boden und Grundwasser. PhD Thesis, 1964, Univ. of Heidelberg.
- EINSELE, G.: Eichung von Grundwasser-Ganglinien zur Bestimmung der Grundwasserneubildung und des Grundwasserabflusses. *Z. dt. geol. Ges.* 126, 1975, 293–315.
- EINSELE, G. & SCHULZ H.D.: Über den Grundwasserhaushalt im norddeutschen Flachland. Teil I: Grundwasserneubildung bewaldeter und waldfreier Sanderflächen Schleswig-Holsteins. *Bes. Mitt. dt. gewk. Jb.* 36, 1973, 1–72.
- EINSELE, G., SEILER, K.-P., BERTLEFF, B., LINDNER, W., PLUM, H., WEBER, E.: Erkundung tiefer Grundwasserzirkulationssysteme. *DVWK Schr.* 81, 1987, 223 p., (Parey) Hamburg, Berlin.
- ELLMER, F., HÜBNER, W. & SANETRA, C.M.: Conservation tillage on sandy soils in north-east Germany. Possibilities and limits. Proc. World Cong.ress on Conservation Agriculture, 2001, Vol. II, 77–81, Cordoba.
- ELLSWORTH, T.R. & JURY, W.A.: A three-dimensional field study of solute transport through unsaturated layered. porous media 2. Characterization of vertical dispersion. *Water Resources Res.* 27, 1991, 967–981.
- ENGELHARDT von., W.: Der Porenraum der Sedimente. 1960, 207 p, (Springer) Berlin.
- EPSTEIN, S.: Variations of the  $^{18}\text{O}/^{16}\text{O}$  ratios of freshwater and ice. In: National Acad. Science, Nuclear Science Series, Report 19, 1956, 20–28.
- ERIKSSON, E.: Composition of atmospheric precipitation. II. Sulphur, chloride, iodine compounds. *Tellus* 4, 1952, 280–303.



- ERIKSSON, E.: The distribution of salinity in groundwaters of the Delhi Region and recharge rates of groundwater. In: *Interpretation of Environmental Isotope and Hydrochemical Data in Groundwater Hydrology*, 1976, 171–177, (IAEA) Vienna.
- ERIKSSON, E. & KHUNAKASEM, V.: Chloride concentrations in groundwater, recharge rate and rate of deposition of chloride in the Israel coastal plain. *J. Hydrol.* 7, 1969, 178–197.
- EVENARI, M., SHANAN, L. & TADMOR, A.: *The Negev. The challenge of a desert*. 1971, 345 p. (Harvard University Press) Cambridge, Mass..
- FALKENMARK, M.: More crops or more ecological flow? In: Proc. on Water Security for cities, food and environment- towards Hydrosolidarity, 2001, Stockholm.
- FANK, J.: Die Bedeutung der ungesättigten Zone für Grundwasserneubildung und Nitratbefruchtung des Grundwassers in quartären Lockersediment-Aquiferen am Beispiel des Leibnitzer Feldes (Steiermark, Österreich). *Beiträge zur Hydrogeologie* 49/50, 1999, 101–388.
- FANK, J.: Tracer investigations at the research station “Wagna” (Leibnitzer Feld, Austria) to detect the role of the unsaturated zone for groundwater protection. In: SEILER, K.-P. & WOHNLIICH, S. (Eds.): *New Approaches Characterizing Groundwater Flow*, 2001, 55–58, (Balkema) Lisse, Abingden, Exten, Tokyo.
- FANK, J. & BERG, W.: Test site Leibnitz, Styria, Austria. *Beiträge zur Hydrogeologie* 52, 2001, 25–38.
- FANK, J. & HARUM, T.: Solute transport and water movement in the unsaturated zone of a gravel filled valley: tracer investigations under different cultivation types. In: SOVERI, J. & SUOKKO, T. (Eds.): *Future Groundwater Resources at Risk*, *IAHS Public.* 222, 1994, 341–354.
- FAO: Food insecurity: When people live with hunger and fear starvation. The state of food insecurity in the world. FAO rep., 2001, 64p., (FAO) Rome.
- FARRINGTON, P. & BARTLE, and G.A.: Water and chloride balance of bonsai woodland on coastal deep sands of South Western Australia. In: SHARMA, M.L. (Ed.): *Groundwater recharge*, 1989, 185–196, (Balkema) Rotterdam, Boston.
- FAYER, M.J. & GEE, G.W.: Predicted drainage at a semi-arid site: sensitivity to hydraulic description and vapor flow. In: Van GNUCHTEN, F.J., LEIJ, F.J. & LUND, L., J. (Eds.): *Indirect methods for estimating the hydraulic properties of unsaturated soils*, US Dept. of Agriculture, 1992, 609–620, Riverside, California.
- FEBRILLET, J., BUENO, E., SEILER, K.-P. & STICHLER, W.: Isotopic and hydro-geologic studies in the South- west of the Dominican Republic to recognize origin and occurrence of groundwater recharge. In: *Isotope Techniques in Water Resources Development*, 1988, 317–334; (IAEA) Vienna.
- FEDDES, R.A., KADAT, P., VAN BAKEL, P.J. T., BRONSWYK, J.J. B. & HALBERTZSMA, J.: Modeling Soil Water Dynamics in the Unsaturated Zone. State of the Art. *J. Hydrol.* 100, 1988, 69–111.
- FEDDES, R.A., KOWALIK, P.J. & ZARADNY, H.: *Simulation of Field Water Use and Crop Yield*. Simulation Monographs 1978, PUDOC, Wageningen.
- FLINT, A.L., FLINT, L.E., HEVESI, J.A. & BLAINEY, J.B.: Fundamental concepts of recharge in the Desert South-west: A regional modeling perspective. In: HOGAN, J.F., PHILLIPS, F.M. & SCANLON, B.R. (Eds.): *Groundwater Recharge in a Desert Environment: The Southwestern United States*, AGU series on Water Science and Applications 9, 2004, 159–184.

- FLURY, M., FLÜHLER, H. & LEUENBERGER, J.: Susceptibility of soils to preferential-flow of water: A field study. *Water Resources Res.* 30, 1994, 1945–1954.
- FONTES, J.-C., & EDMUNDS, W.M.: The use of environmental isotope techniques in arid zone hydrology. A critical review. *Technical Documents in hydrology*. UNESCO Paris, 1989.
- FONTES, J.-C. & GARNIER, J.M.: Determination of the initial  $^{14}\text{C}$  activity of the total dissolved inorganic carbon: A review of existing models and a new approach. *Water Resources Res.* 15, 1979, 399–413.
- FONTES, J.-C., GASSE, F. & ANDREWS, J.N.: Climatic conditions of Holocene ground-water recharge in the Sahel zone of Africa. In: *Proc. on Isotopic Techniques in the Study of Past and Current Environmental Changes in the Hydrosphere and the Atmosphere*, 1993, 231–248, (IAEA) Vienna.
- FONTES, J.-C. & GONFIANTINI, R.: Comportement isotopique au cours de l'évaporation de deux basin sahariens. *Earth and Planet. Sci.* 7, 1967, 325–329.
- FONTES, J.-C., YOUSFI, M. & ALLISON, G.B.: Estimation of long-term diffuse ground-water discharge in the northern Sahara using stable isotope profiles in soil water. *J. Hydrol.* 86, 1986, 315–327.
- FORIZS, I. & DEAK, J.: Origin of bank filtered groundwater resources covering the drinking water demand of Budapest, Hungary. In: *Application of Isotope Techniques to Investigate Groundwater Pollution*, 1998, 133–165, (IAEA) Vienna.
- FÖRSTEL, H.:  $^{18}\text{O}/^{16}\text{O}$  ratio as a tool to study water movement in soil. In: *Recent Investigations in the Zone of Aeration*, Vol. 1, 1984, 281–291, (Dpt. Hydrogeology and Hydrochemistry of the University) Munich.
- FOSTER, S.S.D., BATH, A.H., FARR, J.L. & LEWIS, W.J.: The likelihood of active ground-water recharge in the Botswana Kalahari. *J. Hydrol.* 55, 1982, 113–136.
- FOSTER, S.S.D. & SMITH-CARRINGTON, A.: The interpretation of tritium in the chalk unsaturated zone. *J. Hydrol.* 46, 1980, 343–364.
- FREEZE, R.A.: Groundwater analysis in surface and subsurface hydrology. In: *Groundwater and Man*, Aust. Water Res. Council Conf Series 8, 1983, 101–119, Sidney.
- FREEZE, R.A. & CHERRY, J.A.: *Groundwater*. 1979 (Prentice Hall) Englewood Cliffs, New Jersey.
- FREEZE, R.A. & WITHERSPOON, P.A.: Theoretical analysis of regional groundwater flow: 2. Effect of water table configuration and subsurface permeability variations. *Water Resources Res.* 3, 1967, 623–634.
- FREITAG, D.: *Huminstoffe in der Umwelt*. GSF-Ber. 25/97, 1997, 123 p., (GSF) Neuherberg.
- FRENCH, H.K., LANGSHOLT, E. & KITTEROD, N.O.: A multi-tracer study in the unsaturated zone of a heterogeneous formation. In: *Isotopes in Water Resources Management*, Vol. 1, 1995, 333–349, (IAEA) Vienna.
- FRIEDMAN, I., BENSON, C. & GLEASON, J.: Isotopic change during snow metamorphism, In: *Stable Isotope Geochemistry: A Tribute to Samuel Epstein*, The Geochemical Soc., Special publication No.3. 1991, 211–221.
- FRITZ, P.: The isotopic composition of sulphur compounds in recharge environments. In: *Recent Investigations in the Zone of Aeration*. Vol. 2, 1984, 499–508, (Dpt. Hydrogeology and Hydrochemistry of the University) München.
- FRITZ, P., CHERRY, J.A., WEYER, K.V. & SKLASH, M.G.: Storm runoff analysis using environmental isotopes and major ions. In: *Interpretation of Environmental Isotopes and Hydrochemical Data in Groundwater Hydrology*, 1976, 111–130, (IAEA) Vienna.

- FRÖHLICH, K., GEYH, M.A., VERHAGEN, B.T. & WIRTH, K.: *Isotope Hydrological Methods for the Quantitative Evaluation of Ground Water Resources in Arid and Semi-Arid Areas*. (Weltforum Verl.), München, Köln, London 1987.
- GARDNER, W.R.: Development of modern infiltration theory and application in hydrology. *Trans. Am. Soc. Agric. Engineers* 10, 1967, 379–381.
- GARDNER, W.R.: Field measurement of soil-water diffusivity. *Soil Sci. Soc. Am. J.* 34, 1970, 832.
- GARDNER, W.R. & WIDTSONE, J.A.: The movement of soil moisture. *Soil. Sci.* 11, 1921, 215–232.
- GAT, J.R.: The relationship between surface and subsurface waters: Water quality aspects in areas of low precipitation. *Hydrol. Sci. Bull.* 25, 1980, 257–267.
- GAT, J.R.: Role of the zone of aeration in the recharge and establishment of chemical character of desert groundwater. Proc. *On Recent Investigations in the Zone of Aeration Symp.*, Vol. 2, 1984, 487–498, (Dpt. Hydrogeology and Hydrochemistry of the University) München.
- GAT, J.R.: Variability (in time) of the isotopic composition of precipitation: consequences regarding the isotopic composition of hydrologic systems. In: *Isotope Techniques in Water Resources Development*, 1987, 551–564, (IAEA)Vienna.
- GAT, J.R.: Groundwater recharge under arid conditions. In: YU-SI FOK (Ed.): *Infiltration principles and practice*, ICIDA, 1988, 245–254.
- GAT, J.R.: The chemical structure of arid zone groundwaters: Role of the Aeolian transport, surface flow and of geochemical processes prior to recharge and following discharge. Proc. 6th Symp. Water Rock Interaction, 1989, 251.
- GAT, J.R.: Oxygen and Hydrogen isotopes in the hydrologic cycle. *Annu. Rev. Earth Planet. Sci.* 24, 1995, 225–262.
- GAT, J.R.: Modification of the isotopic composition of meteoric waters at the Land-Biosphere-Atmosphere Interface. In: *Isotope Techniques in the Study of Environmental Change*, 1998, 153–164, (IAEA) Vienna.
- GAT, J.R. & AIREY, P.L.: Stable water isotopes in the atmosphere/biosphere/lithosphere interface: scaling-up from the local to continental scale, under humid and dry conditions. *Global and Planetary Change* 51, 2006, 25–33.
- GAT, J.R. & BOWSER, C.: The heavy isotope enrichment of water in coupled evaporative systems. In: TAYLOR, H.P., O'NEIL, J.R. & KAPLAN, I.R. (Eds.): *Stable isotope Geochemistry. Geochem. Soc., Spec. Publ.* 3, 1991, 159–168.
- GAT, J.R. & CARMI, I.: Evolution of the isotopic composition of atmospheric waters in the Mediterranean Sea area. *J. Geophys. Res.* 76, 1970, 3039–3048.
- GAT, J.R. & DANSGAARD, W.: Stable isotope survey of the freshwater occurrences in Israel and the Jordan Rift Valley. *J. Hydrol.* 16, 1972, 177–211.
- GAT, J.R. & ISSAR, A.: Desert isotope hydrology: Water sources of the Sinai Desert. *Geochim. Cosmochim. Acta* 38, 1974, 1117–1131.
- GAT, J.R. & LEVY, Y.: Isotope hydrology of inland sabkhas in the Bardawil area, Sinai. *Limnology and Oceanography* 23, 1978, 841–850.
- GAT, J.R. & MATSUI, E.: Atmospheric water balance in the Amazon basin: an isotopic evapo-transpiration model. *J. Geophys. Res.* 96, 1991, 13179–13188.
- GAT, J.R., NAOR, H.: The relationship between salinity and the recharge/discharge mechanism in arid low lands. In: *The Hydrology of Areas of Low Precipitation, IAHS Publ.* 128, 1979, 307–312.

- GAT, J.R. & TZUR, Y.: Modification of the isotopic composition of rainwater by processes which occur before groundwater recharge. In: *Proc. Symp. on Isotopes in Hydrology*, 1967, 49–60, (IAEA) Vienna.
- GAYE, C.B. & EDMUNDS, W.M.: Groundwater recharge estimation using chloride, stable isotopes and tritium profiles in the sands of northwestern Senegal. *Environ. Geology* 27, 1996, 246–251.
- GEDZELMAN, S.D., ROSENBAUM, J.H. & LAWRENCE, J.R.: The snowstorm of 11–12 February 1983: isotopic composition of the snow. *J. Atmosph. Sci.* 46, 1989, 1637–1649.
- GEE, G.W. & HILLEL, D.: Groundwater recharge in arid regions: review and critique of estimation methods. *J. Hydrol. Process.* 2, 1988, 255–266.
- GEHRELS, J.C., PEETERS, J.E.M., De VRIES, J.J. & DEKKERS, M.: The mechanism of soil water movement as inferred from  $^{18}\text{O}$  stable isotope studies. *Hydrol. Sci. J.* 43, 1998, 579–594.
- GEIGER, W.F.: Principles for Sustainable Water Management in Urban Areas. In: XI, R.-Z., GU, W.-Z. & SEILER, K.-P. (Eds.): *Research Basins and Hydrological Planning*. 2004, 155–163, (Balkema) Leiden, London, New York, Philadelphia, Singapore.
- GELHAR, L.W., GROSS, G.W. & DUFFY, C.J.: Stochastic methods of analyzing groundwater recharge. In: *The Hydrology of Areas of Low Precipitation*, Proc. of the Canberra Symp., IAHS Public. 128, 1979, 313–322.
- GENUCHTEN van, M.Th.: A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. *Soil Sci. Soc. Am. J.* 44, 1980, 892–898.
- GENUCHTEN van, M.Th.: New Issues and Challenges in Soil Physics Research. Trans. 15th World Congress of Soil Science, Vol. 1, 1994, 5–27, Acapulco, Mexico.
- GEORGII, H.W., ROHBOCK, E. & SCHMITT, G.: Untersuchung des atmosphärischen Schadstoffeintrags in Waldgebieten in der BRD. Umweltforschungsplan des BMI, 1984, 108 p., Berlin.
- GERKE, H.H. & van GENUCHTEN, M.Th.: A dual-porosity model for simulating the preferential movement of water and solutes in structured porous media. *Water Resources Res.* 29, 1993, 305–319.
- GERMAN, P.F.: Preferential-flow and the generation of runoff. 1. Boundary layer flow theory. *Water Resources Res.* 26, 1990, 3055–3063.
- GEYH, M.A., GU, W.-Z. & JACKEL, D.: Groundwater recharge study in the Gobi Desert, China. *Geowissenschaften* 718, 1996, 279–280.
- GHASSEMI, F., JACKEMAN, A.J. & THOMAS, G.A.: Estimation of vertical recharge via mathematical models of groundwater flow. In: SHARMA, M.L. (Ed.): *Groundwater recharge*, 1989, 139–154, (Balkema) Rotterdam, Boston.
- GHERGUT J., MALOSZEWSKI P. & SEILER K.-P.: Age, environmental isotope and contaminants transport uncoupling in heterogeneous aquifers following hydraulic stress. In: SEILER, K-P & WOHNLICH, S. (Eds.): *New Approaches Characterizing Groundwater Flow*, 2001, 327–334, (Balkema) Lisse, Abingdon, Exton (PA), Tokyo.
- GILAT, J. & GAT, J.R.: Sr-90 in rain and soils of Israel. Israel Atomic Energy Report 572, 1960.
- GIESKE, A., SELALO, E. & MCMULLAN, S: Groundwater recharge through the unsaturated zone of southeastern Botswana: a study of chloride and environmental isotopes. Regionalisation in Hydrology. *IAHS Public.*, 1990, 33–43.
- GIRARD, P., HILLAIRE-MARCEL, C. & OGA, M.S.: Determining the recharge of Sahelian aquifers using water isotopes. *J. Hydrol.* 197, 1997, 189–202.

- GLASS, R.J., OOSTING, G.H. & STEENHUIS, T.S.: Preferential solute transport in layered homogeneous sands as a consequence of wetting front instability. *J. Hydrol.* 110, 1989, 87–105.
- GLASS, R.J., STENHUIS, T.S. & PARLANGE, J.-Y.: Mechanism for finger persistence in homogeneous, unsaturated porous media: Theory and verification. *Soil. Sci.* 148, 1989, 60–70.
- GLENNON, R.: *Water follies. Groundwater pumping and the fate of America's fresh-waters.* 314 p., 2002, (Island Press) Washington, Covelo, London.
- GOEL, P.S., DATTA, P.S. & TANWAR, B.S.: Measurements of vertical recharge to groundwater in Haryana State (India) using tritium tracer. *Nord. Hydrol.* 8, 1077, 211.
- GOLDSCHMIDT, M.J. & JACOBS, M.: Precipitation over and replenishment of the Yarkon and Nahal-Tanimim Underground Catchments. Hydrological Paper 3, 1958, (Hydrological Service) Jerusalem.
- GONFIANTINI, R., CONRAD, G., FONTES, J.-C., SAUZAY, G. & PAYNE, P.R.: Etude isotopique de la nappe du Continental Intercalaire et ses relations avec les autres nappes du Sahara septentrional. In: *Isotope Techniques in Groundwater Hydrology*, Vol 1, 1974, 227–241, (IAEA) Vienna.
- GONI, I.B. & EDMUNDS, W.M.: The use of unsaturated zone solute and isotope profiles in the study of groundwater recharge in the semi-arid zone of Nigeria. In: *Isotope Based Assessment of Groundwater Renewal in Water Scarce Regions*, IAEA-TECHDOC-1246, 2001, 85–100, (IAEA) Vienna.
- GOODRICH, D.C., WILLIAMS, D.G., UNKRICH, C.L., HOGAN, J.F., SCOTT, R.L., HULTINE, K.R., POOL, D., COES, A.L. & MILLER, S.: Comparison of methods to estimate ephemeral channel recharge, Walnut Gulch, San Pedro River Basin, Arizona. In: HOGAN, J.F., PHILLIPS, F.M. & SCANLON, B.R. (Eds.): *Groundwater Recharge in a Desert Environment: the Southwestern United States*, AGU series on Water Science and Applications 9, 2004, 77–100.
- GOTTFREUND, E., GOTTFREUND J. & SCHWEISFURTH, R.: Mikrobiologie und Chemie in der ungesättigten und gesättigten Zone. In: *On Recent Investigations in the Zone of Aeration*, Vol. 2, 1984, 427–436, (Dpt. Hydrogeology and Hydrochemistry of the University) Munich.
- GRASSO, D.A., JEANNIN, P.Y. & ZWALEN, F.: A deterministic approach to the coupled analysis of krast spring hydrographs and chemographs. *J. Hydrol.* 271, 2003, 65–76.
- GREENFELT, P. & HULTBERG, H.: Effects of nitrogen deposition on the acidification of terrestrial and aquatic ecosystems. Manusc. Int. Symp. on Acid Precipitation, Muskoka, 15.-20.10.1985.
- GRUNOW, J.: Die Niederschlagszurückhaltung am Hohenpeißenberg und ihre messtechnische Erfassung. *Forstw. Centralbl.* 84, 1965, 212–229.
- GUENDOZ, A., MOULLA, A.S., EDMUNDS, W.M., ZOUARI, K., SHAND, P. & MAMOU, A.: Hydrochemical and isotopic evolution of water in the Complex Terminal aquifer in the Algerian Sahara. *Hydrogeol. J.* 11, 2003, 483–495.
- GUPTA, S.K. & SHARMA, P.: Soil moisture transport through the unsaturated zone: Tritium tagging studies, in Sabarmati Basin, Western India. *Hydrol. Sci. J.* 22, 1984, 177–189.
- GVIRTZMANN, H. & MAGARITZ, M.: Investigation of water movement in the unsaturated zone under an irrigated area using environmental tritium. *Water Resources Res.* 22, 1986, 635–642.
- GVIRTZMAN, H. & MAGARITZ, M.: Water and anion transport of the unsaturated zone traced by environmental tritium. In: BAR-YOSEF, BARROW & GOLDSCHMIDT (Eds.): *Inorganic Contaminants of the Vadose Zone, Ecological Studies* 74, 1990, 190–198.

- HARLAN, R.L.: Dynamics of water movement in permafrost: A review. Proc. Workshop Seminar, Permafrost Hydrology, Can. Nat. Comm. Int. Hydrol., 1974, 69–77.
- HASKELL, C.C. & HAWKINS, R.H.: D<sub>2</sub>O-<sup>24</sup>Na method for tracing soil moisture movement in the field. *Soil Sci. Soc. Am. J.* 28, 1964, 725.
- HAUCK, R.D.: Nitrogen tracers in nitrogen cycle studies, past use and future needs. *J. Environ. Quality* 2, 1973, 317–327.
- HAUCK, R.D., BATHOLOMEW, W.V., BREMNER, J.M., BROADBENT, F.E., CHENG, H.H., EDWARDS, A.P., KEENEY, D.R., LEGG, J.O., OLSEN, S.R. & PASTOF, L.K.: Use of variations in natural nitrogen isotope abundance for environmental studies: a questionable approach. *Science* 177, 1972, 453–454.
- HAUDE, W.: Zur praktischen Bestimmung der aktuellen und potentiellen Evaporation und Evapo-transpiration. *Mitt. dt. Wetterd.* 2, 1954, 3–22.
- HAUDE, W.: Zur Bestimmung der Verdunstung auf möglichst einfache Weise. *Mitt. dt. Wetterd.* 8, 1955, 11–24.
- HAUDE, W.: Die Verteilung der potentiellen Verdunstung in Ägypten. *Erdkunde* 13, 1959, 214–224.
- HEALY, R.W. & COOK, P.G.: Using groundwater levels to estimate recharge. *Hydrogeol. J.* 10, 2002, 91–109.
- HEILWEIL, V.M. & SOLOMON, D.K.: Millimeter to kilometer-scale variations in vadose-zone bedrock solutes: Implications for estimating recharge in arid settings. In: HOGAN, J.F., PHILLIPS, F.M. & SCANLON, B.R. (Eds.): *Groundwater Recharge in a Desert Environment: The Southwestern United States*, AGU series on Water Science and Applications 9, 2004, 49–68.
- HENDERSHOT, W.H., SAVOIE, S. & COURCHESNE, F.: Simulation of stream water chemistry with soil solution and groundwater flow contribution. *J. Hydrol.* 136, 1992, 237–252.
- HERCZEG, A.L., LEANEY, F.W.J., STADTER, M.F., ALLAN, G.L. & FIFIELD, L.K.: Chemical and isotope indicators of point-source recharge to a karst aquifer, South Australia. *J. Hydrol.* 192, 1997, 271–299.
- HERRMANN, A., KOLL, J., LEIBUNDGUT, Ch., MALOSZEWSKI, P., RAU, R., RAUERT, W. & STICHLER, W.: Anwendung von Tracertechniken zur Erfassung des Wasserumsatzes in kleinen Einzugsgebieten. *Dt. gewässerkdl. Mitt* 28, 1984, 65–74.
- HERRMANN, A., MALOSZEWSKI, P. & STICHLER, R.: Changes of <sup>18</sup>O contents of precipitation water during percolation in the unsaturated zone. In: *Groundwater Monitoring and Management* 6, 1987, Dresden.
- HERRMANN, A. & STICHLER, W.: Groundwater-run off relationship. *Catena* 7, 1980, 251–263.
- HESTERBERG, R. & SIEGENTHALER, U.: Production and stable isotopic composition of CO<sub>2</sub> in soil near Bern, Switzerland. *Tellus* 43B, 1991, 197–205.
- HILLEL, D.: *Soil and Water*. 1971 (Academic Press) New York, London.
- HILLEL, D.: *Fundamentals of Soil Physics*. 1980 (Academic Press) New York.
- HOLOCHER, J., PETERS, F., AESCHBACH-HERTIG, W., HOFER, M., BRENNWALD, M., KINZELBACH, W. & KIPFER, R.: Experimental investigation on the formation of excess air in quasi-saturated porous media. *Geochim. Cosmochim. Acta* 66, 2002, 4103–4117.
- HORNVEDT, R., DOLLARD, G.J. & LORAMGER: Atmosphere vegetation interactions. In: DRABLOS, D. & TOLLAN, A. (Eds.): *Ecological Impact of Acid Precipitation*, 1980, 192–194, Oslo.

- HORTON, R.E.: Accuracy of areal rainfall estimates. *Monthly Weather Rev.* 51, 1923, 348–353.
- HORTON, R.E.: The role of infiltration in the hydrologic cycle. *Am. Geophys. Union Trans.* 14, 1933, 446–460.
- HUBERT, M.: Etude hydrologique en vue de l'alimentation en eau des villes de Dakar et Rufisque. Etude, Histoire et Sciences, *IFAN*, 1922, 61–218.
- HUSSAIN, M.F.: Water flow and solute transport using environmental isotopes and modeling. In: *Isotope Based Assessment of Groundwater Renewal in Water Scarce Regions*, IAEA-TECHDOC-1246, 2001, 231–271, (IAEA) Vienna.
- IAEA: *Neutron Moisture gauges. A Guide Book on Theory and Practice*. Technical report series 112, 1970, (IAEA) Vienna.
- IAEA: *Statistical Treatment of Data on Environmental Isotopes in Precipitation*. Technical Report Series 331, 1992, (IAEA) Vienna.
- INGRAHAM, N.L. & MATTHEWS, R.A.: Fog drip as a source of groundwater recharge in Northern Kenya. *Water Resources Res.* 24, 1988, 1406–1410.
- INGRAHAM, N.L. & SHACHEL, C.: A comparison of the toluene distillation and vacuum/heat methods for extraction soil water for stable isotope analysis. *J. Hydrol.* 140, 1992, 371–387.
- IPCC: Intergovernmental Panel on Climate Change. In: HOUGHTON J. & YIHUI, D. (Eds.): *The Scientific Basis, Report Working Group I to IPCC Third Assessment Report (TAR)*, (Cambridge University Press) 2001.
- ISAACSON, R.E., BROWNELL, L.E., NELSON, R.W. & ROETMAN, E.L.: Soil-moisture transport in arid site vadose zones. In: *Isotope Techniques in Groundwater Hydrology*, Vol. I, 1974, 97–114, (IAEA) Vienna.
- ISSAR, A.S., GAT, J.R., KARNIELI, A., NATIV, R. & MAZOR, E.: Groundwater formation under desert conditions. In: *Stable and Radioactive Isotopes in the Study of the Unsaturated Zone*, IAEA-TECDOC-357, 1984, 35–54, (IAEA) Vienna.
- ISSAR, A.S., NATIV, R., KARNIELI, A. & GAT, J.R.: Isotopic evidence of the origin of groundwater in arid zones. In: *Isotope Hydrology*, 1983, 85–104, (IAEA) Vienna.
- IVANKO, S. (1972): Recent progress in the use of <sup>15</sup>N in research on nitrogen balance studies in soil-plant relationship. In: *Isotopes and Radiation in Soil-Plant Relationships Including Forestry*, 1984, 483–497, (IAEA) Vienna.
- IZBICKI, J.A.: Geologic and hydrologic controls on the movement of water through a thick, heterogeneous unsaturated zone underlying an intermittent stream in the western Mojave Desert, southern California. *Water Resources Res.* 38, 2002, 1–14.
- JARDIN, P.M., WILSON, G.U., MCCARTHY, J.F., LUXMOORE, R.J., TAYLOR, D.L. & ZELANY, L.W.: Hydrogeochemical processes controlling the transport of dissolved organic carbon through a forested hillslope. *J. Contam. Hydrol.* 10, 3–19.
- JIRIES, A.: Chemical composition of dew in Amman, Jordan. *Atm. Res.* 57, 2001, 261–268.
- JOB BAGY, E.G. & JACKSON, R.B.: Groundwater use and salinization with grassland afforestation. *Global Change Biology* 10, 2004, 1299–1312.
- JOLLY, I.D., COOK, P.G., ALLISON, G.B. & HUGHES, M.W.: Simultaneous water and solute movement through an unsaturated soil following an increase in recharge. *J. Hydrol.* 111, 1989, 391–396.
- JØRGENSEN, P.R., MCKAY, L.D. & SPLIID, N.H.: Evaluation of chloride and pesticide transport in a fractured clayey till using large undisturbed columns and numerical modeling. *Water Resources Res.* 34, 1998, 539–553.

- JOUZEL, J. & MERLIVAT, L.: Deuterium and oxygen-18 in precipitation: Modeling of the isotopic effects during snow formation. *J. Geophys. Res.* 89, 1984, 11749–11757.
- JUNGE, Ch.: *Air Chemistry and Radioactivity*. International Geophysics series 4, 1963, 382p, (Academic Press) New York.
- JUREN, A., PREGL, M. & VESELIH, M.: Project of an urban hypsometer at the Union brewery, Ljubljana, Slovenia. *RMZ-Materials and Geoenvironment* 50/3, 2003, 153–156.
- KAPPELMEYER, O.: Geothermie. In: BENTZ, A. (Ed.): *Lehrbuch der Angewandten Geologie*, 1961, 863–880, (Enke) Stuttgart.
- KÄSS, W.: *Tracing Technique in Geohydrology*. 581 p., (Balkema) Rotterdam/Brookfield, 1998.
- KAUFMANN, W.J. & TODD, D.K.: Application of tritium tracer to canal percolation measurements. In: *Tritium in the Biological and Physical Sciences*, 1962, 84, (IAEA) Vienna.
- KEELING, C.D., PIPER, S.C. & HEIMANN, M.: A three-dimensional model of atmospheric CO<sub>2</sub> transport based on observed winds. 4. Mean annual gradients and interannual variations. *Geophys. Monograph* 55, 1989, 305–363.
- KEELING, C.D., WHORF, T.P., WHALEN, M. & van der PLICHT, J.: Interannual extremes in the rate of rise of atmospheric carbon dioxide since 1980. *Nature* 375, 1995, 666–670.
- KENDALL, C.: Impact of isotopic heterogeneity in shallow systems on modeling of stormflow generation. PhD. Thesis, Dept. of Geology, University of Maryland, 1993, 270 p.
- KENDALL, C. & GU, W.-Z.: Development of isotopically heterogeneous infiltration waters in an artificial catchment in Chuzhou, China. In: *Isotope Techniques in Water Resources Development* 1991, 61–73, (IAEA) Vienna.
- KENDALL, C. & McDONNELL, J.J.: *Isotope Tracers in Catchment Hydrology*. (Elsevier) Amsterdam/Lausanne/New York/Oxford/Singapore/Tokyo, 1998.
- KENNEDY, V.C.: Silica variation in stream water with time and discharge. In: HEM, J.D. (Ed.): *Nonequilibrium Systems in Natural Water Chemistry. Adv. in Chem. Sci.* 106, 1971, 106–130, Washington.
- KENNETH-SMITH, A., COOK, P.G. & WALKER, G.R.: Factors affecting groundwater recharge following clearing in the south western Murray Basin. *J. Hydrol.* 154, 1994, 85–105.
- KINNIBURG, D.G. & MILES, D.L.: Extraction and chemical analysis of interstitial water from soils and rocks. *Environ. Sci. Technol.* 17, 1983, 362–368.
- KIRSCHENBAUM, I.: *Physical Properties and Analysis of Heavy Water*. 1951 (McGraw-Hill) New York.
- KLEEBERG, H.-B. & OVERLAND, H.: Zur Berechnung des effektiven oder abflusswirksamen Niederschlags. *Mitt. Inst. Wasserwesen* 32, 1989, 19–62, (Univ. Bundeswehr) München.
- KLOTZ, D., DICKOPF, B. & SCHEUNERT, I.: Laborversuche zum Ausbreitungs- und Abbauverhalten ausgewählter Pestizide im unterirdischen Wasser. *GSF-Ber.* 29/95, 1995, 16–33, (GSF) Neuherberg.
- KLUITENBERG, G.J. & HORTON, R.: Effect of solute application method on preferential-flow transport of solutes in soil. *Geoderma* 46, 1990, 283–297.
- KNOTT, J.F. & OLIMPIO, J.C.: Estimation of Recharge Rates to the Sand and Gravel Aquifer Using Environmental Tritium, Nantucket Island, Massachusetts. USGS Water-Supply Paper 1986, 2297, Reston.
- KOHL, D.H., SHEARER, G.B. & COMMONER, B.: Fertilizer nitrogen: Contribution to nitrate in surface water in a corn beer watershed. *Science* 174, 1971, 131–1334.



- KOMOR, S.C. & EMERSON, D.E.: Movements of water, solutes and stable isotopes in the unsaturated zones of two sand plains in the upper Midwest *Water Resources Res.* 30, 1994, 253–267.
- KÖPPEN, W.: *Grundriss der Klimakunde*. 388p. 1931, (Walter de Gruyter) Berlin Leipzig.
- KÖRNER, J.: Abflußbildung, Inter-flow und Stoffbilanz im Schönbuch Waldgebiet. *Tüb. Geowiss. Arbeiten C* 27, 1996, 206 p.
- KOTLYAKOV, V.M.: *World Atlas of Snow and Ice Resources*. Russian Academy of Sciences, Institute of Geography, Vol. I (Atlas), Vol. II (Textbook, 273 p.), 1997, Moscow.
- KRABBENHOFT, D.T., BOWSER, C.J., ANDERSON, M.P. & VALLEY, J.W.: Estimating groundwater exchange with lakes. 1. The stable isotope mass balance method. *Water Resources Res.* 26, 1990, 2445–2453.
- KRAMER, J.H., CULLEN, S.J. & EVERETT, L.G.: Vadose zone monitoring with the neutron moisture probe. *Groundw. Monit. Review* 13, 1992, 177.
- KU, H.F.H., HAGELIN, N.W. & BUXTON, H.T.: Effects of urban storm runoff control on groundwater recharge in Nassau County, New York. *Groundwater* 30, 1992, 507–514.
- KUMAR, B., PATIL, D.J. & MATHUR, R.: Deuterium and chloride content of soil moisture, ground and surface waters from Marvanka Basin, Anantapur, India. In: *Stable and Radioactive Isotopes in the Study of the Unsaturated Soil Zone*, (IAEA)-TECDOC-357, 1985, 71–89, (IAEA) Vienna.
- KUNG, K.-J.S.: Preferential-flow in sandy vadose zone. 1. Field observations. *Geoderma* 46, 1990a, 51–58.
- KUNG, K.-J.S.: Preferential-flow in sandy vadose zone. 2. Mechanisms and Implications. *Geoderma* 46, 1990b, 59–71.
- KUNG, K.-J.S.: Influence of plant uptake on the performance of bromide tracer. *Soil Sci. Soc. Am. J.* 54, 1990, 975–979.
- LABAUGH, J.W., WINTER, T.C., ROSENBERRY, D.O., SCHUSTER, P.F., REDDY, M.M. & AIKEN, G.R.: Hydrological and chemical estimates of the water balance of a closed-basin lake in north central Minnesota. *Water Resources Res.* 33, 1997, 2799–2812.
- LACROIX, M. & MOSORA, F.: Biological effects of deuterium and other stable isotopes. In: *Isotope Ratios as Pollutant Source and Behaviour Indicators*, 1975, 383–387, (IAEA) Vienna.
- LANGE, J., LEIBUNDGUT, C., GRODEK, T., LEKACH, J. & SCHICK, A.P.: Using artificial tracers to study water losses of ephemeral floods in small arid streams. *IAHS Public.* 247, 1997, 31–40.
- LANGE, O.L., KIDRON, G., BÜDEL, B., MEYER, A., KILIAN, E. & ABELOVICH, A.: Taxonomic composition and photosynthetic characteristics of the biological crusts covering sand dunes in the western Negev desert. *Funct. Ecology* 6, 1992, 519–527.
- LARSON, G.L., DELCORE, M.R. & OFFER, S.: Application of the tritium interface method for determining recharge rates to unconfined drift aquifers. I. Homogeneous case. *J. Hydrol.* 91, 1987, 59–72.
- LEANEY, F.W. & ALLISON, G.B.: Carbon-14 and stable isotope data for an area in the Murray Basin: Its use in estimating recharge. *J. Hydrol.* 88, 1986, 129–145.
- LEANEY, F.W. & HERCZEG A.L.: Regional recharge to a karst aquifer estimated from chemical and isotope composition of diffuse and localised recharge. *J. Hydrol.* 164, 1995, 363–387.
- LEANEY, F., WALKER, G., KNIGHT, J., DAWES, W. BRADFORD, A., BARNETT, S. & STADTER, F.: Potential for Groundwater Salinisation in the Tintinara area of South Australia. CSIRO Land and Water Technical Report 33/99, 1999.

- LEDUC, C., FAVREAU, G. & SCHROETER, P.: Long-term rise in a Sahelian water-table: the continental terminal in south-west Niger. *J. Hydrol.* 243, 2001, 43–54.
- LEE DAVISSON, M. & CRISS, R.E.: Stable isotope and groundwater flow dynamics of agricultural irrigation recharge into groundwater resources of the central valley, California. In: *Isotopes in Water Resources Management*, Vol. 1, 1995, 404–418, (IAEA) Vienna.
- LEGUY, C., RINDSBERGER, M., ZANGWIL, A., ISSAR, A. & GAT, J.R.: The relation between the oxygen-18 and deuterium contents of rainwater in the Negev Desert and air mass trajectories. *Isotope Geosciences* 1, 1983, 205–218.
- LELIJ van der, A.: Groundwater accession in the Coleambally irrigation area of N.S.W. In: SHARMA, M.L. (Ed.): *Groundwater Recharge*, 1989, 281–290, (Balkema) Rotterdam, Boston.
- LEOPOLDO, P.R., FRANKEN, W., MATSUI, E. & SALATI, E.: Estimation of water transit time in soils under Amazon forest cover using variations in  $\delta^{18}\text{O}$  values. In: *Isotope Hydrology*, 1984, 125–137, (IAEA) Vienna.
- LERNER, D.N., ISSAR, A.S. & SIMMERS, I.: Groundwater recharge. A guide to understanding and estimating natural groundwater recharge. *IAH.* 8, 1990, 345 p., (Heise) Hannover.
- LEVIN, M., GAT, J.R. & ISSAR, A.: Precipitation, Flood- and Groundwaters of the Negev Highlands: An isotopic study of desert hydrology. In: *Arid-Zone Hydrology: Investigations with Isotope Techniques*, 1980, 3–22, (IAEA) Vienna.
- LIEBSCHER, H.-J.: 20 Jahre Wasserhaushaltsuntersuchungen im Oberharz. *Bes. Mitt. dt. gewässerk. Jb.* 39, 1975, 286 p., (Bundesamt. Gewässerkunde.) Koblenz.
- LIN, R.F. & WEI, K.Q.: Environmental isotope profiles of the soil water in loess unsaturated zone in semi-arid areas of China. In: *Isotope Based Assessment of Groundwater Renewal in Water Scarce Regions*, IAEA-TECHDOC-1246, 2001, 101–118, (IAEA) Vienna.
- LISITZIN, A.P.: Sedimentation in the world ocean: With emphasis on the nature, distribution and behaviour of marine suspensions. *Soc. Econ. Paleontol. Mineral* 17, 1971, 218 p.
- LIST, R.J.: *Smithsonian meteorological tables.* -527 p., (Smithsonian Institute) Washington, 1951.
- LLOYD, J.W.: An examination of recharge mound decay and fossil gradients in arid regional sediment basins. In: *Arid-Zone Hydrology: Investigations with Isotope Techniques*, 1980, 69–75, (IAEA) Vienna.
- LONG, I.F. & FRENCH, B.K.: Measurement of soil moisture in the field by neutron moderation. *J. Soil Sci.* 18, 1967, 149–166.
- LÖPMEIER, F.-J.: Agrarmeteorologisches Modell zur Berechnung der aktuellen Verdunstung (AMBAV). *Beitr. Agrarmeteorologie* 7, 1983, 50 p., (DWD) Braunschweig.
- MA, J. & EDMUNDS, W.M.: Groundwater and lake evolution in the Badain Jaran desert ecosystem. *Hydrogeol. J.* 14, 2006, 1231–1243.
- MACIEJEWSKI, S.: Numerical and experimental study of solute transport in unsaturated soils. *J. Contam. Hydrol.* 14, 193–206.
- MACIEJEWSKI, S., TRIMBORN, P., KLOTZ, D. & MALOSZEWSKI, P.: Investigation of water transport through unsaturated soils using environmental deuterium. In: *Proc. Symp. on Isotopes in Water Resources Management*, Vol. 1, 1995, 303–314, (IAEA) Vienna.
- MACKAY, D.M., FREYBERG, D.L., ROBERTS, P.V. & CHERRY, J.A.: A natural gradient experiment on solute transport in a sand aquifer. 1. Approach and overview of plume movement. *Water Resources Res.* 22, 1986, 2017–2029.
- MAGARITZ, M., KAUFMAN, A., PAUL, M., BOARETTO, E. & HOLLOS, G.: A new method to determine regional evapotranspiration. *Water Resources Res.* 26, 1990, 1759–1762.

- MAILLET, E.: *Mécanique et physique du globe. Essais d'hydraulique souterraine et fluviale*. 1905, 210 p. (Hermann) Paris.
- MAJOUBE, M.J.: Fractionnement en oxygen-18 et en deuterium entre l'eau et sa vapeur. *J. Chim. Phys.* 10, 1971, 1423–1436.
- MALOSZEWSKI, P., MOSER, H., STICHLER, W., BERTLEFF, B. & HEDIN, K.: Modeling of groundwater pollution by river water bank filtration using oxygen-18 data. *Groundwater Monitoring and Management, IAHS Public.* 173, 1990, 153–161.
- MALOSZEWSKI, P., MOSER, H., STICHLER, W. & TRIMBORN, P.: Isotope hydrology investigations in large refuse lysimeters. *J. Hydrol.* 167, 1995, 149–166.
- MALOSZEWSKI, P. & ZUBER, A.: Determining the turnover of groundwater systems with the aid of environmental tracers. 1. Models and their applicability. *J. Hydrol.* 57, 1982, 207–231.
- MALOSZEWSKI, P. & ZUBER, A.: Mathematical modeling of tracer behaviour in short term experiments in fissured rocks. *Water Resources Res.* 26, 1990, 1517–1528.
- MANABE, S.: Climate and ocean circulation: the atmospheric circulation and the hydrology of the earth's surface. *Monthly Weather Review* 97, 1969, 793–805.
- MANN, J.F. (Jr.): Waste Waters in the Vadose Zone of Arid Regions: Hydrologic Interactions. *Ground Water* 14, 1976, 357–372.
- MANNING, A.H. & SOLOMON, D.K.: Constraining mountain-block recharge in the eastern Salt Lake Valley, Utah with dissolved noble gas and tritium data. In: HOGAN, J.F., PHILLIPS, F.M. & SCANLON, B.R. (Eds.): *Groundwater Recharge in a Desert Environment: The Southwestern United States*, AGU series on Water Science and Applications 9, 2004, 139–158.
- MARSHALL, T.J.: *Relations Between Water and Soil*. Commonwealth Agric. Bureau, 1959, (Farnham Royal).
- MASON, J. & SEIP, H.M.: The current state of knowledge on acidification of surface waters and guidelines for further research. *Ambio* 14, 1985, 45–51.
- MATIWIYOFF, N.A. & OTT, D.G.: Stable isotope tracers in the life sciences and medicine. *Science* 181, 1973, 1125.
- MATSUI, E., SALATI, E., RIBEIRO, M.N.G., REIS, C.M., TANCREDI, A.C.N.F. & GAT, J.R.: Precipitation in the Central Amazon Basin. The isotopic composition of rain and atmospheric moisture at Belen and Manaus. *Acta Amazonica* 13, 1983, 307–369.
- MATSUO, S. & FRIEDMAN, I.: Deuterium content of fractionally collected rainwater. *J. Geophys. Res.* 72, 1967, 6374–6376.
- MATTHESS, G.: Geochemical and Transport Processes in the Unsaturated Zone during Groundwater Recharge. In: *Recent Investigations in the Zone of Aeration*. Vol. 1, 1984, 7–17, (Dpt. Hydrogeology and Hydrochemistry of the University) Munich.
- MATTHESS, G., PEKDEGER, A., SCHULZ, H.D., RAST, H. & RAUERT, W.: Tritium tracing in hydrogeochemical studies using model lysimeters. In: *Isotope Hydrology*, Vol. II, 1979, 769–785, (IAEA) Vienna.
- MATTHESS, G. & UBELL, K.: *Allgemeine Hydrogeologie. Grundwasserhaushalt*. 438p, 1983, (Gebr. Bornträger) Berlin, Stuttgart.
- MAZOR, E.: Reinterpretation of  $^{36}\text{Cl}$  data: physical processes, hydraulic interconnections and age estimates in groundwater systems. *Applied Geochemistry* 8, 1992, 351–360.
- MCDONNELL, J.J., BONELL, M. & STEWART, M.K.: Deuterium variations in storm rainfall: Implications for stream hydrograph separation. *Water Resources Res.* 26, 1990, 455–458.

- McNEILAGE, S.D.: The development of a process model for determining groundwater accession. In: SHARMA, M.L. (Ed.): *Groundwater Recharge*, 1989, 85–98, (Balkema) Rotterdam, Boston.
- MICHEL, F.A. & FRITZ, P.: Environmental isotope in permafrost related waters along the Mackenzie Valley corridor. Proc. 3rd Int. Conf. Permafrost, 1978, 207–211, Edmonton.
- MICHEL, F.A. & WILSON, H.C.: Groundwater flow in permafrost regions of Canada. Proc. of Int. Groundwater Symp. of the IAH, Canadian National Chapter, Atlantic Region, Halifax, Nova Scotia, 1988.
- MICHEL, R.L. & TURK, J.T.: Use of  $^{35}\text{S}$  to study rates of sulphur migration in the flat tops wilderness area, Colorado. In: *Isotopes in Water Resources Management*, Vol. 1, 1995, 293–301, (IAEA) Vienna.
- MONTEIT, J.L.: Evaporation and environment. *Symp. Soc. Exp. Biol.*, 1965, 205–234, Nottingham 1965.
- MOOK, W.G.: Stable carbon and oxygen isotopes of natural waters in the Netherlands. In: *Isotope Hydrology 1970*, 163–190 (IAEA) Vienna.
- MOOK, W.G. (Ed.): Environmental Isotopes in the Hydrologic Cycle. *Principles and Application*. Vol. 16, 2001, (IAEA) Vienna.
- MOOK, W.G. (Ed.): Isótopos ambientales en el ciclo hidrológico. *Principios y aplicaciones*. Publ. del Instituto Geológico y Minero de España, Serie: Guías y Manuales 1, 2002, 586 p., (IGME) Madrid.
- MOOK, W.G., GROENEVELD, D.J., BROUWEN, A.E. & VANGANSWIJK, A.J.: Analysis of a runoff hydrograph by mean of natural  $^{18}\text{O}$ . In: *Isotope Techniques in Groundwater Hydrology*, Vol. 1, 1974, 145–155, (IAEA) Vienna.
- MOSER, H. & RAUERT, W.: Isotopenmethoden in der Hydrologie. *Lehrb. Hydrogeol.*, Vol. 8, 1980, 400 p., (Bornträger) Berlin, Stuttgart.
- MOSER, H. & STICHLER, W.: Deuterium measurements on snow samples from the Alps. In: *Isotope Hydrology 1970*, 43–57 (IAEA) Vienna.
- MOSER, H., & STICHLER, W.: Deuterium and oxygen-18 contents as an index of properties of snow covers. *IAHS-Public.* 114, 1975, 122–135.
- MOUTONNET, P., COUCHAT, PH., BRISSAUD, F., PUARD, M. & PAPPALARDO, A.: Observation in situ des mouvements verticaux de l'eau du sol par marquage à l'eau deutériée et mesure gamme/neutrons associée. In: *Symp. on Isotope Hydrology 1978*, Vol. II, 1979, 787–801, (IAEA) Vienna.
- MUALEM, Y.: A new model for predicting the hydraulic conductivity of unsaturated porous media. *Water Resources Res.* 12, 1976, 513–522.
- MÜNNICH, K.-O.: Moisture movement measurement by Isotope tagging. In: *Guidebook on Nuclear Technique in Hydrology*, 1968, 112–117, (IAEA) Vienna.
- MÜNNICH, K.-O.: Use of nuclear techniques for the determination of ground water recharge rates. In: *Guidebook on Nuclear Techniques in Hydrology*, 1968, 191–197, (IAEA) Vienna.
- MÜNNICH, K.-O.: Moisture movement in the unsaturated zone. In: *Guidebook on Nuclear Techniques in Hydrology*, 1983, 203–222, (IAEA) Vienna.
- MÜNNICH, K.-O., SONNTAG, C., CHRISTMANN, D. & THOMA, G.: Isotope fractionation due to evaporation from sand dunes. *Mitt. Zentralinst. f. Isotop. Strahlenforsch.* 29, 1980, 319.
- MUTCHLER, C.K. & HERMSMEIER, L.F.: Review of rainfall simulators. *Trans. Am. Soc. Agri. Eng.* 8, 1969, 67–69.
- NAIR, A.R., NAVADA, S.V. & RAO, S.M.: An injected gamma-tracer method for soil-moisture movement investigations in arid zones. In: *Arid-zone Hydrology: Investigations*

- with *Isotope Techniques*, 1980, 85–92, (IAEA) Vienna.
- NAKAYAMA, F.S. & JACKSON, R.D.: Diffusion of tritiated water in soils. *Soil Sci. Soc. Am. Proc.* 27, 1963, 255.
- NATERMANN, E.: Die Linie des langjährigen Grundwassers und der Trockenwetterabflusslinie (TWL). *Die Wasserwirtschaft* 41, 1951, 12–14.
- NATIV, R., ADAR, E., DAHAN, O. & GEYH, M.A.: Water recharge and solute transport through the vadose zone of fractured chalk under desert conditions. *Water Resources Res.* 31, 1995, 253–261.
- NATIV, R., ISSAR, A. & RUTLEDGE, J.: Chemical composition of rainwater and flood waters in the Negev Desert, Israel. *J. Hydrol.* 62, 1983, 201.
- NAVADA, S.V., NAIR, A.R., SINHA, U.K., KULKARNI, U.P. & JOSEPH, T.B.: Application of isotopes and chemistry in unsaturated zone in arid areas of Rajasthan, India. In: *Isotope Based Assessment of Groundwater Renewal in Water Scarce Regions*, IAEA-TECHDOC-1246, 2001, 119–130, (IAEA) Vienna.
- NEWMANN, B.D., GALLAHER, B.M. & GILKESON, R.H.: Novel Hydrologic Behavior of Semi-arid Mesas. Los Alamos National Laboratory Report LA-UR-00-2294, 2000.
- NIELSEN, D.R. & BIGGAR, J.W.: Analysing soil water and solute movement under field conditions. *Soil-Moisture and Irrigation Studies II*, 1973, 111–127 (IAEA) Vienna.
- NIELSEN, D.R., van GENUCHTEN, M.Th. & BIGGAR, J.W.: Water flow and solute transport processes in the unsaturated zone. *Water Resources Res.* 22, 1986, 89–108.
- NINARI, N. & BERLINER, P.R.: The role of dew in the water and heat balance of bare loess soil in the Negev Desert; quantifying the present dew deposition on the soil surface. *Atmospheric Res.* 64, 2002, 325–336.
- NIR, A. & LEWIS, S.: On tracer theory in geophysical systems in the steady and non steady state I. *Tellus* 27, 1975, 372–383.
- NISWONGER, R.C. & PRUDIC, D.E.: Modeling variable saturated flow using kinematic waves in MODFLOW. In: HOGAN, J.F., PHILLIPS, F.M. & SCANLON, B.R. (Eds.): *Groundwater Recharge in a Desert Environment: The Southwestern United States*, AGU series on Water Science and Applications 9, 2004, 101–112.
- NÜTZMANN, G., MACIEJEWSKI, S. & JOSWIG, K.: Experimental investigations and modeling studies about tracer transport in unsaturated porous media: the dependence of dispersion coefficient on water saturation. In: *Calibration and Reliability in Groundwater Modeling*, ModelCARE99, 1999, 131–137, Zurich.
- NÜTZMANN, G., MACIEJEWSKI, S., STICHLER, W. & ZWIRNMANN, E.: Dual tracer test and modeling studies for determining the unsaturated flow components in a sandy catchment area. In: SEILER, K.-P. & WOHNLICH, S. (Eds.): *New Approaches to Characterizing Groundwater Flow*, 2001, 153–157, (Balkema) Lisse, Abingden, Exten, Tokyo.
- OJEDA, C.G.: Aquifer recharge estimation at the Mesilla Bolson and Guaymas aquifer systems, Mexico. In: *Isotope Based Assessment of Groundwater Renewal in Water Scarce Regions*, IAEA-TECHDOC-1246, 2001, 23–44, (IAEA) Vienna.
- OSTER, H., SONNTAG, C. & MÜNNICH, K.O.: Groundwater age dating with chlorofluorocarbons. *Water Resources Res.* 32, 1996, 2989–3001.
- PEARSON, F.J.(Jr) & HANSHAW, B.B.: Sources of dissolved carbonate species in groundwater and their effects on carbon-14 dating. *Symp. on Isotope Hydrology* 1970, 271, (IAEA) Vienna.
- PECK, A.J.: Groundwater recharge and loss. In: *The Hydrology of areas of Low Precipitation*, Proceedings of the Canberra Symposium, *IAHS Public.* 128, 1979, 361–370.

- PECK, A.J., JOHNSTON, C.D. & WILLIAMSON, D.R.: Analysis of solute distribution in deeply weathered soils. *Agric. Water Manage.* 4, 1981, 83–102.
- PENCK, A.: Versuch einer Klimaklassifikation auf physiographischer Grundlage. *Sitz.-Ber. Preuß. Akad. Wiss., Phys.-Math. Klasse* 12, 1910, 236–246.
- PENMAN, H.L.: Gas and vapor movement in soil. I. *J. Agric. Sci.* 30, 1940, 437.
- PENMAN, H.L.: Natural evaporation from open water, bare soil and grass. *Proc. Roy. Soc. A* 193, 1948, 120–145.
- PETHERAM, C., ZHANG, L., WALKER, G.R. & GRAYSON, R.: Towards a framework for predicting impacts of land-use on recharge: 1. A review of recharge studies in Australia. *Aust. J. Soil Res.* 40, 2000, 397–417.
- PETROV, M.P.: *Deserts of the World*. 447 p., 1976, (Eiley & Sons) New York.
- PFAFF, Th.: Grundwasserumsatzräume im Karst der südlichen Frankenalb. *GSF-Neuherberg Ber.* 3, 1987, 132pp, (GSF) Neuherberg.
- PHILLIPS, F.M.: Environmental tracers for water movement in desert soils of the American Southwest. *Soil. Sci. Soc. Am. J.* 58, 1994, 14–24.
- PHILLIPS, F.M., MATTICK, J.G., DUVAL, T.A., ELMORE, D. & KUBIK, P.W.: Chlorine-36 and tritium from nuclear weapons testing as tracers for long-term liquid and vapor movement in desert soils. *Water Resources Res.* 24, 1988, 1877–1891.
- PHILLIPS, F.M., TROTMANN, K.N., BENTLEY, H.W., DAVIS, S.N. & ELMORE, D.: Chlorine-36 from atmospheric nuclear weapons testing as a hydrologic tracer in the zone of aeration in arid climates. In: *Recent Investigations in the Zone of Aeration*. Vol. 1, 1984, 47–56, (Dpt. Hydrogeology and Hydrochemistry of the University) Munich.
- PHILLIPS, F.M., WALVOORD, M.A. & SMALL, E.E.: Effects of environmental change on groundwater recharge in the Desert Southwest. In: HOGAN, J.F., PHILLIPS, F.M. & SCANLON, B.R. (Eds.): *Groundwater Recharge in a Desert Environment: The Southwestern United States*, AGU series on Water Science and Applications 9, 2004, 273–294.
- PHILIP, J.R.: The theory of infiltration. 4. Sorptivity and algebraic infiltration equation. *Soil Sci.* 84, 1957, 257–264.
- PIONKE, H.B. & DeWALLE, D.R.: Intra and inter-storm <sup>18</sup>O trends for selected rainstorms in Pennsylvania. *J. Hydrol.* 138, 1992, 131–143.
- PLUMMER, L.N., SANFORD, W.E., BEXFIELD, L.M., ANDERHOLM, S.K. & BUSENBERG, E.: Using geo-chemical data and aquifer simulation to characterize recharge and groundwater flow in the Middle Rio Grande Basin, New Mexico. In: HOGAN, J.F., PHILLIPS, F.M. & SCANLON, B.R. (Eds.): *Groundwater Recharge in a Desert Environment: The Southwestern United States*, AGU series on Water Science and Applications 9, 2004, 185–216.
- POL van de, R.M., WIERENGA, P.J. & NIELSEN, D.R.: Solute movement in a field soil. *Soil Sci. Soc. Am. J.* 41, 1977, 10–14.
- PRILL, R., C.: Movement of moisture in the unsaturated zone in a dune area, southeastern Kansas. USGS Profess. Paper D, 1968, p. D1–0.
- PRYCH, E.A.: Using chloride and chlorine-36 as soil water tracers to estimate deep percolation at selected locations on the U.S. Department of Energy Hanford Site, Washington. U.S. Geol. Survey Water – Supply Paper 2481, 1998, 67 p., Denver.
- RAATS, P.A.C.: The kinematics of soil water. In: *On Isotope and Radiation Techniques in Soil Physics and Irrigation Studies*, 1967, 191–200, (IAEA) Vienna.
- RADHAKRISHNAN NAIR, A., PENDHARKAR, A.S., NAVADA, S.V. & RAO, S.M.: Groundwater recharge studies in Maharashtra. In: *Isotope Hydrology*, Vol. II, 1979, 803–826, (IAEA) Vienna.

- RAKOTOFIRINGA, H. & MOUTONNET, P.: Essai de détermination neutronique de l'évapotranspiration réelle d'un terrain gazonné des hauts plateaux malgaches. *Terre Malgache* 12, 1971, 147.
- RAMESH, R. & SARIN, M.M.: Stable isotope study of the Ganga (Ganges) river system. *J. Hydrol.* 139, 1992, 49–62.
- RANGARAJAN, R. & ATHAVALE, R.N.: Annual replenishable ground water potential of India An estimate based on injected tritium. *J. Hydrol.* 234, 2000, 38–53.
- RANK, D., ADLER, A., ARAGUÁS-ARAGUÁS, L., FROELICH, K., ROZANSKI, K. & STICHLER, W.: Hydrological parameters and climatic signals derived from long-term tritium and stable isotope time series of the river Danube. In: *Isotope Techniques in the Study of Environmental Change*, 1998, 191–205, (IAEA) Vienna.
- RAPPER, G.P. & SHARMA, M.L.: Prediction of groundwater recharge to a sandy aquifer using a simulation model. In: SHARMA, M.L. (Ed.): *Groundwater Recharge*, 1989, 99–108, (Balkema) Rotterdam, Boston.
- REILLY, T.E., PLUMMER, L.N., PHILLIPS, P.J. & BUSENBERG, E.: The use of simulation and multiple environmental tracers to quantify groundwater flow in a shallow aquifer. *Water Resources Res.* 30, 1994, 421–433.
- RENNIE, D.A. & PAUL, E.A.: Nitrogen isotope ratios in surface and sub-surface soil horizons. In: *Isotope Ratios as Pollutant Source and Behaviour Indicators*, 1975, 441–453, (IAEA) Vienna.
- REVESZ, K. & WOODS, P.H.: A method to Extract Soil Water for Stable Isotope Analysis. *J. Hydrol.* 115, 1990, 397–406.
- RHODE, A.: The origin of streamwater traced by Oxygen-18. *Uppsala University Rep. Ser. A*, No 41, 1987.
- RICHTER, W. & LILLICH, W.: *Abriss der Hydrogeologie*. 281 pp., 1975, (Schweizerbart) Stuttgart.
- RIGHTMIRE, C.T.: Changes in formation gas composition and isotope content as indicators of unsaturated-zone chemical reactions related to recharge events. In: *Isotope Hydrology*, Vol. II, 1979, 711–732, (IAEA) Vienna.
- RIJTEMA, P.-E.: On the relation between transpiration, soil physical properties and crop production as a basis of water supply plans. *Inst. voor Cultuurtechniek en Waterhuishouding* 58, 1968, Waageningen.
- RINDSBERGER, M., JAFFE, M., RAHAMIM, S. & GAT, J.R.: Patterns of the isotopic composition of precipitation in time and space: data from the Israeli storm water collection program. *Tellus* 42B, 1990, 263–271.
- RINDSBERGER, M. & MAGARITZ, M.: The relation between air-mass trajectories and the water isotope composition of rain in the Mediterranean Sea area. *Geophys. Res. Lett.* 10, 1983, 43–46.
- RITSEMA, C.J., DEKKER, L.W., HENDRICKX, J.M.H. & HAMMINGA, W.: Preferential-flow Mechanism in a Water Repellent Sandy Soil. *Water Resources Res.* 29, 1993, 2183–2193.
- ROBERTSON, W.D. & CHERRY, J.A.: Tritium as an indicator of recharge and dispersion in a groundwater system in central Ontario. *Water Resources Res.* 25, 1989, 1097–1109.
- RORABAUGH, M.I.: Estimating bank storage and groundwater contribution to streamflow. *IAHS Public.* 63, 1964, 432–441.
- ROTH, K. & HAMMEL, K.: Transport of conservative chemical through an unsaturated two-dimensional Miller-similar medium with steady state flow. *Water Resources Res.* 32, 1994, 1653–1663.

- ROTH, K., FLÜHLER, H., JURY, W.A. & PARKER, J.C. (Eds.): *Field-Scale Water and Solute Flux in Soils*. 1990, (Birkhäuser Verlag) Basel.
- ROZANSKI, K., SONNTAG, C. & MUNNICH, K.-O.: Factors controlling stable isotope composition of modern European precipitation. *Tellus* 34, 1992, 142–150.
- RUSSO, D. & DAGAN, G. (Eds.): *Water Flow and Solute Transport in Soils*. Advanced Series in Agricultural Sciences 20, 1993, (Springer) Berlin.
- SAJJAD, M.I., HUSSAIN, S.D., WAHEED, R., SEILER, K.-P., STICHLER, W. & TANSEEN, M.A.: Study of downward movement of soil moisture in unsaturated zone. In: *Stable and Radioactive Isotopes in the Study of the Unsaturated Soil Zone*, 1985, 89–121, (IAEA) Vienna.
- SALAMA, R., HATTON, T. & DAWES, W.R.: Predicting land use impacts on regional scale groundwater recharge and discharge. *J. Environ. Qual.* 28, 1999, 446–460.
- SALATI, E., DALL'OLLIO, A., MATSUI, E. & GAT, J.R.: Recycling of water in the Amazon Basin, an isotopic study. *Water Resources Res.* 15, 1979, 1250–1258.
- SANFORD, W.E.: Recharge and groundwater model. An overview. *Hydrogeol. J.* 10, 2002, 110–120.
- SAXENA, R.K.: Estimation of canopy reservoir capacity and oxygen-18 fractionation in throughfall in a pine forest. *Nordic Hydrol.* 17, 1986, 251–260.
- SAXENA, R.K. & DRESSIE, Z.: Estimation of groundwater recharge and moisture movement in sandy formations by tracing natural oxygen-18 and injected tritium profiles in the unsaturated zone. In: *Isotope Hydrology*, 1984, 139–150, (IAEA) Vienna.
- SCANLON, B.R.: Evaluation of moisture flux from chloride data in desert soils. *J. Hydrol.* 128, 1991, 137–156.
- SCANLON, B.R.: Evaluation of liquid and vapor flow in desert soils based on chlorine-36 and tritium in an arid unsaturated zone. *Water Resources Res.* 28, 1992, 285–297.
- SCANLON, B.R.: Uncertainties in estimating water fluxes and residence times using environmental tracers in an unsaturated zone. *Water Resources Res.* 36, 2000, 395–409.
- SCANLON, B.R.: Evaluation of methods of estimating recharge in semi-arid and arid regions in the Southwest USA. In: HOGAN, J.F., PHILLIPS, F.M. & SCANLON, B.R. (Eds.): *Groundwater Recharge in a Desert Environment, Water Science and Application* 9, 2004, 235–254.
- SCANLON, B.R. & GOLDSMITH, R.S.: Field study of spatial variability in unsaturated flow beneath and adjacent to playas. *Water Resources Res.* 33, 1997, 2239–2252.
- SCANLON, B.R., HEALY, R.W. & COOK, P.G.: Choosing appropriate techniques for quantifying groundwater recharge. *Hydrogeol. J.* 10, 2002, 18–39.
- SCANLON, B.R., KEESE, K., REEDY, R.C., SIMUNEK, J. & ANDRASKI, B.J.: Variations in flow and transport in thick desert vadose zones in response to paleoclimatic forcing (0–90kyr); field measurements, modeling and uncertainties. *Water Resources Res.* 33, 2003, 1179.
- SCANLON, B.R., LANGFORD, R.P. & GOLDSMITH, R.S.: Relationship between geomorphic settings and unsaturated flow in an arid setting. *Water Resources Res.* 35, 1999, 983–999.
- SCANLON, B.R., TYLER, S.W. & WIERENGA, P.J.: Hydrologic issues in arid, unsaturated systems and implications for contaminant transport. *Rev. Geophys.* 35, 1997, 461–490.
- SCHMALZ, B.L. & POLZER, W.L.: Tritiated water distribution in unsaturated soil. *Soil Sci.* 108, 1969, 43.
- SCHMUGGE, T.J., JACKSON, T.J. & MCKIM, H.L.: Survey of methods for soil moisture determination. *Water Resources Res.* 16, 1980, 961–969.



- SCHNOOR, J.L., SIGGL, L., STUMM, W. & ZOBRIST, J.: Saure Niederschläge und ihr Einfluss auf die Schweizer Seen. *Mitt. EAWAG* 15, 1983, 6–13.
- SCHOELLER, H.: L'influence du climat sur la composition chimique des eaux souterraines vadose. *B.S.G.F.* 11, 1941, 267–289.
- SCHOELLER, H.: Arid zone hydrology: recent developments. UNESCO Series on Arid Zone Research, No. 12, 1959, 125 p., Paris.
- SCHOELLER, H.: Salinité des eaux souterraines, évapo-transpiration et alimentation des nappes. *IAHS Public.* 52, 1960, 488–494.
- SCHOELLER, H.: *Les eaux souterraines.* 642 p., 1962, (Masson) Paris.
- SCHOELLER, M.: Calculs du bilan des nappes d'eau des Sables des Landes en utilisant la teneur en chlore de l'eau des nappes et celles de l'eau de pluie. *C.R.Ac.Sc.* 253, 1961, 1598–1599.
- SCHOELLER, M.: *Recherches sur l'acquisition de la composition chimique des eaux souterraines.* 231 p., (Imprimerie Drouillard) Bordeaux.
- SCHROEDER, M.: Methodische Untersuchungen am Beispiel der Grosslysimeteranlage Castricum. *Forstwiss. Zentralbl.* 89, 1970, 200–210.
- SCHÜLEIN, J.: Untersuchungen zum lateralen Transport von Herbiziden und Herbizidmetaboliten in einem Agrarökosystem. *FAM-Ber.* 24, 1998, 145 p., (GSF) Neuherberg.
- SCHULZ, H.-D.: Grundwasserneubildung berechnet aus der Chlorid-Bilanz. *Geol. Mitt.* 12, 1972, 53–60.
- SCHUMANN, S., HERRMANN, A., STICHLER, W. & PRAJAPATIS, B.: Tracer hydrological investigations in a small irrigated agricultural basin in Nepal to evaluate environmental risks of pesticides. In: SEILER, K.-P. & WOHNLICH, S. (Eds.): *New Approaches Characterizing Groundwater Flow*, 2001, 189–194, (Balkema) Lisse, Abingden, Exten, Tokyo.
- SCOGING, H.M. & THORNES, J.B.: Infiltration characteristics in semi-arid zones. In: The Hydrology of areas of Low Precipitation, Proc. of the Canberra Symp., *IAHS Public.* 128, 1979, 159–168.
- SCOTTER, D.R.: Preferential solute movement through larger soil voids. I. Some computations using simple theory. *Austr. J. Soil. Res.* 16, 1978, 257–267.
- SEILER, K.-P.: Kluft- und Porenwasser im Mittleren Buntsandstein des Südlichen Saarlands. *Geol. Mitt.* 9, 1968, 75–96.
- SEILER, K.-P.: Results of field experiments on hydrodynamic dispersion in Quaternary gravels of southern Germany. Proc. Scient. Basis for Water Res. Management, 1985, 351–360, Jerusalem.
- SEILER, K.-P.: Transport und Immobilisierung von Huminstoffen in quartären und tertiären Lockergesteinen. In: FREITAG, D. (Ed.): *Huminstoffe in der Umwelt. GSF-Neuherberg Ber.* 25/97, 1997, 23–32, (GSF) Neuherberg.
- SEILER, K.-P.: Die Kolmatierung von Flussbetten. *GSF- Neuherberg Ber.* 3/97, 1997, 22–29; (GSF) Neuherberg.
- SEILER, K.-P.: *Man's Impact on Groundwater Systems.* UNESCO/IAEA Series on Environmental Isotopes in the Hydrological Cycle, Vol. V, 2000, 105 p., (UNESCO) Paris.
- SEILER, K.-P.: Qualitative and quantitative impact of irrigation on groundwater resources. In: GAT, J.R. & NETHANYAHU, S. (Eds.): *Water and Environment: Resolving Conflicts in the Development of Drylands*, Conference Proceedings, CWST-Ben-Gurion University of the Negev, 2000, p 30, Beer Sheba.
- SEILER, K.-P., ALVARADO RIVAS, J.: Ground water exploration and exploitation of the Caracas aquifer, Venezuela. In: *Int. Symp. on Isotope Techniques in the Study of Past and Current Changes in the Hydrosphere and the Atmosphere.*, 1998, 856–863, (IAEA) Vienna.

- SEILER, K.-P. & BAKER, D.: Der Einfluss der Schichtung auf die Sickerwasserbewegung bei punkt- und linienförmiger Infiltration. *Z. dt. geol. Ges.* 136, 1985, 659–672.
- SEILER, K.-P., BERTLEFF, B., EINSELE, G., NN, M., LAZIK, D., MALOSZEWSKI, P. & PLUM, H.: Speicher-Durchfluss-Modelle zur Bewertung des Stoffein- und Stoffaustrags in unterschiedlichen Grundwasser-Zirkulationssystemen. *DVWK Schriften* 109, 1995, 95 p., (Wirtschafts- und Verlagsgesellschaft Gas und Wasser mbH) Bonn.
- SEILER, K.-P. & HELLMEIER, C.: Humic substances and agro-chemical in the discharge components of Scheyern. *Freiburger Schriften zur Hydrologie* 13, 2001, 367–374.
- SEILER, K.-P., GU, W.-Z. & STICHLER, W.: Transient response of groundwater systems to climate changes (in press by BGS).
- SEILER, K.-P. & LINDNER, W.: Near surface and deep groundwater. *J. Hydrol.* 165, 1995, 33–44.
- SEILER, K.-P., von LOEWENSTERN, S. & SCHNEIDER, S.: The role of bypass- and matrix-flow in the unsaturated zone for groundwater protection. In: SILLO, O. (Ed.): *Groundwater: Past Achievements and Future Challenger* (2000), 307–311 (Balkema) Rotterdam, Brookfield.
- SEILER, K.-P., von LOEWENSTERN, S. & SCHNEIDER, S.: Matrix and bypass-flow in quaternary and tertiary sediments of agricultural areas in south Germany. *Geoderma* 105, 2002, 299–306.
- SEILER, K.-P., TRIMBORN, P., & ALVARADO, J.: Das Grundwasser im Umfeld des Lago de Valencia, Venezuela und seine anthropogene und geogene, nachteilige Beeinflussung. *Z. dt. geol. Ges.* 143, 1992, 398–403.
- SEILER, K.-P. & ZOJER, H.: Role of Tracers in the Unsaturated Zone. *Beiträge zur Hydrogeologie* 52, 2001, 11–15, Graz.
- SHARMA, M.L.: Measurement and prediction of natural groundwater recharge an overview. *J. Hydrol. (N.Z.)* 25, 1987, 49–56.
- SHARMA, M.L.: Groundwater recharge. In: *Groundwater Recharge*, 1989, 323 p. (Balkema) Rotterdam, Brookfield.
- SHARMA, M.L. & CRAIG, A.B.: Comparative recharge rates beneath banksia woodland and two pine plantations on the Gangara mound, Western Australia. In: SHARMA, M.L. (Ed.): *Groundwater Recharge*, 1989, 171–184, (Balkema) Rotterdam, Brookfield.
- SHARMA, M.L., CRESSWELL, I.D. & WATSON, J.D.: Estimates of natural groundwater recharge from depth distribution of an applied tracer, subsurface flow, pollutant transport and salinity. Proc. Nat. Conf. Institute of Engineers, Publ 85/13, 1985, 64–70, Melbourne, Victoria.
- SHARMA, M.L. & HUGHES, M.W.: Groundwater recharge estimation using chloride, deuterium and oxygen-18 profiles in the deep costal sands of Western Australia. *J. Hydrol.* 81, 1985, 93–109.
- SHARMA, P. & GUPTA, S.K.: Soil water movement in semi-arid climate an isotopic investigation. In: *Stable and Radioactive Isotopes in the Study of the Unsaturated Soil Zone*, (IAEA)-TEC-DOC-357, 1985, 55–71, (IAEA) Vienna.
- SHARON, D.: The spottiness of rainfall in a desert area, *J. Hydrol.* 17, 1972, 161–175.
- SHIKLOMANOV, I.A.: Global water resources. *Nature and Resources* 26, 1990, 34–43.
- SHIKLOMANOV, I.A., GU, W.-Z., TANG, H.I.X., MARUNICH, S.V. & LUO, J.J.: Experimental research on the role of dew in arid ecosystem of Gobi desert, Inner Mongolia. In: XI, R.-Z., GU, W.-Z. & SEILER, K.-P. (Eds.): *Research Basins and Hydrological Planning* 2004, 329–332, (Balkema) Leiden, London, New York, Philadelphia, Singapore.

- SHULIN, R., van GENUCHTEN, M.T., FLÜHLER, H. & FERLIN, P.I.L.: An experimental study of solute transport in a stony field soil. *Water Resources Res.* 23, 1987, 1785–1794.
- SIMMERS, I.: *Recharge of Phreatic Aquifers in (Semi-)Arid Areas*. 1997 (Balkema) Rotterdam, Brookfield.
- SKLASH, M.G. & FARVOLDEN, R.N.: The role of groundwater in storm runoff, *J. Hydrol.* 43, 1979, 45–65.
- SKLASH, M.G., FARVOLDEN, R.N. & FRITZ, P.: A conceptual model of watershed response to rainfall, developed through the use of oxygen-18 as a natural tracer. *Can. J. Earth Sci.* 13, 1976, 271–283.
- SLATYR, R.O. & MABBUT, J.A.: Hydrology of arid and semi-arid regions. In: CHOW, V.T. (Ed.): *Handbook of Applied Hydrology* 24, 1964, (McGraw-Hill) New York.
- SMETEM, K.R.J., TRUDGILL, S.T. & PICKEL, A.M.: Nitrate loss in soil drainage waters in relation to by-passing flow and discharge on arable site. *J. Soil Sci.* 34, 1983, 499–509.
- SMEDT, F.D.E. & WIERENGA, P.J.: A Generalized Solution for Solute Flow in Soils with Mobile and Immobile Water. *Water Resources Res.* 15, 1979, 1137–1141.
- SMITH, D.B., WEARN, P.L., RICHARDS, J.H. & ROWE, P.C.: Water movement in the unsaturated zone of high and low permeable strata by measuring natural tritium. In: *Isotope Hydrology*, 1970, 73–87, (IAEA) Vienna.
- SOLOMON, D.K., SCHIFF, S.L. POREDA, R.J. & CLARK, W.B.: A validation of the  $^3\text{H}/^3\text{He}$  method for determining groundwater recharge. *Water Resources Res.* 29, 1993, 2951–2962.
- SOLOMON, D.K. & SUDICKY, E.A.: Tritium and helium-3 isotopic ratios for direct estimation of spatial variations of groundwater recharge. *Water Resources Res.* 27, 1991, 2309–2019.
- SONNTAG, C., CHRISTMANN, D. & MÜNNICH, K.-O.: Laboratory and field experiments on infiltration and evaporation of soil water by means of deuterium and oxygen-18. In: *Stable and radioactive isotopes in the study of the unsaturated soil zone*, TECDOC-357, 1985, 145–161, (IAEA) Vienna.
- SOPHOCLEOUS, M. & PERRY, C.A.: Experimental studies in natural groundwater-recharge dynamics: the analysis of observed recharge events. *J. Hydrol.* 81, 1985, 297–332.
- SPRINGUEL, I.: Determination and growth model of *Tamarix nilotica* and *Balanites argyptiaca* in Wadi Allaqi, Lake Nasser area, Aswan, Egypt. In: BRECKLE et al. (eds.): *Ökologische Optimierung der Wassernutzung bei Bewässerungsverfahren mit salzhaltigem Wasser in ariden Gebieten*. *Bielefelder ökol. Beitr.* 16, 2003, 45–54.
- STALL, J.B.: An analysis of water availability in semi-arid zones. In: The Hydrology of areas of Low Precipitation, Proc. of the Canberra Symp, *IAHS Public.* 128, 1979, 191–196.
- STARKEL, L.: Introduction to global pale hydrological changes. GREGORY, K.J., STARKEL, L. & BAKER, V.R. (Eds.): *Global Continental Paleohydrology*, 1995, 1–20, (Wiley & Sons) Chichester, New York, Brisbane, Toronto, Singapore.
- STARR, J.L., BROADBENT, F.E. & STOUT, P.R.: A comparison of  $^{15}\text{N}$ -depleted and  $^{15}\text{N}$ -enriched fertilizers as tracers. *Soil Sci. Soc. Am. Proc.* 38, 1974, 266.
- STEPHENS, D.B., & KNOWLTON, R.J.: Soil water movement and recharge through a sand at a semi-arid site in New Mexico. *Water Resources Res.* 22, 1986, 881–889.
- STEWART, G.L.: Fractionation of tritium and deuterium in soil water. *Geophysical Monograph Ser.* 11, 1967, 159.
- STICHLER, W., MOSER, H. & SCHROEDER M.: Measurements of percolation velocity in a sand lysimeter by means of  $^{18}\text{O}$ -content. In: *Recent Investigations in the Zone of Aeration*. Vol. 1, 1984, 191–204, (Dpt. Hydrogeology and Hydrochemistry of the University) Munich.

- STICHLER, W., OERTER, H. & RAUERT, W.: Bestimmung von Abflußkomponenten in einem Vorfluter mit Messungen des Isotopengehalts und der elektrolytischen Leitfähigkeit. *GSF-Neuherberg Ber. R 290*, 1982, 188–200, (GSF) Neuherberg.
- STICHLER, W., SCHOTTERER, U., FRÖHLICH, K., GINOT, P., KULL, C., GÄGGELER, H. & POUYAU, B.: Influence of sublimation on stable isotope records covered from high altitude glaciers in the tropical Andes. *J. Geophys. Res.* 106, 2001, 22613–22620.
- STONE, W.J.: Paleohydrologic implications of some deep soil-water chloride profiles, Murray Basin, South Australia. *J. Hydrol.* 132, 1994, 201–223.
- STONESTROM, D., PRUDIC, D.E., LACZNIAK, R.J. & AKSTIN, K.C.: Tectonic, climatic and land-use controls on groundwater recharge in an arid alluvial basin: Amargosa Desert, USA. In: HOGAN, J.F., PHILLIPS, F.M. & SCANLON, B.R. (Eds.): *Groundwater Recharge in a Desert Environment: The Southwestern United States*, AGU series on Water Science and Applications 9, 2004, 29–48.
- STONESTROM, D., PRUDIC, D.E., LACZNIAK, R.J., AKSTIN, K.C., BOYD, R.A. & HENKELMAN, K.K.: Estimates of deep percolation beneath native vegetation, irrigated fields and the Amargosa-River channel, Amargosa Desert, Nye County, Nevada. USGS Open-File report 03–104, 2003.
- STUART, M.E. & MILNE, C.J.: Groundwater quality implications of wastewater irrigation in León, Mexico. In: CHILTON et al. (Eds.): *Groundwater in the Urban Environment: Problems, Processes and Management*, 1997, 193–198, (Balkema) Rotterdam Brookfield.
- STUMM, W. & MORGAN, J.J.: *Aquatic Chemistry*. 1983 (Wiley) New York etc.
- STUTE, M., CLARK, J.F., PHILIPS, F.M. & ELMORE, D.: Reconstruction of late glacial climates from the groundwater archive:  $\text{Cl}^-$  and  $^{36}\text{Cl}$  in the Carrizo Aquifer, Texas. In: *Isotope Techniques in the Study of Past and Current Environmental Changes in the Hydrosphere and the Atmosphere*, 1993, 259–270, (IAEA) Vienna.
- STUTE, M., CLARK, J.F., SCHLOSSER, P., BROECKER, W.S. & BONANI, G.: A 30,000yr continental paleotemperature record derived from noble gases dissolved in groundwater from the San Juan Basin, New Mexico. *Quat. Res.* 43, 1995, 209–220.
- STUYFZAND, P.J.: Groundwater quality evolution in the upper aquifer of the coastal dune area of the western Netherlands. In: *Hydrochemical Balances of Freshwater Systems (The Uppsala Symposium)*, *IAHS Public.* 150, 1984, 87–98.
- SUECKER, J.A.: Chemical hydrograph separation during snowmelt for three headwater basins in Rocky Mountain National Park, Colorado. In: TONNESSEN, K.A., WILLIAMS, M.W. & TRANTER, M. (Eds.): *Biogeochemistry of seasonally snow covered catchments*, *IAHS- Public.* 228, 1995, 271–281.
- SUGIMOTO, A., YANAGISAWA, N., NAITO, D., FUJITA, N. & MAXIMOV, T.C.: Importance of permafrost as a source of water for plants in the Siberian taiga. *Ecol. Res.* 17, 2002, 493–503.
- SUKHIJA, B.S. & RAMA, F.A.: Evaluation of groundwater recharge in semi-arid region of India using environmental tritium. *Indian Acad. Sci 77 Ser. A* 6, 1973, 279–292.
- SUKHIJA, B.S., REDDY, D.V. NADAKUMA, V. & RAMA, F.A.: A method for evaluation of artificial recharge through percolation tanks using environmental chloride. *Ground Water* 35, 1997, 161–165.
- SUKHIJA, B.S., REDDY, D.V. NAGABHUSHANAM, P. & CHAND, R.: Validity of environmental chloride method for recharge evaluation of coastal aquifers. *India J. Hydrol.* 99, 1988, 349–366.

- SUKHIJA, B.S., REDDY, D.V. NAGABHUSHANAM, P, HUSSEIN, S., GIRI, VY & PATIL, D.J.: Environmental and injected tracers methodology to estimate direct precipitation recharge to a confined aquifer. *J. Hydrol.* 117, 1996, 77–97.
- SUKHIJA, B.S., REDDY, D.V., NAGABHUSHANAM, P. & HUSSEIN, S.: Recharge processes: Piston flow vs preferential-flow in semi-arid aquifers of India. *Hydrogeol. J.* 11, 2003, 387–395.
- SUKHIJA, B.S. & SHAH, C.R.: Conformity of groundwater recharge rate by tritium method and mathematical modeling. *J. Hydrol.* 30, 1976, 167–178.
- TAMERS, M.A.: Radiocarbon ages of groundwater in an arid zone unconfined aquifer. In: Isotope Techniques in the Hydrological Cycle, *AGU Monograph* 11, 1967, 143–152.
- TANDIA, A.A.: Revue critique des méthodes d'évaluations de la recharge des nappes. Contribution de l'approche géochimique et isotopique. Louga-Nord Sénégal. Thèse du 3ème cycle Univ. Dakar. 138p + annexes, 1980.
- TANDIA, A.A., ARANYOSSY, J.F. & GAYE, C.B.: Evaluation de la recharge des nappes phréatiques sous climat semi-aride. Exemple du Nord-Senegal. In: *Les ressources en eau au Sahel*, 1993, 39–51, (IAEA) Vienna.
- TANWAR, B.S.: Effects of irrigation on the groundwater system in the semi-aridzone of Haryana, India. In: The Hydrology of areas of Low Precipitation, Proc. of the Canberra Symp., *IAHS Public.* 128, 1979, 375–384.
- TAYLOR, R.G. & HOWARD, K.W.F.: Groundwater recharge in the Victoria Nile basin of east Africa: support for the soil moisture balance approach using stable isotope tracers and flow modeling. *J. Hydrol.* 180, 1996, 31–53.
- THIESSEN, A.H.: Precipitation for large areas. *Monthly Weather Rev.* 39, 1911, 1082–1084.
- THOMA, G., ESSER, N., SONNTAG, C., WEISS, W., RUDOLPH, J. & LEVENE, P.: New technique of in situ soil moisture sampling for environmental isotope analysis: applied at Pilat sand dune near Bordeaux. In: *Isotope Hydrology*, Vol. II, 1979, 753–768, (IAEA) Vienna.
- THOMAS, G.W. & SWOBODA, A.R.: Anion exclusion effects on chloride movements in soils. *Soil Sci.* 110, 1970, 163.
- THORNSWAITE, C.W.: Problems in the classification of climate. *Geogr. Rev* 33, 1943, 233–255.
- THORNSWAITE, C.W.: An approach towards a rational classification of climate. *Geogr. Rev.* 38, 1948, 55–91.
- THORPE, P.M.: Tritium as an indicator of groundwater recharge to the Gangara groundwater mound on the Swan coastal plain, Perth, Western Australia. In: SHARMA, M.L. (Ed.): *Groundwater Recharge*, 1989, 41–55, (Balkema) Rotterdam, Boston.
- TODOROVIC, Z. & FILPI, A.: Movement of complex compounds through different soil types. In: *On Isotope and Radiation Techniques in Soil Physics and Irrigation Studies*, 1967, 241–250, (IAEA) Vienna.
- TOTH, J.: A theoretical analysis of groundwater flow in small drainage basis. *J. Geophys. Res.* 68, 1963, 4795–4812.
- TOTH, J.: Hydraulic continuity in large sedimentary basins. *Hydrogeol. J.* 3, 1995, 4–16.
- TURC L.: Le bilan d'eau de sols, relation entre les précipitations, l'évaporation et l'écoulement. *Ann. Agron.* 1954, 36–43, Alger.
- TYLER, S.W., CHAPMAN, J.B., CONRAD, S.H., HAMMERMEISTER, D.P., BLOUT, D.O., MILLER, J.J., SULLY, M.J. & GINANI, J.N.: Soil-water flux in the southern Great Basin, United States: Temporal and spatial variations over the last 120 000 years. *Water Resources Res.* 32, 1996, 1481–1499.

- TYLER, S.W. & WALKER, G.R.: Root zone effects on tracer migration in arid zones. *Soil Sci. Soc. Am. J.* 58, 1994, 25–31.
- TZUR, Y.: Isotopic composition of water vapour. Ph.D. thesis, Feinberg Graduate School at the Weizmann Institute of Science, Rehovot, Israel, 1971.
- UHLIG, S.: Berechnung der Verdunstung aus klimatologischen Daten. *Mitt. dt. Wetterd.* 6, 1954, 24 p.
- ULRICH, B. & BÜTTNER, G.: Waldsterben Konsequenzen für die forstliche und landwirtschaftlicher Ertragskraft. *Inf. zur Raumentw.* 10, 1985, 879–891.
- ULRICH, B. & MATZNER, E.: Abiotische Folgewirkungen der weiträumigen Ausbreitung von Luftverunreinigungen. Umweltforschungsplan des BMI, Forschungsber. Nr. 10402615, 1982/1983, 221p text, 141p data, (Berlin).
- UNEP: *World Atlas of Desertification*. 1992, (E.Arnold) London.
- UNESCO: *World Map of Hydro-geological Conditions and Groundwater Flow*. 1999, (Hydro Science Press) Paris.
- UNESCO/IHP: Environmental isotopes in the hydrological cycle, Principles and Applications. IHP-V Technical Documents 39, 2000, volumes I-VI.
- UNESCO/WMO: *Hydrological Maps. Studies and Reports in Hydrology* 20, 1977, 204 p., Paris.
- US SOIL CONSERVATION SERVICE: Urban hydrology for small watersheds. Tech. Rep. 55, 1975, (US Department of Agriculture) Washington.
- VACHAUD, G., DANCETTE, C., SONKO, S. & THONY, J.L.: Méthodes de caractérisation hydrodynamique in-situ d'un sol non saturé. Application à deux types de sol du Sénégal en vue de la détermination des termes du bilan hydrique. *Ann. Agron.* 29, 1979, 1–36.
- VACHAUD, G., ROYER, J.M. & COOPER, J.D.: Comparison of methods of calibration of a neutron probe by gravimetry or neutron-capture model. *J. Hydrol.* 34, 1977, 344–356.
- VACHAUD, G., VAUCLIN, M. & COLOMBANI, J.: Bilan hydrique dans le Sud Tunisien. Caractérisation expérimentale des transferts dans la zone non saturée. *J. Hydrol.* 49, 1981, 31–52.
- VACHIER, P. & DEVER, L.: Isotopic Approach for Water Movement in the Chalk unsaturated Zone. In: *Recent Investigations in the Zone of Aeration*, Vol. 1, 1984, 37–46, (Dpt. Hydrogeology and Hydrochemistry of the University) Munich.
- VACHIER, P., DEVER, L. & FONTES, J.-C.: Mouvements de l'eau dans la zone non saturée et alimentation de la nappe de la craie de Champagne (France). In: *Proc. Symp. on Isotope Techniques in Water Resources Development*, 1987, 367–379, (IAEA) Vienna.
- VEN van de, F.H.M.: Water balances of urban areas. *IAHS Public.* 198, 1990, 21–23.
- VERHAGEN, B.Th., BREDENKAMP, D.B., VAN RENSBURG, H.J. & FARR, J.I.: Recharge quantification with radiocarbon: Independent corroboration in three karoo aquifer studies in Botswana. In: *Isotope Techniques in Water Resources Development and Management*, (IAEA) Vienna 1999.
- VERHAGEN, B.Th., SMITH, P.E., McGEORGE, I.L. & DZIEMBOWSKI, Z.: Tritium profiles in Kalahari Sands as a measure of rain-water recharge. In: *Isotope Hydrology*, Vol. II, 1979, 733–751, (IAEA) Vienna.
- VESELIC, M. & CENCUR CURK, B.: Test studies of flow and solute transport in the unsaturated fractured and karstified rock on the experimental field site Sinji Vrh, Slovenia. In: SEILER, K.-P. & WOHNLICH, S. (Eds.): *New Approaches Characterizing Groundwater Flow*, 2001, 211–214, (Balkema) Lisse, Abingden, Exten, Tokyo.

- VILLA NOVA, N.A., SALATI, E. & MATSUI, E.: Estimativa de evapotranspiracao na basia Amazonica. *Acta Amazonica* 6, 1976, 215–228.
- VOLKERING, F., van BREUKELEN, B.M., GROEN, K., MEIJER, H.A.J., AHAD, J.M.E., SHERWOOD-LOLAR, B. & KRAMERS, J.D.: Application of natural isotope analysis in soil pollution research. In: *Contaminated Soil 2000*. Vol. 1, 2000, 214–221, Leipzig.
- VRBA, J. & VERHAGEN, B.Th.: Groundwater resources for emergency situations. *IHP VI, Series on groundwater* 12, 2006, 94 p., (UNESCO) Paris.
- VUUREN van, W.E.: Problems involved in soil moisture determinations by means of a neutron depth probe. In: *Recent Investigations in the Zone of Aeration*. Vol. 1, 1984, 271–280, (Dpt. Hydrogeology and Hydrochemistry of the University) Munich.
- WASEL, Y.: Dew absorption by plants of arid zones. *Bull. Res. Council Israel* D6, 1958, 180–186.
- WALKER, G.R., JOLLY, I.D. & COOK, P.G.: A new chloride leaching approach to the estimation of diffuse recharge following a change in land use. *J. Hydrol.* 128, 1991, 49–67.
- WALKER, G.R., JOLLY, I.D. STADTER, M.H., LEANEY, F.W., DAVIE, R.F., FIFIELD, L.K., OPHEL, T.R. & BIRD, J.R.: Evaluation of the use of chlorine-36 in recharge studies. In: *Isotope Techniques in Water Resources Development*, 1992, 19–29, (IAEA) Vienna.
- WALKER, C.D. & RICHARDSON, S.B.: The use of stable isotopes of water in characterising the source of water in vegetation. *Chem. Geol.* 94, 1991, 145–158.
- WALKER, G.R., WOODS, P.H. & ALLISON, G.B.: Interlaboratory comparison of methods to determine the stable isotope composition of soil water. *Chem. Geol.* 111, 1994, 297–306.
- WALVOORD, M.A., PLUMMER, M.A., PHILLIPS, F.M. & WOLFSBERG, A.V.: Deep arid system hydrodynamics, 1, Equilibrium states and response times in thick desert vadose zones. *Water Resources Res.* 38, 2002, 1308.
- WALVOORD, M.A. & SCANLON, B.R.: Hydrologic processes in deep vadose zones in interdrainage arid environments. In: HOGAN, J.F., PHILLIPS, F.M. & SCANLON, B.R. (Eds.): *Groundwater Recharge in a Desert Environment: the Southwestern United States*. AGU series on Water Science and Applications 9, 2004, 15–28.
- WANG, J.S.Y.: Flow and transport in fractured rocks. *Rev. Geophys.* 29, 1991, 254–262.
- WARD, R.S., LAWRENZE, A.R., WILLIAMS, A.T. & BARKER, J.A.: Transport of microbiological contaminants in the unsaturated zone of the Chalk aquifer: investigation by tracer test. In: SEILER, K.-P. & WOHNLICH, S. (Eds.): *New Approaches Characterizing Groundwater Flow*, 2001, 221–224, (Balkema) Lisse, Abingden, Exten, Tokyo.
- WELLINGS, S.R. & BELL, J.P.: Movement of water and nitrates in the unsaturated zone of upper chalk near Winchester, Hants, England. *J. Hydrol.* 48, 1980, 119–136.
- WELLMAN, B.P., COOK, F.O. & KROUSE, H.R.: Nitrogen-15: Microbial alteration of abundance. *Science* 161, 1968, 269–270.
- WESSELING, J.: Hydrology, soil properties, crop growth and land drainage. *Inst. voor Cultuurtechniek en Waterhuishouding* 57, 1958, Waageningen.
- WESSOLEK, G., RENGER, M., STREBEL, O. & SPONAGEL, H.: Einfluss von Boden, Pflanzenbestand und Grundwasserflur-Abstand auf die Grundwasserneubildung. In: *Recent Investigations in the Zone of Aeration*. Vol. 2, 1984, 767–775, (Dpt. Hydrogeology and Hydrochemistry of the University) Munich.
- WHITE, R.E.: The influence of macropores on the transport of dissolved and suspended matter through soil. *Adv. Soil Sci.* 3, 1985, 95–119.
- WHITE, W.B.: Groundwater flow in karstic aquifers. In: DELLEUR, J.W. (Ed.): *The Handbook of Groundwater Engineering* 1998, 18/1–18/36, (CRC Press) Boca Raton.

- WIEDEY, G., & GEHRMANN, J.: Vergleich eines geschädigten und bis 1983 symptomfreien Fichtenbestands im Hills: Deposition, Bodeninventar, Durchwurzelung. *Mitt. dt. bodenk. Ges.* 42, 1985, 112–122.
- WIGLEY, T.M.L., PLUMMER, L.N. & PEARSON, F.J.: Mass transfer and carbon isotope evolution in natural water systems. *Geochim. Cosmochim. Acta* 42, 1978, 1117–11139.
- WILSON, J.L. & GUAN, H.: Mountain-block hydrology and mountain front range. In: HOGAN, J.F., PHILLIPS, F.M. & SCANLON, B.R. (Eds.): *Groundwater Recharge in a Desert Environment, Water Science and Application* 9, 2004, 113–137.
- WINTER, T.C.: Effect of groundwater recharge on configuration of the water table beneath sand dunes and on percolation in lakes in the sandhills of Nebraska, U.S.A. *J. Hydrol.* 86, 1986, 221–237.
- WOOD, W.W. & BASSET, R.L.: Water quality changes related to the development of anaerobic conditions during artificial recharge. *Water Resources Res.* 11, 1975, 553.
- WOOD, W.W. & IMES, J.L.: Dating of Holocene Ground-water recharge in western part of Abu Dhabi (United Arab Emirates): Constraints on global climate-change models. In: ALSHARHAN A.S. & WOOD, W.W. (Eds.): *Water Resources Perspectives: Evaluation, Management and Policy*, 2003, 379–385.
- WOOD, W.W. & NATIV, R.: An isotopic and solute paradox? Or is there evidence for macropore flow in the Southern High Plains, USA. *Geol. Soc Amer. Annual Meeting Report*, 1994; 390 (Elsevier) Amsterdam.
- WOOD, W.W. & OSTERKAMP W.R.: Playa-lake basins on the Southern High Plains of Texas and New Mexico: Part II. A hydrologic model and mass-balance arguments for their development. *Bull. Geol. Soc. Am.* 99, 1987, 224–230.
- WOOD, W.W., RAINWATER, K.A. & THOMPSON, D.B.: Quantifying macropore recharge: Examples from a semi-arid area. *Ground Water* 35, 1997, 1097–1106.
- WOOD, W.W., RIZK, Z.S. & ALSHARHAN, A.S.: Timing of recharge, and the Origin, Evolution and Distribution of Solutes in a Hyperarid Aquifer System. In: ALSHARHAN A.S. & WOOD, W.W. (Eds.): *Water Resources Perspectives: Evaluation, Management and Policy*, 2003, 295–312 (Elsevier) Amsterdam..
- WOOD, W.W. & SANFORD, W.E.: Chemical and isotopic methods for quantifying groundwater recharge in a regional semi-arid environment. *Ground Water* 33, 1995, 458–468.
- WOOD, W.W. & SIGNOR, D.C.: Geochemical factors affecting artificial ground water recharge in the unsaturated zone. *Transactions ASAE* 18, 1975, 677.
- WOODCOCK, A.H. & FRIEDMAN, I.: The deuterium content of raindrops. *J. Geophys. Res.* 68, 1963, 4477.
- WUNDT, W.: Die Niedrigwasserführung in Baden-Württemberg als Maß für die verfügbaren Grundwassermengen. *Gas-Wasserfach* 24, 1953, 719–722.
- WUNDT, W.: Die Kleinstwasserführung der Flüsse als Maß für die verfügbaren Grundwassermengen. *Forsch. dt. Landesk.* 104, 1958, 47–54, Remagen.
- YAIR, A.: Runoff generation in a sandy area. The Nizzana sands, western Negev. Israel. *Earth Surf. Proc. Landforms* 15, 1990, 597–609.
- YAIR, A., SHARON, D. & LAVEE, H.: An instrumented watershed for the study of partial area contribution of runoff in an arid zone. *Z. Geomorphol.*, Suppl. 29, 1978, 71.
- YAIR, A., KARNIELI, A. & ISSAR, A.: The chemical composition of precipitation and runoff water on an arid limestone hillside, northern Negev, Israel. *J. Hydrol.* 129, 1991, 371–388.
- YAIR, A., SHARON, D. & LAVEE, H.: Trends in runoff and erosion processes over an arid limestone hillside, Northern Negev, Israel. *Israel. Hydrol. Sci. Bull.* 25, 1980, 243 p.



- YANG, I.C., RATTRAY, G.W. & PEI, Y.: Interpretation of chemical and isotope data from boreholes in the unsaturated zone at Yuka Mountain, Nevada. USGS Water Resources Invest. Rep 98-4132, 1996, 57 p.
- YOUSFI, M., ARANYOSSI, J.F., DJERMOUNI, B. & FONTES, J.-C.: Etude isotopique des mouvements de l'eau en zone non saturée sous climat aride (Algérie). In: *Stable and radioactive isotopes in the study of the unsaturated soil zone*, (IAEA)-TECDOC-357, 1985, 161-179, (IAEA) Vienna.
- YURTSEVER, Y.: Worldwide survey of isotopes in precipitation. IAEA report, 1975, (IAEA) Vienna.
- YURTSEVER, Y. & GAT, J.R.: Atmospheric Waters. In: *Stable Isotope Hydrology; Deuterium and Oxygen-18 in the Water Cycle*, Technical Report Series No.210, 1981, 103-143, (IAEA) Vienna.
- ZANGVIL, A.: Six years of dew observation in the Negev Desert, Israel. *J. Arid. Environ.* 32, 1996, 361-371.
- ZEKTSER, I. S. & DZHAMALOV, R.G.: Groundwater discharge to the world's oceans. UNESCO, *Nature and Resources* 27, 1981, 18-20.
- ZHU, C., WINTERLE, J.R. & LOVE, E.I.: Late Pleistocene and Holocene groundwater recharge from chloride mass balance method and chlorine-36 data. *Water Resources Res.* 39, 2003, 1182.
- ZIMMERMANN, U., EHHALT, D. & MÜNNICH, K.-O.: Soil-water movement and evapo-transpiration: Changes in the isotopic composition of the water. In: *Isotope Hydrology*, 1967, 567-583, (IAEA) Vienna.
- ZIMMERMANN, U., MÜNNICH, K.-O. & ROETHER, W.: Downward movement of soil moisture traced by means of hydrogen isotopes. *Geophys. Monogr.* No. 11, Isotope Techniques in the Hydrologic Cycle, AGU, 1967, 28-36, Washington.
- ZIMMERMANN, U., MÜNNICH, K.-O. & ROETHER, W.: Tracer determines movement of soil moisture and evapo-transpiration. *Science* 152, 1966, 346.
- ZOELLMANN, K., KINZELBACH, W. & FULDA, C.: Environmental tracer transport ( $^3\text{H}$  and  $\text{SF}_6$ ) in the saturated and unsaturated zones and its use in nitrate pollution management. *J. Hydrol.* 240, 2001, 187-205.
- ZOUARI, K., ARANYOSSY, J.F., MAMOU, A. & FONTES, J.-C.: Etude isotopique et géochimique des mouvements et de l'évolution des solutions de la zone aérée des sols sous climat semi-aride (Sud Tunisien). In: *Stable and radioactive isotopes in the study of the unsaturated soil zone*, IAEA-TECDOC-357, 1985, 121-145, (IAEA) Vienna.
- ZOUARI, K., MALIKI, M.A., MOUMNI, L. & ARANYOSSY, J.F.: Chemical (Cl) and isotopic ( $^{18}\text{O}$ ,  $^2\text{H}$ ,  $^3\text{H}$ ) study of the unsaturated zone in the arid region of Nefta, south Tunisia. In: *Isotope Based Assessment of Groundwater Renewal in Water Scarce Regions*, IAEA-TECHDOC-1246, 2001, 71-84, (IAEA) Vienna.
- ZUBER, A.: Mathematical models for the interpretation of environmental radioisotopes in groundwater systems. In: FRITZ, P. & FONTES, J.-C. (Eds.): *Handbook of Environmental Isotope Geochemistry*, Volume 2, The Terrestrial Environment B., Elsevier Publ. Comp., 1986, 1-55.

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