

**ENVIRONMENTAL  
ISOTOPES**  
**in the**  
**HYDROLOGICAL CYCLE**

**Principles and Applications**

**W. G. Mook**

**editor**

**VOLUME V**  
**MAN'S IMPACT**  
**ON**  
**GROUNDWATER SYSTEMS**

**by**

**Klaus-Peter Seiler**

**GSF-Institute of Hydrology, Neuherberg**

**Germany**

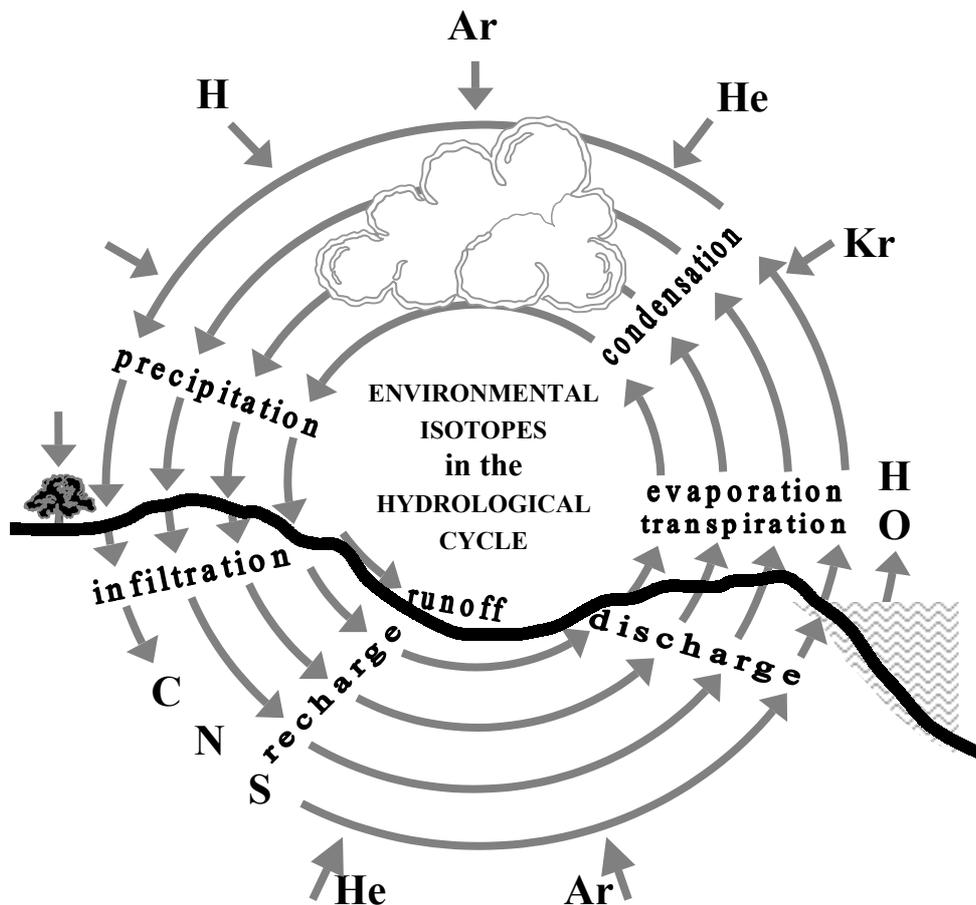
UNESCO/IAEA Series on

# Environmental Isotopes in the Hydrological Cycle

## Principles and Applications

÷

<b>Volume I</b>	<b>:Introduction: Theory, Methods, Review</b>
<b>Volume II</b>	<b>:Atmospheric Water</b>
<b>Volume III</b>	<b>:Surface Water</b>
<b>Volume IV</b>	<b>:Groundwater, Saturated and Unsaturated Zone</b>
<b>Volume V</b>	<b>:Man's Impact on Groundwater Systems</b>
<b>Volume VI</b>	<b>:Modelling</b>



### Contributing Authors

E.Müller, A.Hartmann, P.Trimborn, GSF-National Research Centre, Neuherberg, Germany -  
F.Decarli, J.Alvarado Rivas, Ministerio del Ambiente y de los Recursos Naturale Renovables

(MARNR) Caracas, Venezuela - A. Jiriez, University of Muta, Jordan -  
I. Sajjad, Pakistan Institut of Nuclear Technology, Rawalpindi, Pakistan

# PREFACE

The availability of freshwater is one of the great issues facing mankind today - in some ways the greatest, because problems associated with it affect the lives of many millions of people. It has consequently attracted a wide scale international attention of UN Agencies and related international/regional governmental and non-governmental organisations. The rapid growth of population coupled to steady increase in water requirements for agricultural and industrial development have imposed severe stress on the available freshwater resources in terms of both the quantity and quality, requiring consistent and careful assessment and management of water resources for their sustainable development.

More and better water can not be acquired without the continuation and extension of hydrological research. In this respect has the development and practical implementation of isotope methodologies in water resources assessment and management been part of the IAEA's programme in nuclear applications over the last four decades. Isotope studies applied to a wide spectrum of hydrological problems related to both surface and groundwater resources as well as environmental studies in hydro-ecological systems are presently an established scientific discipline, often referred to as "Isotope Hydrology". The IAEA contributed to this development through direct support to research and training, and to the verification of isotope methodologies through field projects implemented in Member States.

The world-wide programme of the International Hydrological Decade (1965-1974) and the subsequent long-term International Hydrological Programme (IHP) of UNESCO have been an essential part of the well recognised international frameworks for scientific research, education and training in the field of hydrology. The International Atomic Energy Agency (IAEA) and UNESCO have established a close co-operation within the framework of both the earlier IHD and the ongoing IHP in the specific aspects of scientific and methodological developments related to water resources that are of mutual interest to the programmes of both organisations.

The first benchmark publication on isotope hydrology entitled "Guidebook on Nuclear Techniques in Hydrology" was realised in 1983 through the activity of the joint IAEA/UNESCO Working Group on Nuclear Techniques established within the framework of IHP, and it has been widely used as practical guidance material in this specific field.

In view of the fact that the IHP's objectives include also a multi-disciplinary approach to the

assessment and rational management of water resources and taking note of the advances made in isotope hydrology, the IAEA and UNESCO have initiated a joint activity in preparation of a series of six up-to-date textbooks, covering the entire field of hydrological applications of natural isotopes (environmental isotopes) to the overall domain of water resources and related environmental studies.

The main aim of this series is to provide a comprehensive review of basic theoretical concepts and principles of isotope hydrology methodologies and their practical applications with some illustrative examples. The volumes are designed to be self-sufficient reference material for scientists and engineers involved in research and/or practical applications of isotope hydrology as an integral part of the investigations related to water resources assessment, development and management. Furthermore, they are also expected to serve as “Teaching Material” or text books to be used in universities and teaching institutions for incorporating the study of "isotopes in water" in general into the curriculum of the earth sciences. Additionally the contents can fulfil the need for basic knowledge in other disciplines of the Earth Sciences dealing with water in general.

These six volumes have been prepared through efforts and contributions of a number of scientists involved in this specific field as cited in each volume, under the guidance and co-ordination of the main author/co-ordinating editor designated for each volume. W.G.Mook (Netherlands), J.Gat (Israel), K.Rozanski (Poland), W.Stichler (Germany), M.Geyh (Germany), K.P.Seiler (Germany) and Y.Yurtsever (IAEA, Vienna) were involved as the main author/co-ordinating editors in preparation of these six volumes, respectively. Final editorial work on all volumes aiming to achieve consistency in the contents and layout throughout the whole series was undertaken by W.G.Mook (Netherlands).

Mr.Y. Yurtsever, Staff Member of the Isotope Hydrology Section of the IAEA; and Ms. A. Aureli, Programme Specialist, Division of Water Sciences of UNESCO, were the Scientific Officers in charge of co-ordination and providing scientific secretariat to the various meetings and activities that were undertaken throughout the preparation of these publications.

The IAEA and UNESCO thank all those who have contributed to the preparation of these volumes and fully acknowledge the efforts and achievements of the main authors and co-ordinating editors.

It is hoped that these six volumes will contribute to wider scale applications of isotope methodologies for improved assessment and management of water resources, facilitate incorporation of isotope hydrology into the curricula of teaching and education in water sciences and also foster further developments in this specific field.

Paris / Vienna, March 2000

# PREFACE TO VOLUME V

Water is an essential component of ecosystems and man's health. As the world population is growing, the need for more food, man's shift to urban areas and the progressive industrialisation all affect water resources in a qualitative and quantitative way. Connected to these general developments the following problems arise:

- water exploitation increasingly concentrates on local areas with high water demands at low cost;
- urbanisation contributes to the disequilibrium of groundwater recharge, either by sealing the surface against infiltration or by leakage processes from the underground water transport system;
- the groundwater quality is affected by leakage and accidental spills of liquid and solid wastes gathered in a few places, generally untreated or unconditionally released, thus presenting serious dangers of pollution;
- the excessive use of agrochemicals influences the natural functioning of both the soil and the aquifer, thus hampering the self-attenuation processes;
- emissions from fuel and waste combustion are concentrated in few places, in the vicinity of the emission source provoking strong and quasi immediate contamination, also in the more distant surroundings slowly increasing impacts on water resources and ecosystems by dry or wet deposition;
- the expansion of man's activities in arid and semi-arid regions often lead to the deterioration of resources, either by overexploitation or by desertification;
- deforestation disturbs the water balance and water quality, and enhances erosion.

Since water resources react on changes of land and water use with a long delay time, man's activities should be better adapted to basic hydrodynamic conditions in order to better satisfy the needs of a safe drinking water supply, flood protection, and the food and industrial production. Such basic hydrodynamic conditions comprise e.g. resource replenishment, steady state or transient dynamics and chemical stratification, which all may contribute to develop exploration and exploitation strategies that guarantee sustainable water availability in a qualitative and quantitative way.

It is well known that remediation techniques of water resources imply costly but crucial efforts with often low efficiency to restore the health of ecosystems and to provide a healthy water supply on the basis of existing guidelines. To avoid such efforts fundamental and

process-oriented research on the physical, chemical, microbial and hydraulic behaviour of water resources must advance to provide effective and long-term strategies of water resource protection.

Hydrogeological research is strongly interdisciplinary and based on geological, hydraulic, hydrochemical, microbial and isotopic research, each with its specific efficiency and scope of application.

- geological investigations provide essential boundary conditions for setting up and developing conceptual models for strategic mathematical modelling,
- hydraulic investigations provide system inherent parameters, generally based on local information, that must be extrapolated into time and space and, therefore, need long-term data series; these are to be processed statistically by mathematical models to approach a better understanding of the system dynamics;
- environmental isotopes introduce space and time integral information that may close the gap and provide the link between missing data series;
- hydrochemistry brings information on the reactive behaviour of water constituents and certain compounds in the water reservoir;
- microbial and chemical studies are needed to understand the resilience (natural attenuation capacity) of water resources.

Since in many areas of the world relevant long-term data on water resources are missing, the traditional and isotope methods in combination with mathematical modelling often answer pressing questions about groundwater origin, chemical reactions, fluxes, ages and mixing processes occurring in reservoirs, naturally and caused by man. Only on this basis can relevant strategies for exploration, exploitation and protection of subsurface waters be developed.

This volume aims to demonstrate how the choice of applying combined disciplines and methods should be made in the case of specific, man-made perturbations of the natural environment.

Neuherberg, March 2000

K.-P. Seiler

# CONTENTS

<b>1</b>	<b>POLLUTION SUSCEPTIBILITY OF AQUIFERS AND POLLUTION ASSESSMENT</b>	<b>1</b>
1.1	Introduction.....	1
1.2	Role of groundwaters in human and ecosystem sectors.....	2
1.3	Transport potential of discharge components .....	4
1.4	Rock properties and the susceptibility of aquifers to contaminants.....	6
1.5	Reactive behaviour of pollutants in aquifers.....	8
1.6	Microbial activities in aquifers.....	10
1.7	Dynamics of groundwater in aquifer systems .....	11
1.8	Contaminant sources .....	19
<b>2</b>	<b>GROUNDWATER EXPLOITATION AND OVEREXPLOITATION</b>	<b>21</b>
2.1	Groundwater abstraction from deep wells in the Molasse Basin of S. Germany	28
2.1.1	Introduction.....	28
2.1.2	The TNL in the study area .....	28
2.1.3	Hydrodynamic flow field in the vicinity of deep wells .....	30
2.2	The origin of saline ground waters in the area of the Valenci lake, Venezuela .	32
2.2.1	Introduction.....	32
2.2.2	Hydrogeologic overview. ....	33
2.2.3	The origin of groundwaters.....	34
2.2.3.1	Hydrochemistry and isotopes E. and SE of the lake.....	34
2.2.3.2	Groundwater W. and N. of the lake .....	36
2.2.4	Water balance for the study area.....	37
<b>3</b>	<b>IRRIGATION AND THE IMPACT ON GROUNDWATER QUALITY</b>	<b>41</b>
3.1	The impact of irrigation on percolation in dry lands with various sediments .....	43
3.1.1	Experimental boundary conditions and performance .....	44
3.1.2	Discussion of results on percolation .....	45
3.1.3	The contribution of irrigation and channel waters in the area between Chenab and Ravi, Punjab, to groundwater logging .....	53
<b>4</b>	<b>IMPACT OF URBANISATION ON GROUNDWATER</b>	<b>55</b>
4.1	Groundwater management below the city of Caracas, Venezuela .....	56
4.1.1	Geology of the Caracas valley .....	57
4.1.2	Water balance and the origine of groundwaters beneath the city .....	58
4.1.3	Stable isotope concentrations in the groundwater .....	58
4.1.4	Dynamics of the groundwater .....	59
4.1.5	Contaminants in the groundwater .....	61

<b>5</b>	<b>IMPACT OF LAND USE ON GROUNDWATER QUALITY</b>	<b>65</b>
5.1	The role of sediment facies in storage and disintegration of agrochemicals in the karst of South Germany.....	66
5.1.1	Introduction.....	66
5.1.2	The malm carbonates of the Franconian Alb.....	67
5.1.3	Results of tracer experiments.....	67
5.1.4	The dilution of dye tracers.....	68
5.1.5	Tritium in groundwaters from bedded and reef facies.....	70
5.1.6	Fate of nitrates in the reef facies.....	71
5.1.7	Bacterial populations in the underground.....	71
5.1.8	Laboratory denitrification experiments.....	73
<b>6</b>	<b>SAMPLING OF WATER – QUANTITIES, METHODS, POINTS OF ATTENTION</b>	<b>77</b>
6.1	Well construction and sampling.....	77
6.2	Sampling devices.....	79
6.3	Sampling quantities and water storage.....	80
6.4	Sampling of seepage waters.....	81
<b>7</b>	<b>OUTLOOK TO FURTHER APPLICATIONS</b>	<b>85</b>
	<b>REFERENCES</b>	<b>87</b>
	<b>LITERATURE</b>	<b>95</b>
	<b>IAEA PUBLICATIONS</b>	<b>97</b>
	<b>CONSTANTS</b>	<b>100</b>
	<b>SYMBOLS AND UNITS</b>	<b>101</b>
	<b>SUBJECT INDEX</b>	<b>103</b>

# 1 POLLUTION SUSCEPTIBILITY OF AQUIFERS AND POLLUTION ASSESSMENT

## 1.1 INTRODUCTION

The largest reservoirs on earth are formed by groundwater, the oceans and the atmosphere; for the most part, the atmosphere and to some extent groundwater are transient and the oceans are mostly final depots for pollutants.

In many areas of the world, groundwater is the only resource available for irrigation, for manufacturing industrial and agriculture products, for producing energy and also for domestic use. This is especially true for semi-arid and arid regions (dry lands) with their characteristic wide basins as well as for all regions with infiltration capacities (e.g. soluble rocks and Quaternary gravels) higher than for generating runoff. A review of the average distribution of waters on the continents is given in [Table 1.1](#).

**Table 1.1** Review of approximate freshwater quantities on the Earth. Ice is not considered.

<b>Groundwater</b>	96.3 %	8 000 000 km <sup>3</sup>
<b>Lake water</b>	2.7 %	226 000 km <sup>3</sup>
<b>Soil Moisture</b>	0.8 %	62 000 km <sup>3</sup>
<b>Air Humidity</b>	0.2 %	15 000 km <sup>3</sup>
<b>River water</b>	0.01 %	1 000 km <sup>3</sup>
<b>Annual average discharge from continents</b>		<b>45 000 km<sup>3</sup></b>

Comparing the groundwater quantities with the annual discharge from the continents ([Table 1.1](#)) and assuming both that discharge contributes totally to groundwater recharge and that all of the groundwater participates evenly in the subsurface water cycle, the minimum turnover time would be ca. 180 years; in case of smaller groundwater recharge this turnover time increased. With these assumptions, the groundwater reservoirs on the continents had a tremendous dilution capacity and would not yet significantly show measurable effects of

pollutants released since the beginning of the industrial age. Although this holds true for certain regions of the continents, in general this is not the case. Obviously on a short-term and a long-term groundwater responds systematically different to contamination impacts. The causes for this are diverse and lie in

- the transport and export potential of overland flow, interflow and groundwater recharge,
- the intensity, with which the groundwater of different aquifers in different depths is incorporated in the subsurface branch of the water cycle and is exploited by men,
- the hydrodynamic and dilution properties of aquifers and aquifer systems,
- particle favoured transport mechanisms,
- the physical and chemical behaviour of pollutants at the solid-liquid interface,
- microbial activities in biofilms in the underground and
- the intensity of the pollution sources.

All these parameters and their influence on groundwater pollution must be considered from a short-term and long-term point of view in order to elaborate actual as well as sustainable strategies of groundwater management and protection measures. These information have to be obtained using traditional hydrogeologic, hydrochemical, artificial and environmental tracer methods in combination and must be linked to mathematical modelling.

In the acquisition and use of these parameters small- and large-scale information must be distinguished. On the small scale mostly process oriented studies are executed in very detail; in the large scale weighted processes are considered; only the latter results can be regionalised.

## **1.2 ROLE OF GROUNDWATERS IN HUMAN AND ECOSYSTEM SECTORS**

The importance of groundwater becomes obvious, if one looks at its usage in the different continents (Table 1.2); surface water usage is also included in this account. Table 1.2 shows (Global 2000), that in the developing countries the demand for irrigation water is the highest. In the industrialised nations, however, the demand for water for energy and industrial production is the highest; world-wide, the water used for human consumption is the lowest. The totalled average water demand in 1980 of ca. 3000 km<sup>3</sup>/year amounts to only 6%, the drinking water demand to only 0.5% of the average yearly discharge from continents. Recent statistics prove an increase of global water demand in 1996 to 5500 km<sup>3</sup> corresponding to a total water demand per capita of 1000 m<sup>3</sup>/year. As compared to this number the individual water demand for households is about 55 m<sup>3</sup>/year and the demand for drinking and food processing about 5 m<sup>3</sup>/year. Of course, these statistics do not incorporate the uneven

distribution of renewable waters in the different climatic and geological zones on earth. It was, however, also a misuse to import water on a large scale to water-scarce regions or to produce excessively fresh water by desalinisation, because this would create new problems linked to waste waters and changes in the infiltration water quantities.

Besides **water quantity** problems we are often faced with **water quality** problems. Water quality is primarily dependent upon geogenic factors and is nowadays also strongly influenced by anthropogenic factors. There exist international standards ([WHO 1997](#)) for the quality of irrigation, drinking and surface waters in order to sustain

- 1) soil fertility, plant growth and soil biodiversity,
- 2) human health and
- 3) the self cleaning potential of subsurface and surface waters.

These standards also contribute to some extent to protect the atmosphere and the oceans from contaminants released from subsurface waters. Demands on groundwater quality are the highest for drinking water as well as for waters for food processing and much lower for all the other water usage. Some of the most important anthropogenic factors on groundwater quality are that

- the used water can not (e.g. after irrigation) or often is not treated (e.g. waste water from industry or households) or enters the water cycle by hazards,
- low quality waters are attracted by overexploitation and
- agrochemicals are excessively used.

World-wide, this led to a decrease in the water quality on the continents especially in coastal, agricultural and urban regions.

In many regions of the world, the high demand for water for non-domestic use has drawn away attention from maintaining groundwater quality and by that way led to an unequilibrated competition between water usage for production purposes, consumption and maintenance of the natural ecological elements and functions for self cleaning processes within water resources.

By nature, groundwater close to the land's surface is low in nutrients and rare elements. Due to anthropogenic impacts, however, groundwater can suffer considerable losses in quality. Generally, these appear only slowly underground and once begun, these processes require much more time to fade away than they needed to build up.

Today's refined techniques to use groundwater, the prevailing production- instead of ecosystem-oriented usage of water resources and the lack of sewage water treatment in many countries, have significantly reduced the available waters for the private sector and for food processing. Therefore, it has become important to evaluate the susceptibility and vulnerability

of the groundwater reservoirs, when developing, exploiting, protecting and managing these resources.

**Table 1.2** Water demand statistics for individual regions in km<sup>3</sup> (Global 2000).

	<b>Irrigation</b>	<b>Energy production</b>	<b>Industrial production</b>	<b>Households</b>	$\Sigma$
<b>Asia</b>	1400	68	31	98	1597
<b>Africa</b>	61	11	4	12	88
<b>Australia</b>	13	8	6	2	29
<b>South America</b>	35	6	4	11	56
<b>North America</b>	205	232	77	38	552
<b>Europe</b>	116	176	184	40	516
$\Sigma(1980)$	1830	501	306	201	2838
$\Sigma(1996)$					5500

### 1.3 TRANSPORT POTENTIAL OF DISCHARGE COMPONENTS

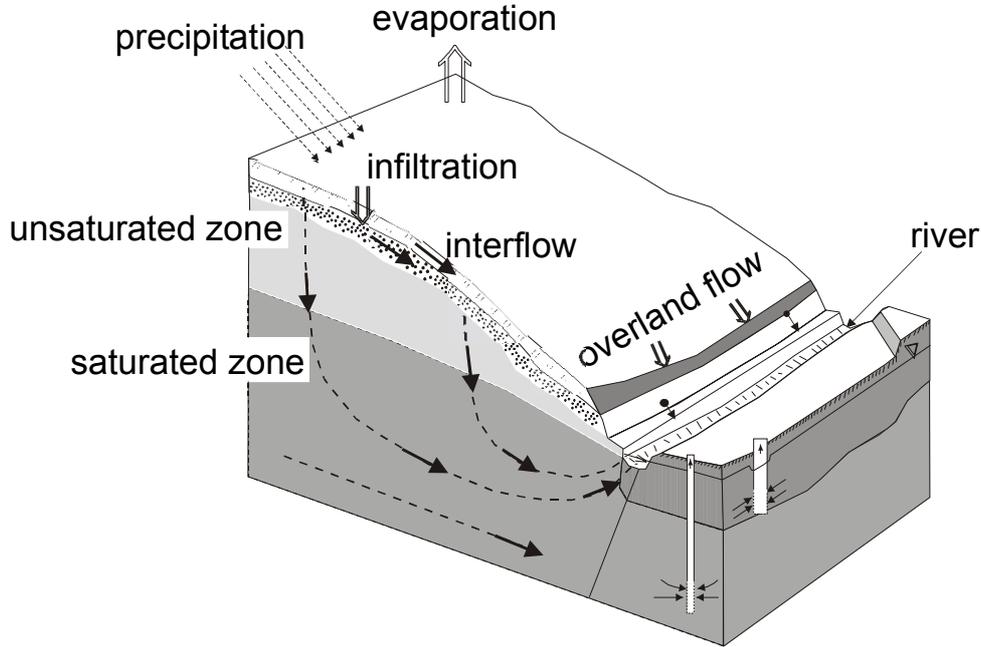
Discharge on continents is made up of a maximum of four components (Fig.1.1)

- 1) evapotranspiration
- 2) overland flow
- 3) interflow and
- 4) groundwater recharge.

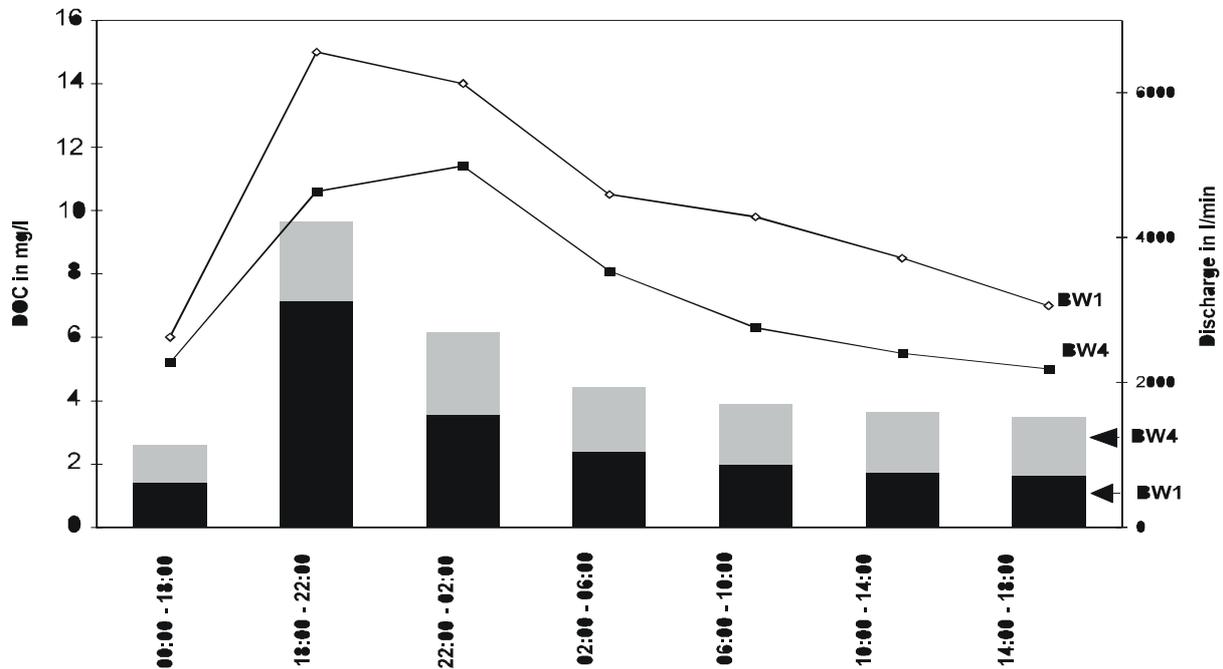
All of these discharge components occur in consolidated, fissured and unconsolidated sediments. They transport dissolved pollutants or, after remobilisation, sorbed pollutants with slow sorption kinetics (Fig.1.2). The impacts on ground and surface waters are therefore quite variable. The main pools of contaminants for these discharge components are waste disposals, cultivated soils and the effective root zone beneath (Luckner 1994).

Overland flow and interflow are mostly found in sediments and soils of hilly terrains with limited infiltration capacity; they rarely occur in flat areas. Under normal precipitation

conditions both of these discharges develop flow velocities of decimetres to meters per day. Contrary, groundwater recharge (matrix flow) in non-fissured sediments has flow velocities of less than millimetres per day; in this respect flow velocities in the matrix of the seepage zone and the passive groundwater recharge zone (Sect.1.7) are similar to some extent.



**Fig.1.1** Block diagram of a landscape with the four most important discharge components.



**Fig.1.2** Humate discharge after a precipitation event. BW1 = 100% firs, BW4 = 80% firs and 20% agriculture. The DOC concentrations during discharge events are higher than in the unsaturated zone beneath the effective root zone, but equal the DOC in soil waters of the effective root zone. DOC has a high co-transport potential for heavy metals, agrochemicals and organics.

Infiltration always produces slow matrix flow (millimetres per day) (Hillel 1971, Feddes et al. 1988) and quick bypass (preferential) flow (meters to decimetres per day) (Beven & German 1982, White 1985, German 1990, van Genuchten 1994). Bypass-flow either transforms into slow matrix flow by existing capillary gradients - in hilly terrains with permeability discontinuities paralleling the morphology - or produces interflow with mean residence times close to overland flow. This interflow can flush a considerable amount of pollutants and particles from soils (Matthess et al. 1991, Kim et al. 1994) and the effective root zone, thus contributing to some extent to groundwater protection. On the other hand, it often leads to shock impacts (Fig.1.2)

- to rivers, ponds and lakes in hilly terrains as well as
- to groundwater in plains with a water table close to the land's surface.

Flow components are separated by classical hydrograph (Linsley et al. 1949) as well as by chemical and environmental isotope methods (Sklash et al. 1976, Sklash & Vervolden 1979, Kendall & McDonnal 1998). Comparison of both methods shows that they are based on different basic assumptions and, therefore, do not necessarily provide congruent results. Hydrograph separation is only based on differences in flow velocities or mean residence times; on the contrary, isotope and chemical methods include also mixing processes between storm and chemically or isotopically equilibrated pre-storm waters both from the unsaturated and saturated zone. This mixing takes place to some extent independent of flow velocities by concentration gradients driving molecular diffusion exchanges. Therefore, hydrograph separation methods usually deliver more direct discharges (overland flow + interflow) than chemical and isotope methods.

Hydrograph separation is a reliable tool if only few flow components with very distinct and different mean residence times produce discharge during storm events in a catchment area; it mostly applies to separate quick and slow discharges and does not clearly relate to any further specific process, as chemical and isotope separation does.

## **1.4 ROCK PROPERTIES AND THE SUSCEPTIBILITY OF AQUIFERS TO CONTAMINANTS**

Water bearing rocks are called aquifers and normally they are subdivided into unconsolidated and consolidated aquifers (see Volume IV). Unconsolidated aquifers are generally porous, but may have uneven pore size distributions resulting in remarkable differences between total and hydrodynamic effective porosities. Consolidated aquifers, on the other hand, were physically or chemically solidified after sedimentation (sedimentary rocks) or crystallised (crystalline rocks) by metamorphic or complete melting processes. They got fissured (secondary porosity) by cooling process, mostly, however, as a consequence of tectonic stress. In soluble rocks, the fissures can widen into solution cavities (carbonate and gypsum karst). Some of the consolidated aquifers have also a primary porosity, such as e.g. many sandstones, carbonate

reefs, or Cretaceous chalks (Stille 1903, Seiler 1969, Matthes 1970, Seiler et al. 1991). Rocks with fissures and matrix pores are classified as heterogeneous-porous or biporous media, in which flow velocities are not continuous, but have usually a pronounced bimodal or polymodal frequency distribution, often resulting in very short and quite long residence times of groundwaters site by site.

The role of rock porosities (pores, fissures, solution cavities) with regard to any pollutant behaviour and thus the susceptibility of the aquifers to pollution is closely connected with the groundwater flow velocities and the hydrodynamic dispersion.

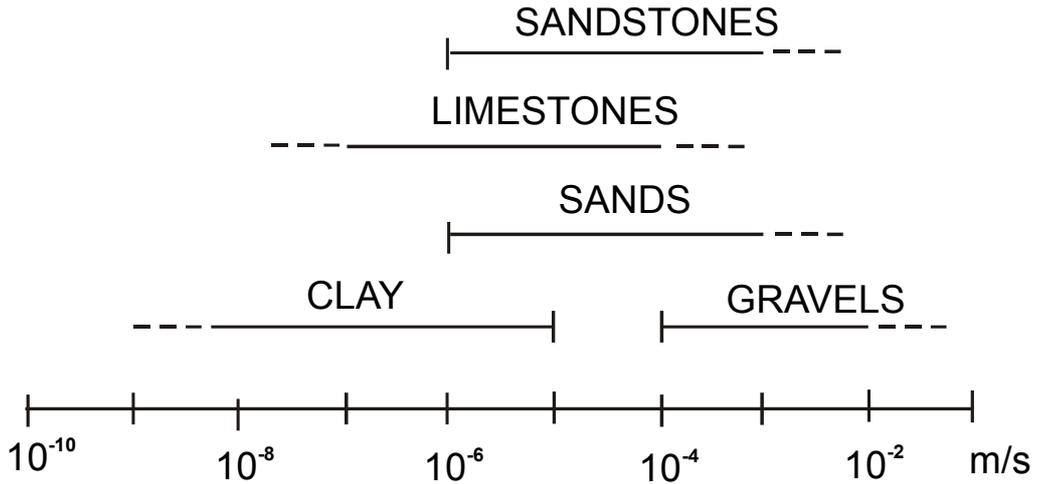
- 1) The movement of the groundwater is positively correlated with the groundwater recharge and the geometry of the rock pores. In general, the hydraulic conductivity of the rock changes proportionally to the square of the porosity. The proportionality constant is closely coupled with the sediment genesis and the subsequent diagenesis of the rocks. Fig.1.3 gives a review of some often occurring rock hydraulic conductivities.
- 2) Pollutions become diluted in aquifers by hydrodynamic dispersion or by mixing processes. The larger the rock pores are and the less sediment structures are obstacles for groundwater flow, the lower is the lateral hydrodynamic dispersion. Examples for the hydrodynamic dispersion of non-reactive tracers are shown in Fig.1.4 (Lallemant-Barres & Peaudecerf 1978, Freeze & Cherry 1979, Seiler 1985, Seiler et al. 1989, Glaser 1998).

All these aquifer parameters are either deduced from hydraulic tests or have been measured with non-reactive tracers. Both methods, however, give only local or sectoral insights into the subsurface system and must apply to many points in the catchment to issue representative, catchment wide information.

In biporous media (heterogeneous-porous media), in addition to the hydrodynamic dispersion, there is also a preferential lateral component (Foster 1975, Sudicky & Frind 1981) stimulated by molecular diffusion. As a result molecular diffusion enhances the dilution process

- as long as a concentration gradient exists between the draining (e.g. fissures) and storing section (e.g. porous matrix) in heterogeneous-porous media,
- the larger the hydraulic conductivity differences and the longer the flow distances are getting and
- the higher the matrix porosity and the lower the flow velocity is.

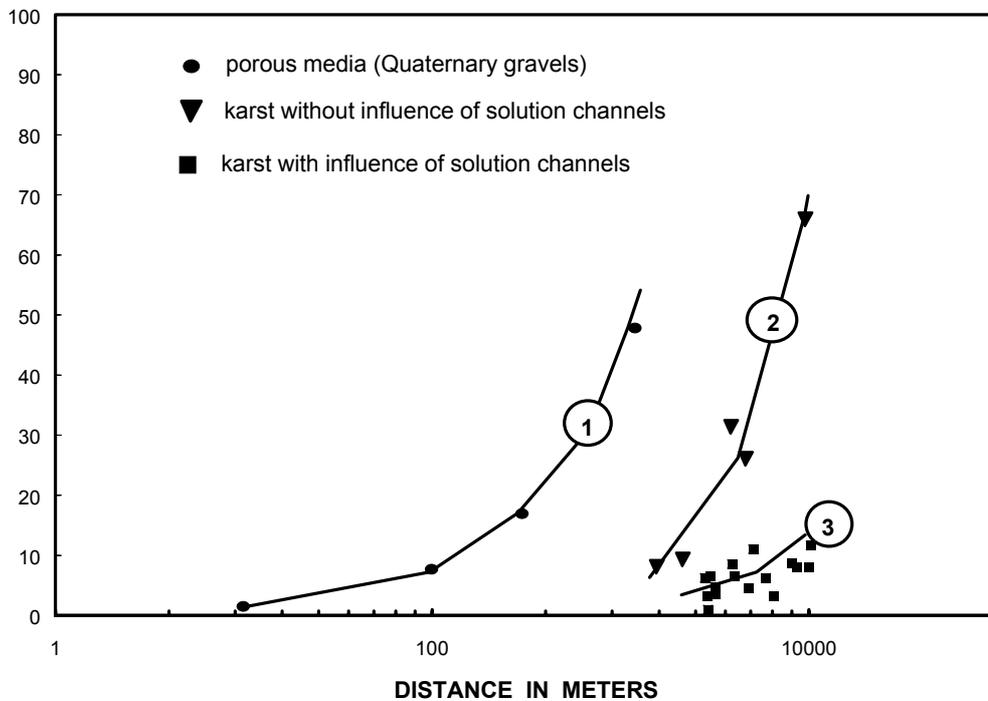
The geologic boundary conditions of heterogeneous-porous media can lead to a creeping pollutant charge in rocks, which cannot be discovered in time using only conventional investigations of groundwaters. Through a suitable combination of classical hydrogeological, geochemical, tracer and environmental isotope investigations (Sect.5.1), the process of charge of the matrix with pollutants can be determined and process-orientated numerically modelled (Sudicky & Frind 1981, Maloszewski & Zuber 1985, Seiler et al. 1991).



**Fig.1.3** Overview of hydraulic conductivities in various types of rock.

## 1.5 REACTIVE BEHAVIOUR OF POLLUTANTS IN AQUIFERS

Non-reactive or conservative pollutants do not interact with the rock matrix and are not transformed or disintegrated by chemical and microbial reactions; they flow as water does. Most of the environmental isotopes, especially those being part of the water molecule ( $^2\text{H}$ ,  $^3\text{H}$ ,  $^{18}\text{O}$ ), belong to this group.



**Fig.1.4** Dispersivities of non-reactive tracers in solution cavities (bottom curve), in gravels (middle curve) and in fissured-porous reef rocks.

On the contrary, reactive pollutants undergo chemical, microbial or physical reactions in the unsaturated zone and in aquifers. They experience changes either in chemical species or become vaporised or sorbed on surfaces of the rock matrix, thus diminishing their initial concentration in the liquid phase. All these processes may occur either instantaneously or with slow kinetics; they depend on the chemical environment, especially on pH and Eh, and may be reversible or not.

Porous aquifers with a very high specific surface contribute much more to sorption than fissured aquifers without matrix porosity. With respect to the mineralogy of aquifers, clay minerals, especially montmorillonites, and Fe-, Mn- and Al-mixed oxides favour the retention of cationic and anionic pollutants. Since under natural conditions the migration of geogenic substances that may harm water quality is not abundant in groundwaters within the active recharge zone, sorption capacities never have been exhausted within very long time scales.

This may change with anthropogenic emissions of pollutants in high concentrations in the long run. Instantaneous sorption processes may be described by comparing the tracer velocity ( $v_{\text{tracer}}$ ) with the pollutant velocity ( $v_{\text{pollutant}}$ ); this ratio is defined as the retardation factor  $R_f$  and applies as far as sorption is an instantaneous process

$$R_f = \frac{v_{\text{tracer}}}{v_{\text{pollutant}}} \quad (1.1)$$

The retardation factor equals or exceeds 1; only in the case of any self motion of e.g. bacteria (Alexander & Seiler 1983), of very high molecular diffusion, or of ion exclusion it may drop to values between 0.9 and 1.

Instantaneous sorption may also be characterised by the distribution coefficient  $K_d$ , relating the pollutant concentration  $C_{\text{solid}}$  fixed on solid surfaces to the pollutant concentration in the liquid phase  $C_{\text{liquid}}$ :

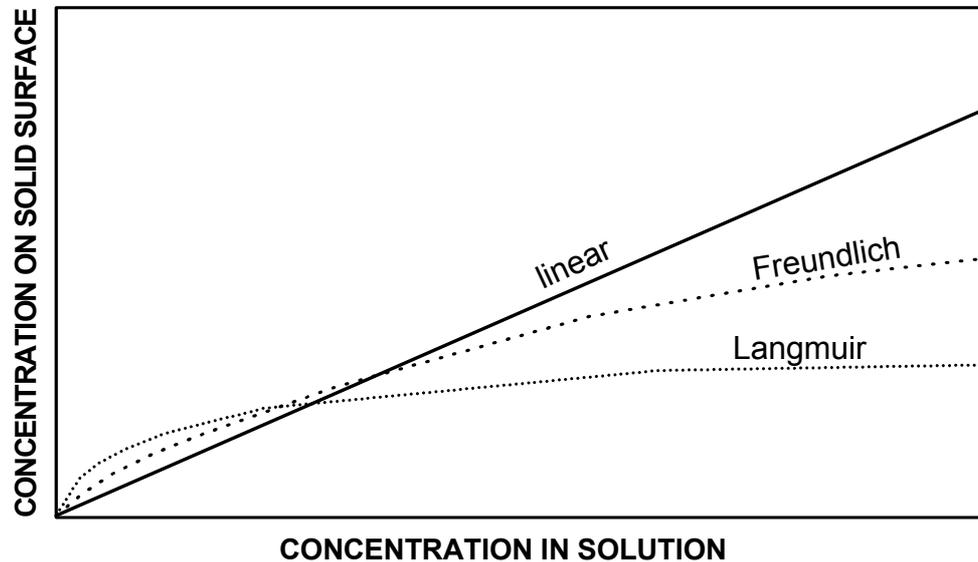
$$K_d = \frac{C_{\text{solid}}}{C_{\text{liquid}}} \quad [\text{cm}^3/\text{g}] \quad (1.2)$$

Retardation factor and distribution coefficient in water rock systems are related by

$$R_f = 1 + \frac{K_d \gamma}{p} \quad (1.3)$$

Additionally to instantaneous reactions this concept of retardation for numerical modelling supposes linear sorption isotherms or very low concentrations of pollutants to approximate linear sorption. Very often, however, sorption follows either Langmuir or Freundlich (Fig.1.5) or even more complicated isotherms. As a rule highly contaminated groundwaters do not

follow this simple concept and kinetics of reaction should be introduced in numerical models using mostly reactions of the first order. Often, however, data sets are insufficient and the reactive behaviour can only be approximated.



**Fig.1. 5** Typical isotherms to describe instantaneous sorption.

## 1.6 MICROBIAL ACTIVITIES IN AQUIFERS

Common scientific teaching states that aquifers and most of the unsaturated zone are poor in micro-organisms. In contrast, the soil zone with abundant organic material has a very high, microbial disintegration potential. Since the soil has a limited retention potential due to bypass-flow exporting pollutants from soils into ground- and surface waters (Sect.1.3), the self cleaning processes would become slowed down below the soil zone, thus decreasing the ability of subsurface systems in digesting pollutants. Recent research, however evidenced that about 92% of all micro-organisms life subsurface and 8% at continental surfaces and the oceans (Müller 1999).

It is known from recent investigations, that the unsaturated zone beneath the soil and above the capillary fringe has a pronounced filtering capacity for micro-organisms (Schaefer et al. 1998) with body sizes e.g. of bacteria ranging between 0.5 and 5  $\mu\text{m}$ ; therefore, this zone is poor in microbial activities, especially at low water contents. Significant microbial activities, however, exist again in the capillary fringe of the unsaturated zone (Rietti-Shati et al. 1996) and in aquifers with slow groundwater movement, as well as in heterogeneous-porous aquifers like karst (Sect.5.1), sandstone, chalk and gravel aquifers with disconform grain size distributions (Seiler & Alvarado 1997). The link between the soil zone and the capillary

fringe for microbial transports very probably is provided by bypass-flow transporting 20 - 50% of infiltrated waters quickly either to ground or to surface waters (Sect.1.3).

Most aquifers appear to have originally a microbial population small in numbers, which can increase as a whole or selectively, as soon as nutrient (N, C, P) and energy sources are available. This can easily or effectively happen through the influx of organic and inorganic pollutants, disintegrating after a certain incubation time through this increase of the microbial population (Sect.4.1 and 5.1).

Most micro-organisms are fixed on solid surfaces (>90%) and become active in the reductive environment of biofilms (few tens of micrometers in thickness and mostly discontinuous in appearance). The ongoing reduction processes in biofilms can often not be recognised by redox measurements in the flowing groundwater. However, using the stable isotopes  $^{34}\text{S}$ ,  $^{15}\text{N}$  and  $^{18}\text{O}$  in  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ , the disintegration process in biofilms is reflected by a respective isotope fractionation with an increase of the isotope concentrations in the low energetic and a decrease in the high energetic phase, respectively (Sect.5.1.8).

Microbial activities as a rule increase the elasticity (resilience) of the underground system. The extent of this elastic behaviour

- depends on the intensity of the land use and
- on the release of the pollution source, and
- will become limited by a too fast increase of the pollutant concentrations.

## 1.7 DYNAMICS OF GROUNDWATER IN AQUIFER SYSTEMS

We have to clearly distinguish between infiltration of precipitation and groundwater recharge (Sect.1.3), although infiltration may contribute to groundwater recharge as well. However, in arid to semi-arid regions of the world infiltration often contributes only to the unsaturated zone and does mostly not break through to the groundwater table.

A portion of the existing groundwater (Table 1.1) is directly recharged by infiltration of precipitation or undergoes indirect recharge (bank filtration, artificial groundwater recharge, see Volume III); the majority of the groundwater belongs to a long-term reserve (Toth 1963, Freeze & Witherspoon 1967, Toth 1995, Seiler & Lindner 1995, Alvarado et al. 1996). On a long run, only the recharged portion of groundwater is available for management purposes comprising water supply as well as the conservation of important ecological functions of groundwaters returning to the surface. Any management of the long-term reserve (groundwater mining), which started recently in many countries of the world, presents mostly an irretrievable groundwater consumption that is often followed by quality degradation.

Groundwater recharge occurs in all regions of the continents; the desert regions (Verhagen et al. 1973) receive very small amounts ( $< 5$  mm/a) very irregularly, the tropical regions receive an annual average of less than 150 mm and the humid regions an annual average of less than 300 mm. Recent investigations even have shown that groundwater recharge occurs also through permafrost, albeit only little.

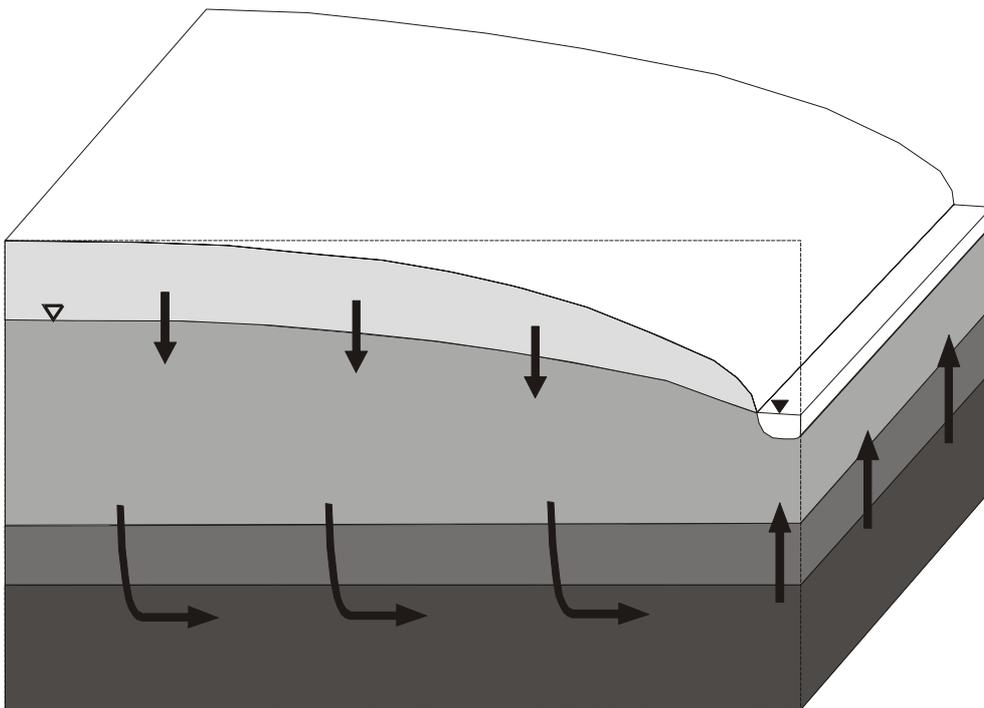
However, this groundwater recharge, which can also transport pollutants into the underground, does not flow through the entire thickness of the aquifers. Instead, it predominantly flows through the aquifer systems close to the groundwater surface (Seiler & Lindner 1995).

The groundwater flows in aquifer systems that each has its individual hydraulic properties. In unconsolidated aquifers, the hydraulic conductivity and porosity generally decrease with increasing depth; statistically, also the hydraulic conductivities of the fissures decrease with depth. Only in areas with deep reaching tectonic faults high hydraulic conductivities of fissures may reach several 1000 m of depth. This general and discontinuous decrease in the hydraulic conductivities with depth has soil and rock mechanical reasons. Therefore, the groundwater recharge is not distributed equally among all aquifers: it focuses on high conductive near surface layers.

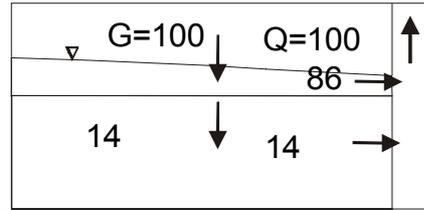
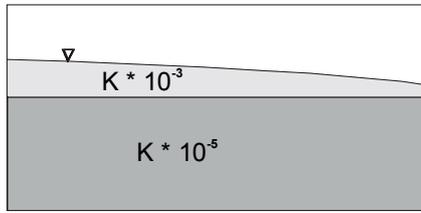
To represent the quantitative turnover of groundwater recharge in the individual sections of aquifer systems (Fig.1.6), the groundwater movement between the underground water divide and the receiving stream with layers of different hydraulic conductivities has been simulated numerically in two dimensions ( $z = 400\text{m}$ ,  $x = 15000\text{m}$ ). In these examples the groundwater surface receives a recharge of 150 mm/a, having access to each of the geologic layers. Finally the groundwater reaches the receiving stream as surface discharge. The numerical simulation of scenarios with generally known hydraulic conductivity/depth distributions (Fig.1.7) and the calculated amounts of groundwater turnover in the individual layers (in percent of groundwater recharge) leads to the conclusion, that generally more than 85% of it occurs in near-surface layers and that less than 15% of the groundwater recharge reaches also deeper lying aquifers. Related to this, groundwaters in near-surface aquifers are relatively young and always old in the deeper aquifers ( $>100$  years). Thus, groundwater recharge is divided into an active, near-surface zone, and a passive, deep groundwater recharge zone (Fig.1.8), both occurring world-wide. Only in dry lands groundwater recharge is often of a patchy type and the active and passive recharge zone are not easy to distinguish. In semi-arid regions, the active groundwater recharge zone has a thickness of a few metres or decimetres, increases in the tropics to few metres or decametres and is in humid areas less than 100 m thick; the thickness of the active recharge zone finally depends upon effective recharge and the storage, drainage properties of the aquifer system in which it occurs.

The passive groundwater recharge zone can achieve a thickness of several 100 m and is underlain by the connate groundwaters or formation waters (v. Engelhardt 1960). These are groundwaters, which did not return into the biosphere for millions of years (Fig.1.8).

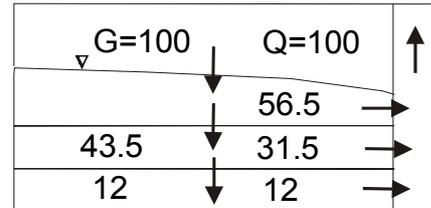
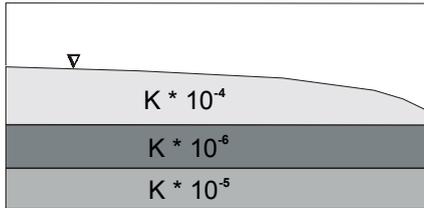
As a consequence of the above considerations groundwater recharge as determined by field measurements mostly refers to near-surface groundwater systems; effective groundwater recharge diminishes with depth. If in deep groundwater exploitation no notice is taken of this depth related distribution of groundwater recharge, significant and on a long run transient changes occur in the groundwater flow field.



**Fig.1.6** The modelling plane for representing the influence of hydraulic conductivity distributions in rocks upon the distribution of groundwater recharge in the individual layers. A groundwater recharge of 150 mm/a was assumed with no overland and bypass discharge, no interflow and no underflow of the receiving stream.

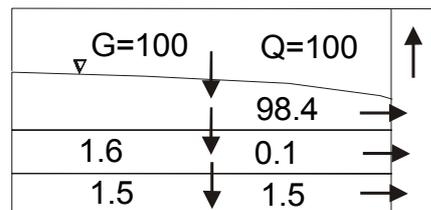
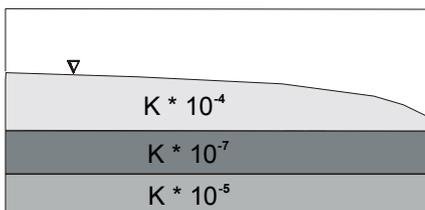
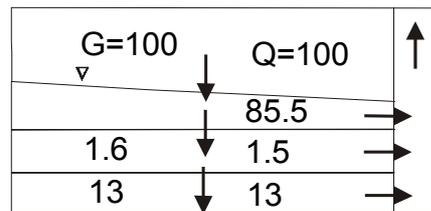
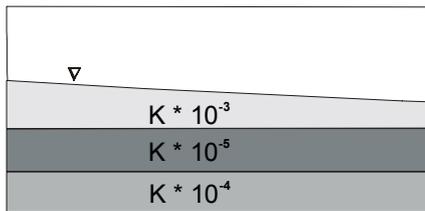


Permeabilities (k)  
in m/s

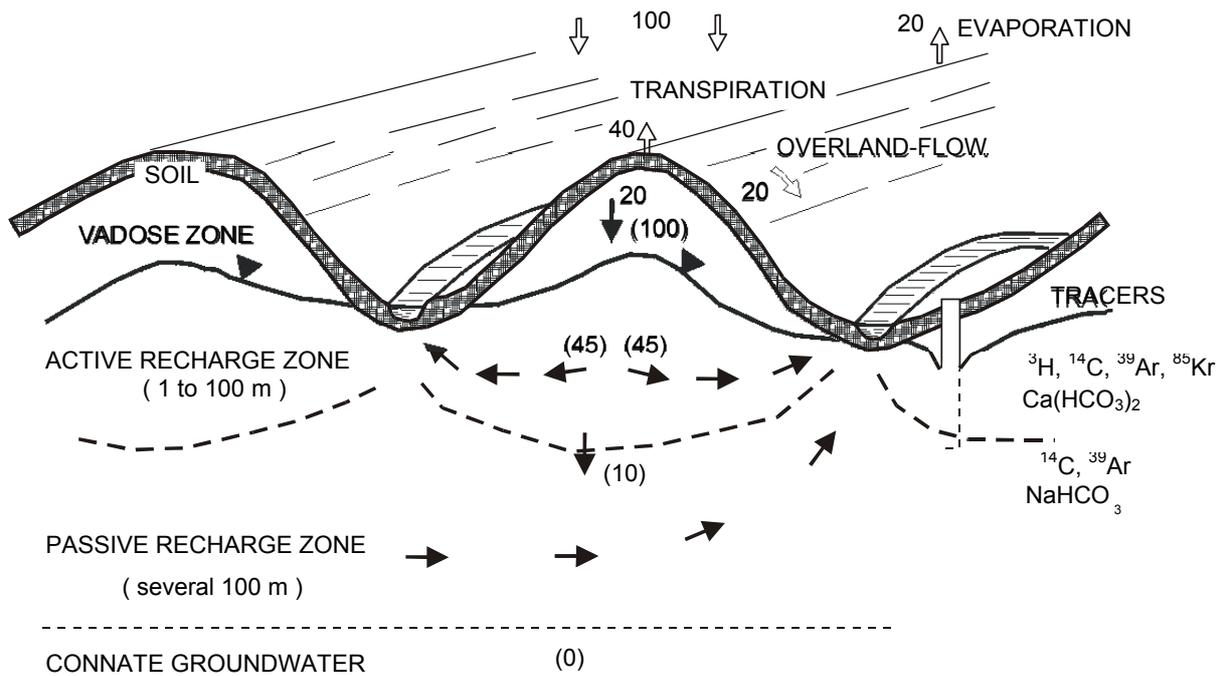


Recharge G = 100 ‰

Discharge Q = 100 ‰



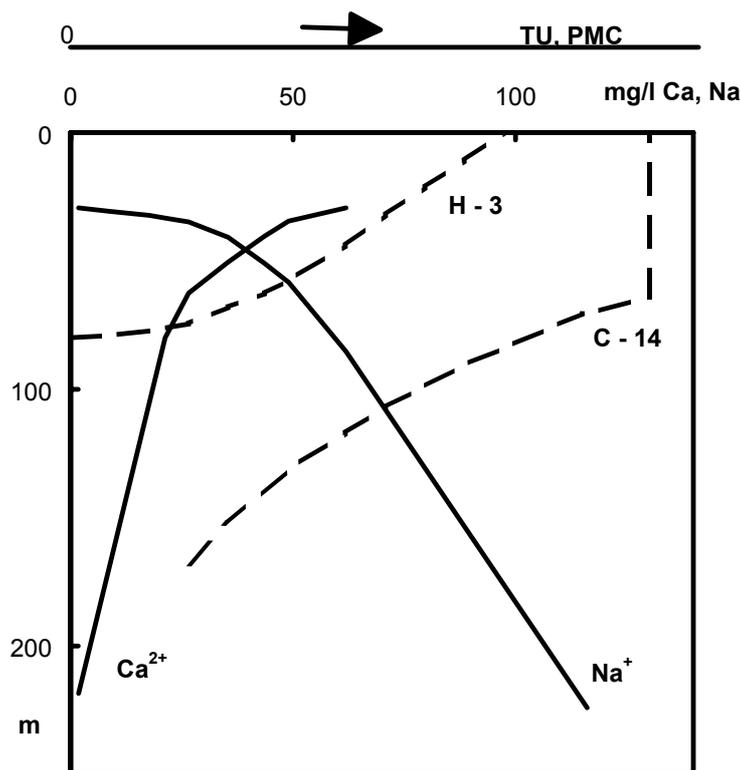
**Fig.1.7** Selected examples of hydraulic conductivity series, as frequently occurring in nature (left columns) and the distribution of the groundwater recharge (in percent of recharge) upon the individual layers. G = recharge, Q = discharge.



**Fig.1.8** Subdivision of aquifer systems in active and passive groundwater recharge zones and connate groundwaters (not to scale). 100 = 100% of precipitation, (100) = 100% of groundwater recharge.

As far as pollution is concerned, near-surface aquifer systems offer easy access, whereas the deep aquifers beneath dispose of a long-term significant dilution and reaction potential covering hundreds and thousands of years. This is often disregarded in planning groundwater extraction measures, which then may lead to significant hydraulic short cuts between aquifers producing an undesired access of either polluted or high mineralised waters to deep groundwater systems.

The interface between the active and passive recharge zone can be identified by very sudden changes in the concentrations of  $^3\text{H}$ ,  $^{14}\text{C}$  and ion exchange waters ( $\text{Ca}^{2+}$  replaced by  $\text{Na}^+$ ) (Fig.1.9), all indicating an abrupt change in groundwater ages. If isochrones are incorporated in the numerical simulation of scenarios (Fig.1.10), it can be seen that water ages indeed change rapidly from near-surface, to deep aquifers, i.e. from the active to the passive groundwater recharge zone. It is practicable to define the boundary between these two zones with  $^3\text{H}$ . To do this, the TNL (Tritium-Null-Line, Tritium nought line) is defined as an interface below which the  $^3\text{H}$  concentrations have fallen to values under the usual detection limit (Seiler & Lindner 1995) of  $\pm 0.5$  TU. Frequently this boundary is also defined with the saltwater/freshwater interface under the continents (Richter & Lillich 1975). This requires, however, that salt rocks exist within the rock sequence and reach from beneath till the active groundwater recharge zone.

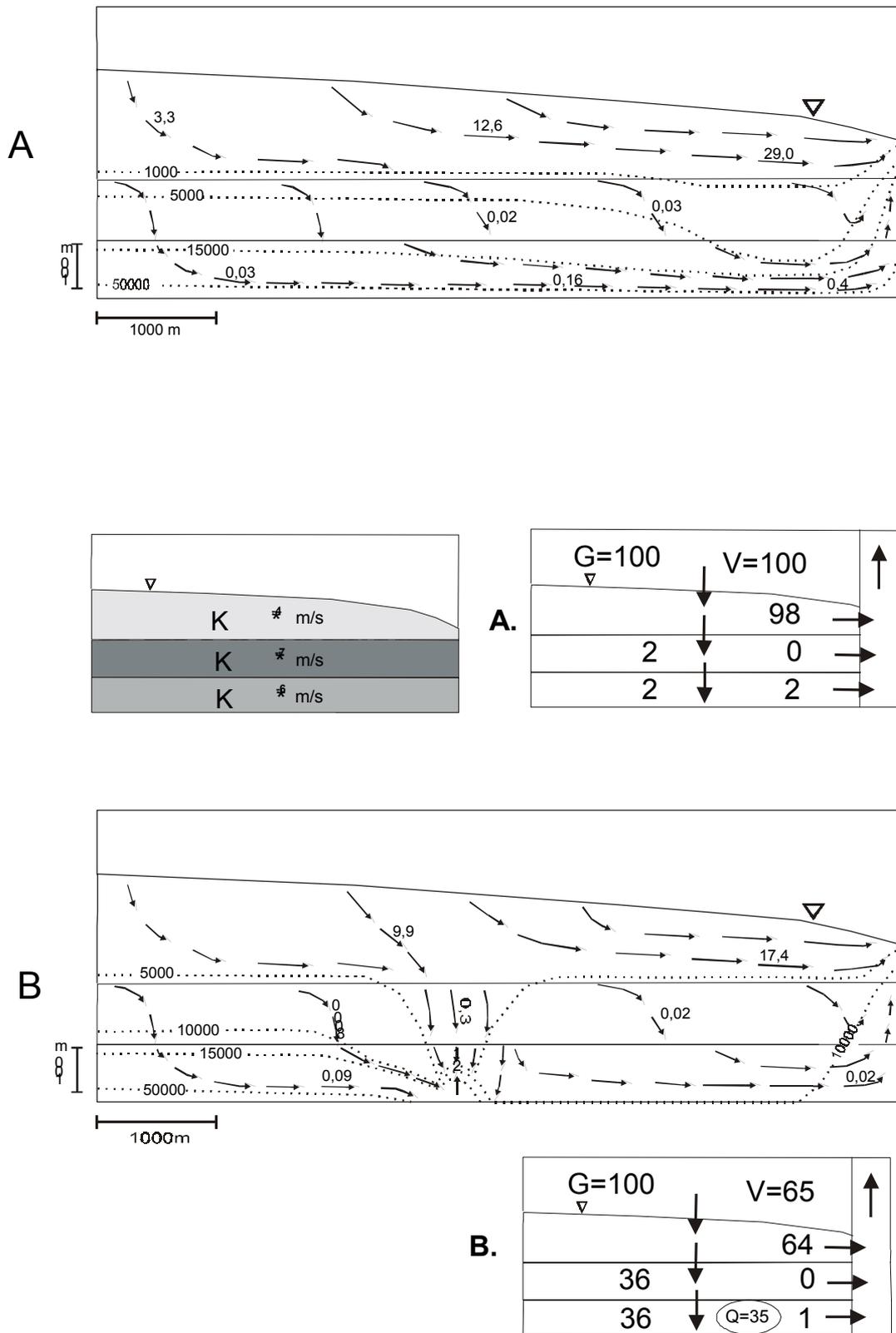


**Fig.1.9** Changes in  $^3H$ ,  $^{14}C$ ,  $Ca^{2+}$  and  $Na^+$  concentrations with groundwater depth;  $^3H$  concentrations in TU,  $^{14}C$  concentrations in pMC (Modified after Egger 1978).

Contrary to salts or the mineralisation of groundwaters,  $^3H$  is an external tracer. It is produced by cosmic radiation and is radioactive with a half-life of 12.43 years. Only through the water cycle is it introduced into groundwater in considerable concentrations. It occurs world-wide in precipitation, albeit in different concentrations (Moser & Rauert 1980). Under natural conditions it occurs in concentrations of 5 and 20 TU in tropical and polar zones, respectively. Thus, groundwater ages in the active recharge zone comprise some ten and drop below the TNL rapidly to some hundred or thousand years.

The active groundwater recharge zone is thin (< 100 m) and has high groundwater flow velocities (distance velocities > 0.1 m/day). The passive groundwater recharge zone is much thicker (mostly > 300 m) and has groundwater flow velocities of less than millimetres per day.

Due to the high dilution volume, which results from the low groundwater flow velocities and the large groundwater thickness, the passive groundwater recharge zone reacts much slower to pollutant inputs than the active groundwater recharge zone. Only the connate water remains free of pollutants - in principle. Connate groundwaters (v. Engelhardt 1960), however, are usually not used as drinking or industrial water, because of their chemical composition. On the contrary, they are being used balneologically (for medical baths).



**Fig.1.10** Flow lines, distance velocities of the groundwater (m/d) and age distribution (years) in groundwater at a certain hydraulic conductivity distribution (m/s) in the aquifer systems. A. without and, B. with a groundwater exploitation from the passive groundwater recharge zone of 35 % of the recharge.

The low flow velocities in the passive groundwater recharge zone also produce low leaching capacities. Therefore, mineralisation of groundwaters out of the passive recharge zone often show higher concentrations and comprise also specific rare elements (e.g. As, I, F), missing as geogenic component in the active recharge zone through leaching.

Following the development of water supply in the last 150 years, it turns out that in many countries at the beginning river waters, later waters of springs and shallow wells and finally of deep wells, that penetrate the passive groundwater recharge zone, are used for water supply. The reason for this development was, among others, impairment of the groundwater quality for drinking water purposes. Mostly, the sources of contamination have been disregarded; thus, digging deeper wells or providing larger dilution volumes does not solve the water quality problems on a long run. Contrary, it produces first an increase of dilution for pollutants followed by a creeping increase of pollution of the passive recharge zone, lasting for years or centuries, depending on depth and quantities of exploitation.

As a consequence of these recent findings, drilling of wells should not only refer to hydraulic conductivities of aquifers but also recognise the role of the active and passive recharge zone. Mostly groundwater abstraction from the passive groundwater recharge zone is not based on the low, yet available or effective groundwater recharge (< 15%). Instead, it is based on the calculated groundwater recharge for the landscape. The consequence of such groundwater exploitation from deep layers was also calculated in scenarios (Fig.1.10). 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 recharge. The resulting groundwater deficit must then be compensated (DVWK 1983, DVWK 1987). This compensation process reaches equilibrium only after several years to decades or even centuries, thus keeping the hydrodynamic system for a long run under transient conditions. It appears that a quantitatively and qualitatively secure water supply from the passive zone is possible if applied in accordance with the aquifer specific recharge. If not, it leads to a long-term contamination input into a groundwater zone, that would otherwise have been naturally protected on a long term.

The process of short cut between the active and passive recharge zone can be monitored in a process-oriented way (early warning system), using the natural stratification of environmental isotopes or chemicals in groundwaters (see Chapter 2) and their dislocation with groundwater exploitation. This monitoring, however, becomes only process oriented if the results feed mathematical models (Seiler 1998).

## 1.8 CONTAMINANT SOURCES

Common groundwater contaminating sources are:

- 1) urban areas,
- 2) agricultural and industrial activities,
- 3) waste waters discharged into rivers and sinkholes,
- 4) waste disposal and
- 5) saline or geogenic polluted water attracted by overexploitation of groundwater resources.

Additionally, certain activities in urban and agricultural areas are difficult to control as they often coincide with hazards like

- accidental spills,
- particle favoured transport,
- undetected or non-locatable leakages and
- unpredictable weather conditions after incidents or applications, respectively.

In groundwater such incidents are directly detectable using chemical survey. The potential consequences of such incidents, however, are best recognised by applying isotope studies in combination with hydrogeologic investigations and numerical modelling.

Chemical monitoring usually refers to the contaminant itself or its metabolites; thus it is restricted to the contamination but not to the process of hydrodynamic system changes. The knowledge of the hydrodynamic system changes, however, is essential, because e.g. from organic pollutants less than 15% of the metabolites are known and many metabolites of lower molecule size may be more toxic and even more mobile than the mother substance. This demonstrates that chemical monitoring may deliver uncompleted insights. On the contrary, isotope methods are species independent and allow either directly ( $^{15}\text{N}$ ,  $^{34}\text{S}$ ,  $^{13}\text{C}$ ,  $^{18}\text{O}$  in  $\text{SO}_4^{2-}$  or  $\text{NO}_3^-$ ) or indirectly ( $^{39}\text{Ar}$ ,  $^{18}\text{O}$ ,  $^2\text{H}$ ,  $^3\text{H}$ ) or in combination with non-reactive chemical tracers ( $\text{Cl}^-$ , sometimes  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ ) to recognise the potential as well as any existing contaminant impact on groundwaters. Generally spoken, isotopes offer an integrating and statistically well-based interpretation where pollution studies often lead to a sectoral and sometimes uncompleted interpretation of the system. Such studies should also comprise microbial considerations, because microbial activities in the subsurface, also depending on changes in land use, may mask real contamination assessment.

Waste water-incidences originating from rivers (water quality requirements for rivers are not as strong as for groundwaters) and the access of saline waters to drinking or irrigation waters need special control of groundwater management. The analytical results of this monitoring should feed mathematical models that make a process-oriented prediction of the development

of the groundwater regime (early warning system). Such studies should be based on artificial and environmental tracers in accordance to the task of obtaining information on mass transport in groundwater systems (see Chapter 2). Contrary, the exclusively hydrodynamic consideration comprises both mass transport and pressure equilibration in the system and may disregard problems like transient conditions and colmatation of interfaces.

Contrary to the afore mentioned contamination sources, waste disposals produce only local impacts of groundwater systems. Chemical monitoring and the conservative investigation of the groundwater flow field by means of artificial and environmental tracers best describe this impact.

## 2 GROUNDWATER EXPLOITATION AND OVEREXPLOITATION

The advantage of groundwater exploitation for water supply by wells as compared to the use of river or spring waters consists of being widely independent from short-term variations

- in precipitation and its immediate consequences for discharges or storage in open reservoirs and
- in the chemical and microbial composition of waters.

Water supply from natural or artificial lakes occupies an intermediate position in between ground and surface water exploitation.

Contaminant reach rivers and springs faster than groundwater and may affect groundwaters much longer than spring and river waters. These differences arise from mean residence times that are important for physical, chemical and microbial elimination and disintegration processes with slow kinetics. Mean residence times of lake waters are longer than river- and springwaters, but still shorter than in groundwaters. Although surface contaminations have easy access to lakes, elimination processes and remediation techniques in lakes are usually quite efficient, because microbial processes occur quite efficiently in the presence of light (photolytic processes).

Mean residence times can be determined using artificial or environmental tracer techniques. Generally the first deliver sectorial information of the system ([Moser & Rauert 1980](#), [Kaess 1998](#)). Environmental isotope techniques, on the contrary, provide integrated and mostly time-invariant data on mean residence times.

- In rivers and springs often variations of environmental isotopes in the isotopic input and output are compared to determine mean residence times. Applying the stable isotopes  $^2\text{H}$  and  $^{18}\text{O}$ , the mean residence time can be calculated using damping effects from the input to the output function ([Oeschger & Siegenthaler 1972](#)) or from the phase shift between both functions. This method is limited by the measuring accuracy of the stable isotopes (routinely  $\delta^{18}\text{O}: \pm 0.1\text{‰}$ ,  $\delta^2\text{H}: \pm 1\text{‰}$ ) and consequently, mostly covers not more than 4 years.
- For determining somewhat larger mean residence times radioactive environmental isotopes with short half-lives are more appropriate ( $^3\text{H}$ : 12.43 years,  $^{85}\text{Kr}$ : 10.6 years). The input functions of both radioactive isotopes are well known (e.g. [IAEA 1975](#)), however, both isotopes behave in the unsaturated zone somewhat different. With  $^3\text{H}$  the

mean residence time of water since infiltration is determined, with  $^{85}\text{Kr}$  the time since percolation water reaches the groundwater surface. Evaluation of longer mean residence times using  $^{39}\text{Ar}$  (half-life 269 years),  $^{14}\text{C}$  (half-life 5730 years) or  $^{36}\text{Cl}$  (half-life 301000 years) requires an exact knowledge of the long-term input function which mostly is supposed to be constant over geologic periods of time. To evaluate these functions, an appropriate hydrogeological concept is needed to select the respective hydraulic model. Best-known models in this respect are the piston flow, the exponential, the dispersion model (Maloszewski & Zuber 1982), all for unconsolidated rocks, and the single fissure model for consolidated fissured rocks with matrix porosity (Maloszewski & Zuber 1993). All these models are low parameterized and do not substitute high-parameterized numerical or analytic models. A comparison of the results of both types of models is documented in detail in DVWK (1995).

For hydrodynamic and economic reasons groundwater exploitation requires hydraulic conductivities exceeding  $10^{-6}$  m/s and a water table not too far from land's surface. It cannot be recommended to orient the drilling and screening of wells only on depth-related hydraulic conductivities, although this might be considered a favorable economic prerequisite. Groundwater exploitation should be based on the effective, aquifer related recharge (Sect.1.7) and not on the overall groundwater recharge. High hydraulic conductivities in the passive recharge zone facilitating groundwater abstraction (e.g. aquifers in desert areas or deep aquifers in humid climates) should not be misinterpreted as an abundant availability of groundwaters for sustainable exploitation.

Operation wells deform a groundwater flow field by gathering streamlines (Fig.2.1). The stronger the abstraction from an individual well, the more streamlines become focused and the width of the flow field contributing to the well increases. In an excess state of exploration, however, groundwater flow may convert from laminar into turbulent first at the well and later in the surroundings of the well. Such turbulent flow may accelerate subsurface erosion (suffusion) in the aquifer, thus locally increasing its hydraulic conductivity, and possibly harming the stability of the bore hole or pumping system, or favor fouling and corrosion of the screen by iron, manganese or carbonate precipitation, thus reducing hydraulic conductivities of the abstraction installation (McLaughlan et al. 1993).

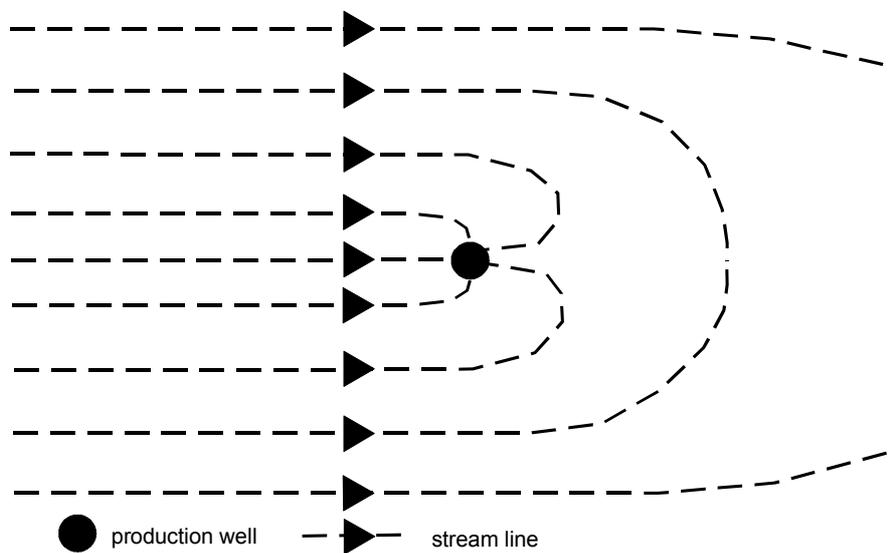
As an empirical rule in practice, the draw down for exploitation in the active groundwater recharge zone should be less than half the thickness of the aquifer system encountered by the well. This does not apply in the passive groundwater recharge zone.

The geometry and degree of the deformation of the groundwater flow field through pumping depends not only from the pumping rate, but also from the depth in which the screen is sited in the well or the construction of the well itself (Sect.2.1.3).

Groundwater exploitation of an individual well creates a local cone of depression of hydraulic heads; exploitation of well groups additionally creates a zone of depression of the groundwater table. As a rule the cone of depression develops within short times; contrary, the

zone of depression provokes transient conditions for longer times (months to years). Both phenomena have to be considered individually in judging the assessment of exploitation of groundwater on the groundwater flow field.

Overexploitation occurs as far as groundwater abstraction exceeds available groundwater recharge from precipitation or surface water contribution. In such a case one aquifer of the aquifer system undergoes pressure reduction changing the effective stresses in aquifers (grain to grain stress) and initiating subsidence in fine grained, unconsolidated silt and clay aquifers (Magara 1978) (Fig.2.2). This may endanger constructions (e.g. Mexico City), move coast lines (e.g. Maracaibo Lake, Venezuela) and change even the surface drainage system of catchment areas (Leipzig area, Germany).



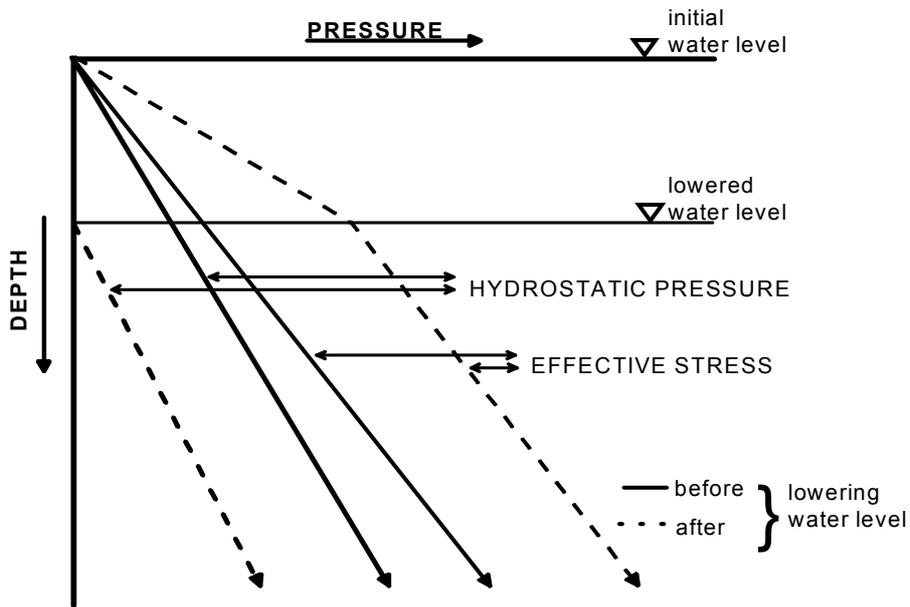
**Fig.2.1** Typical deformations of groundwater flow lines in the vicinity of wells with (A) and without (B) groundwater abstraction.

Subsidence of sediments reduces the storage capacity of aquifers. If overexploitation finishes, the reduced porosity will mostly not return to initial conditions, because in unconsolidated rocks plastic deformations dominate over elastic deformations. Therefore, groundwater levels rise after finishing overexploitation often closer to the surface and changes in coastal lines will never restore to their original position. Thus in some cases a stop of overexploitation after a long run of groundwater mining might even create hygienic and geotechnical problems.

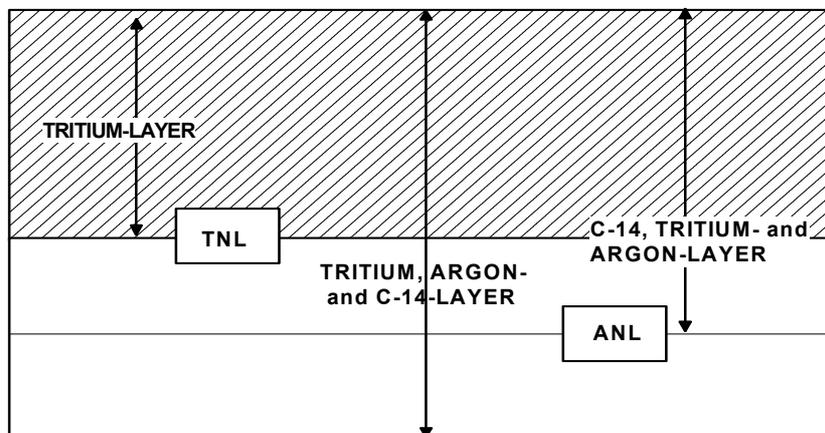
Overexploitation of groundwater resources may also favor the subsurface inflow of saline waters either from deep aquifers (Fig. 2.14) or from oceans, thus harming crops, soil fertility and drinking water quality as well (e.g. costal aquifer of Israel and Gaza, Caribbean islands).

Overexploitation of groundwater resources - also named groundwater mining because a non-rechargeable portion of extracted groundwater is lost - causes mostly long-term transient hydrodynamic conditions and provokes hydraulic short cuts between different aquifer systems. This may lead to undesired water quality changes (Sect.1.7).

Often overexploitation of groundwater resources exceeds the available groundwater recharge only slightly. It may even not result in an immediate draw down of the groundwater table because the aquifer is linked to adjacent aquifers substituting the missing groundwaters (Andres & Egger 1985). These processes, however, become well documented in their respective changes of the isotope stratification of groundwaters. They may be evaluated in a process-oriented manner, using mathematical models that include isotope information.



**Fig.2.2** Increase of effective stresses in unconsolidated aquifers due to lowering the hydraulic head.

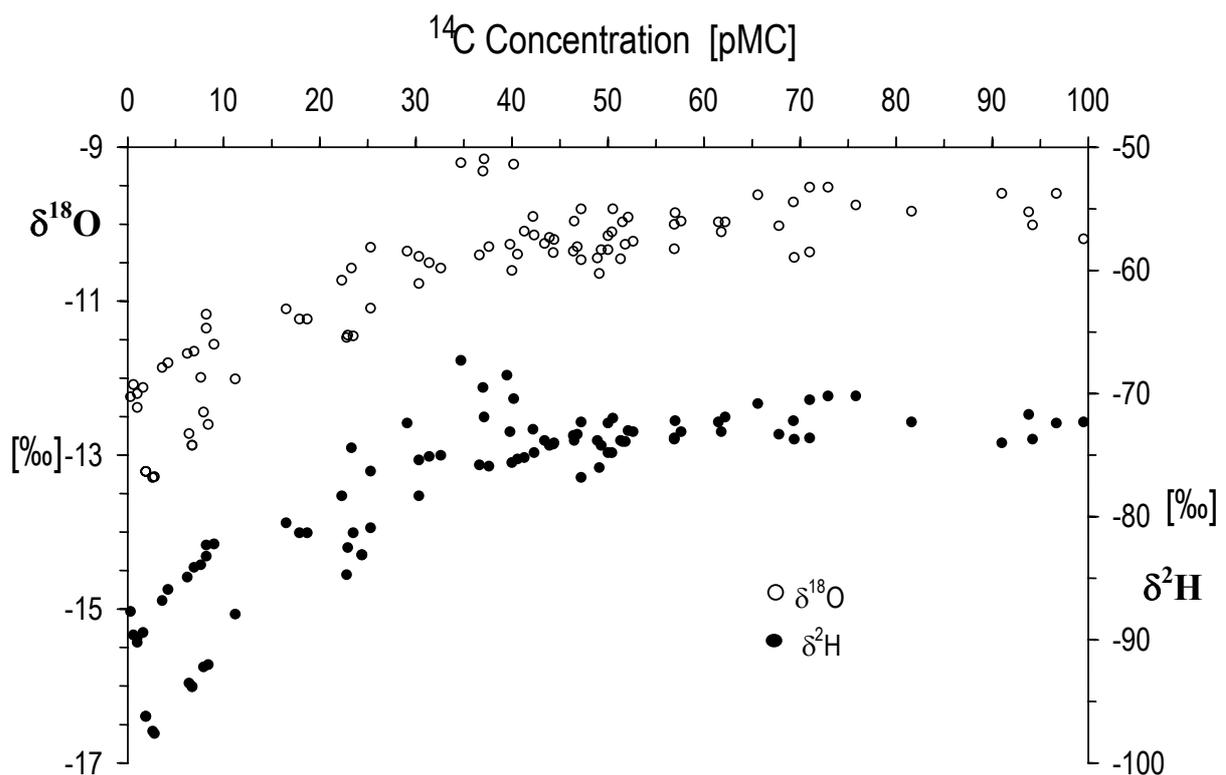


**Fig.2.3** Stratification of environmental isotopes and non-reactive chemical tracers in an aquifer system.

In groundwater chemical, stable and radioactive isotope stratification exists (Fig.2.3). All of these ( $\text{Na}_2\text{CO}_3/(\text{Ca}(\text{HCO}_3)_2)$ ,  $\text{Cl}^-$ ,  $^{34}\text{S}$ ,  $^{18}\text{O}$ ,  $^2\text{H}$ ,  $^{39}\text{Ar}$ ,  $^{14}\text{C}$ , noble gases) are linked either to changes in climatic conditions affecting groundwater recharge (Fig.2.4) or to water rock interactions with slow kinetics or differences in the half-life of radioactive isotopes. These natural chemical and isotope patterns changes with overexploitation and may be used as an indicator to assess the development of hydrodynamic changes linked to overexploitation.

In overexploited groundwater systems process-oriented evaluations of hydrodynamic changes, as indicated by environmental isotopes, require proper sampling (Sect.6.1). By field experience and scenario modelling

- sampling should take place very close to the production well (Fig.1.10), or
- in profiles along the general flow direction in the catchment and
- the repetition of sampling should cover time spans of 2 to 10 years; only in cases of strong decline of the groundwater table, sampling is recommended at each 5 m of decline of hydraulic head in order to better recognise how the aquifer becomes evacuated.



**Fig.2.4** Change of  $^{18}\text{O}$  and  $^{14}\text{C}$  concentrations in groundwaters as a consequence of temperature changes in the recharge area (Andres & Egger 1982) during late Quaternary.

Changes in the hydraulic properties of sediments due to subsidence or compaction as well as the overall array of influence of groundwater abstraction can be controlled using the single well dilution technique (Fig.2.5, Box 2.1). This technique (Moser & Rauert 1980) allows determining flow velocities and directions of groundwater in a single borehole. These flow velocities ( $v_b$ ) can be transformed into a filter velocity ( $v_f$ ) in the aquifer as far as the aquifer is unconsolidated and the deformation of the groundwater flow field ( $\alpha$ ) through the well - without exploitation - can be calculated (Drost et al. 1973, Klotz 1977) (see box 2.1).

Within consolidated fissured aquifers the transformation of the borehole flow velocity into a filter velocity is hardly possible, but the measurement of flow directions indicate the direction of fissures involved in groundwater flow.

The single well dilution techniques apply only for sections of the well screen no larger than the length of the scintillation or Geiger-Mueller counter. This section is limited by packers (Fig.2.5), which suppress - if possible - vertical flow along the well axis. Reliable data are obtained with this method if the following boundary conditions are fulfilled:

- 1) laminar groundwater flow,
- 2) homogeneous distribution of the tracer concentrations in the measuring volume,
- 3) non-reactive tracers that do not produce density flow,
- 4) horizontal flow through the measuring volume, and
- 5) dilution exceeding that of molecular diffusion.

### BOX 2.1

#### SINGLE WELL DILUTION TECHNIQUE

##### 1) *Determination of flow velocity in the well*

Measured concentration decline of a tracer within a defined level of the filter with diameter  $r_1$

$$C_t = C_0 e^{-\beta t} \quad (2.1)$$

$$\ln C_t = -\beta t + \ln C_0$$

$$\beta t = \ln C_0 - \ln C_t \quad (2.2)$$

With  $\beta = \frac{Q}{V} \quad (2.3)$

and  $Q = v_b A_b = v_b 2r_1 H \quad (2.4)$

and  $V = \pi r_1^2 H \quad (2.5)$

**Continuation Box 2.1**

Inserting 2.4 and 2.5 in 2.3 gives:

$$\beta = \frac{v_b 2r_1 H}{\pi r_1^2 H} = \frac{2v_b}{\pi r_1} \quad (2.6)$$

Inserting Eq. 2.6 in 2.2 results in:

$$v_b = \frac{\pi r_1}{2t} \ln \frac{C_0}{C_t} \quad (2.7)$$

**2) Transformation of flow velocity in the well into the filter velocity of unconsolidated rocks**

**Discharge in the well = discharge in the aquifer**

$$Q_{\text{well}} = Q_{\text{aquifer}}$$

$$v_b A_{\text{well}} = v_f A_{\text{aquifer}}$$

$$v_b = \frac{A_{\text{aquifer}}}{A_{\text{well}}} v_f$$

Supposing that H of  $A_{\text{well}}$  equals H of  $A_{\text{aquifer}}$  leads to

$$V_b = \frac{B_{\text{aquifer}}}{2r_{1\text{well}}} v_f = \alpha v_f \quad (2.8)$$

Insert Eq. 2.8 into 2.7 results in

$$V_f = \frac{\pi r_1}{2\alpha t} \ln \frac{C_0}{C_t}$$

**3) Calculation of  $\alpha$  from borehole and aquifer data**

$$\alpha = \frac{8}{\left[1 + \frac{k_3}{k_2}\right] \left[1 + \left(\frac{r_1}{r_2}\right)^2 + \frac{k_2}{k_1} \left\{1 - \left(\frac{r_1}{r_2}\right)^2\right\}\right] + \left[1 - \frac{k_3}{k_2}\right] \left[\left(\frac{r_1}{r_2}\right)^2 + \left(\frac{r_2}{r_3}\right)^2 + \frac{k_2}{k_1} \left\{\left(\frac{r_1}{r_2}\right)^2 - \left(\frac{r_2}{r_3}\right)^2\right\}\right]}$$

The single-well dilution method covers the range of filter velocities from 0.01 to about 50 m/d. Mostly radioactive  $^{82}\text{Br}$  is used as tracer, which has a short half-life (36 h), is a gamma emitter and thus allows direct measurement in the bore hole, is non-reactive in aquifers and allows simultaneous measurement of the groundwater flow and direction. Principally also non-radioactive, non-reactive tracers can be used (e.g. fluoresceine or chloride); these tracers, however, do not allow measuring simultaneously groundwater flow and direction.

## 2.1 GROUNDWATER ABSTRACTION FROM DEEP WELLS IN THE MOLASSE BASIN OF SOUTH GERMANY

### 2.1.1 INTRODUCTION

The Molasse Basin in south Germany forms the immediate foreland of the Alps and is overthrust by the Alps in its southern part. The Molasse sediments exceed 6000 m in thickness in the South and crop out along the Danube river in the North (Fig.2.6). Sediments are alternatively of marine and continental origin and end to the actual surface with a limno-fluviatile sand to clay facies. Groundwaters of marine origin are still to be met in 400 to 500 m depth below floor, as connate waters.

### 2.1.2 THE TNL IN THE STUDY AREA

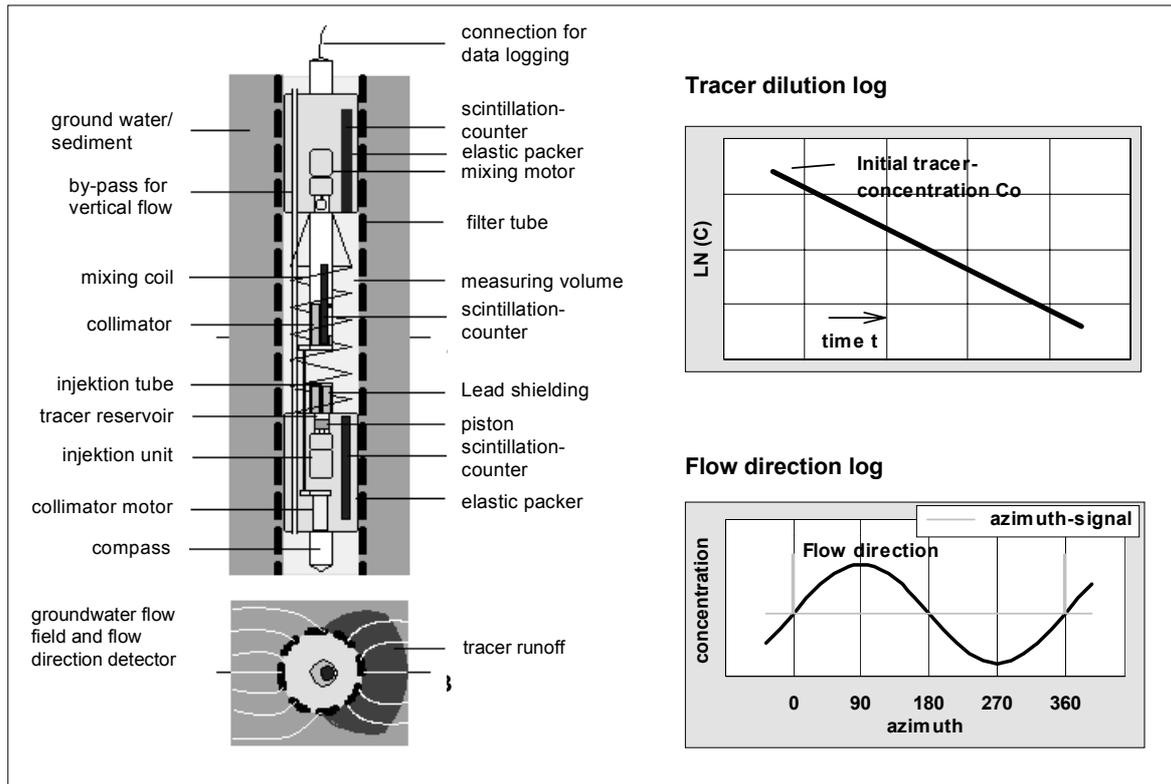
Groundwater exploitation was first focused on the active groundwater recharge zone and shifted in the urban areas of Munich and Augsburg (Fig.2.6) and also in areas with intensive agricultural activities to an exploitation depth of up to 200 m. Groundwater recharge at the surface of the Molasse sediments averages to 5 L/s km<sup>2</sup> or 155 mm/a; the TNL (Tritium naught line, Sect.1.7) is situated at about 50 m depth (Fig.2.7). Consequently, exploitation at 100 m to 200 m depth takes place in the passive groundwater recharge zone, which does not dispose of the total groundwater recharge determined at the ground surface of a catchment area.

Most of the wells in the study area have been sampled to analyze stable and radioactive environmental isotopes as well as the chemical composition of waters. As a result of all this sampling the chemical/isotope profiles (Figs. 1.9 and 2.7) have been drawn (Egger 1978).

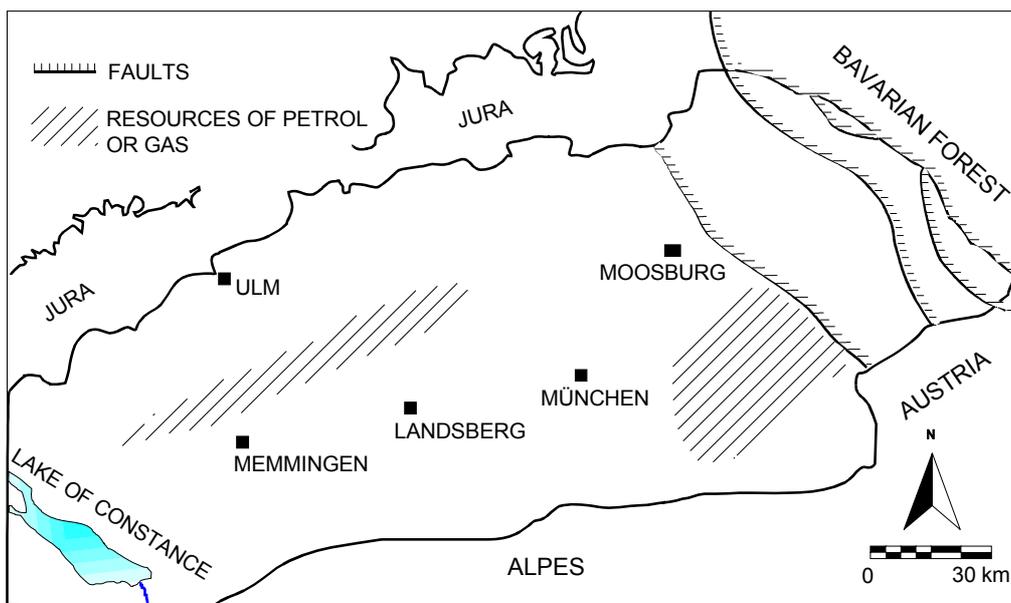
They indicate that all investigated compounds change more or less simultaneously and significantly along the TNL.

A profile in the investigation area (Fig.2.7) shows (Egger 1978) that the TNL is straight running from Munich to Augsburg at 50 m below surface, but declines below both towns because of a significant exploitation from the passive recharge zone (1977: 2.8 m<sup>3</sup>/s in Munich and 1.5 m<sup>3</sup>/s in Augsburg). This decline of the TNL is not accompanied with any significant decline of the water table in the Quaternary/Tertiary aquifer systems, but shows only by the abnormal environmental isotope distribution an additional input from the active to the passive recharge zone as compared to the normal. As a consequence not only <sup>3</sup>H but also contaminants like hydrocarbons may significantly enter the passive recharge zone with originally old (> 100 years) waters (Rauert et al. 1993).

From this decline of the TNL Egger and Andres (1985) calculated an additional contribution of the active recharge zone to the effective, depth related groundwater recharge in the passive zone of 2 L/(s km<sup>2</sup>).



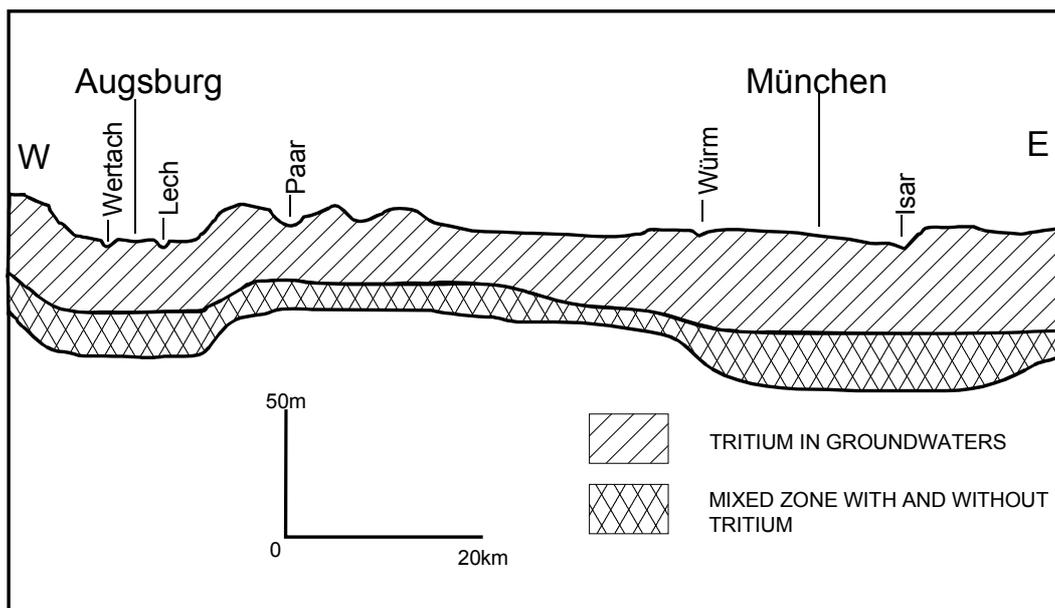
**Fig.2.5** The single well dilution probe. The semi logarithmic decline of the radioactive tracer concentration is due to in- and out flowing groundwater within the measuring section. The maximum in the distribution of radioactivity along the filter screen expresses the outflow, the minimum the inflow site of groundwater.



**Fig.2.6** The Molasse Basin in South Germany.

### 2.1.3 HYDRODYNAMIC FLOW FIELD IN THE VICINITY OF DEEP WELLS

Deep wells are mostly only screened at great depth. Mathematical modelling has been performed to simulate the consequences of deep groundwater extraction for the inflow area to a well. Wells screened from the water table to any depth have a flow field in which the groundwaters of all depths contribute to the operating well. However, as shown in Fig.2.8, with increasing depth of the screened area, the groundwater surface above the screen overflows the production horizons (Fig.1.10B). This type of flow field is also known from horizontal filters or Ranney wells (Nemecek 1961 1964) and is rarely considered in delineating groundwater protection zones for deep well exploitation.



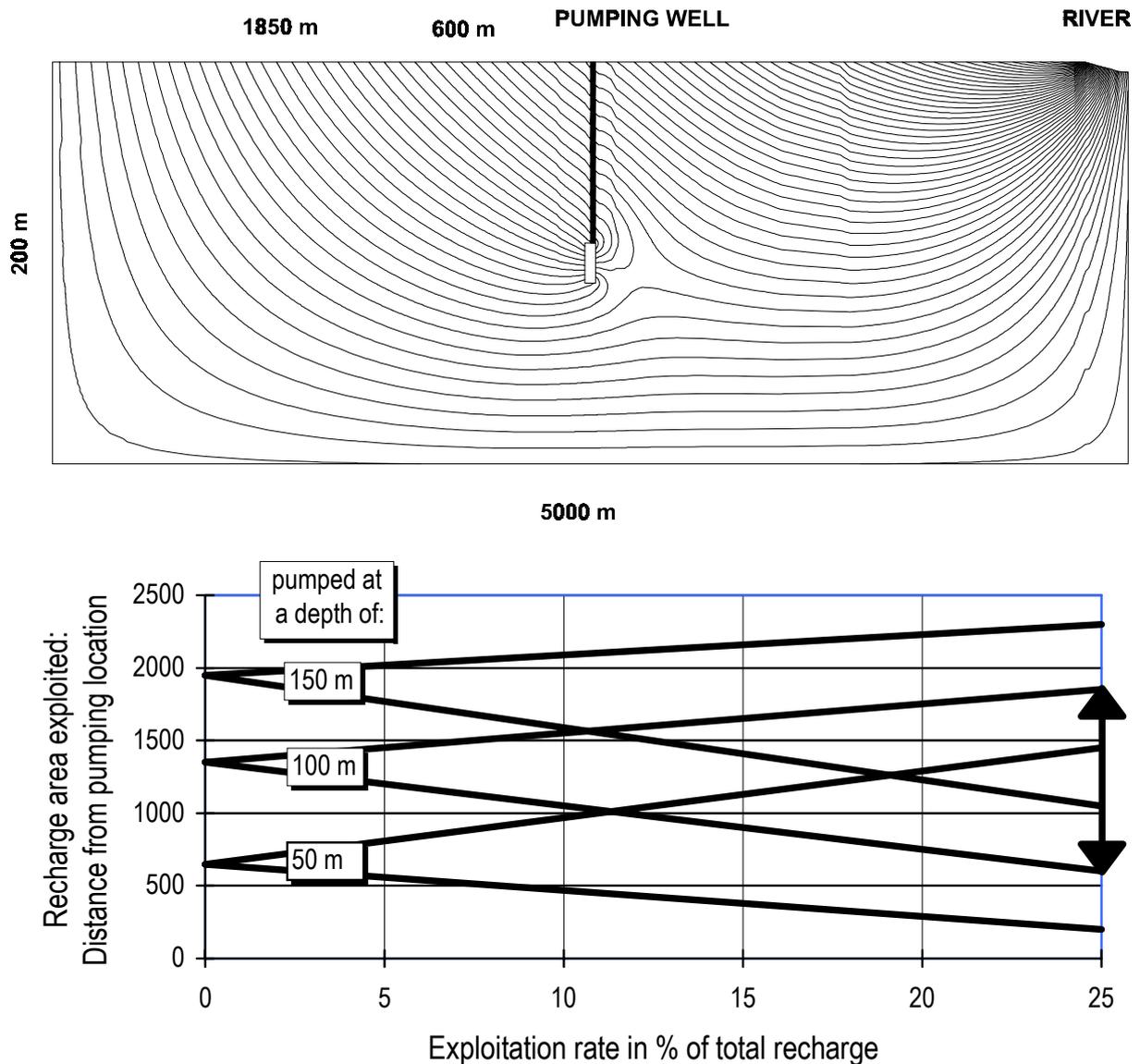
**Fig.2.7** Cross-section through the Molasse between Munich and Augsburg and the TNL (Tritium Naught Line) (after Egger 1978).

It may, on the contrary, be a useful tool to provide an efficient protection of water quality in areas exposed to pollution impacts (see Sect.4.1), although it is difficult to control (e.g. urban areas, agriculture activities in river valleys).

Model results in Fig.2.8 have been calculated for a homogeneous aquifer. Introducing changes in hydraulic conductivities will accentuate these facts. This modelling illustrates that, as a consequence of non-equilibrium extraction of groundwaters, possible contaminations of the passive recharge zone do not necessarily derive from the immediate vicinity of the respective well as for instance the gravel pack (Rauert et al. 1993).

Comparing the flow and isochrone fields in an inhomogeneous aquifer system without (Fig. 1.10A) and with 35% extraction of groundwater recharge (Fig. 1.10B) demonstrates that upstream of the production well hydrodynamic and isotope changes are not as significant as downstream. Experience has shown (Evin & Vuillaume 1970) that, on a long run, these changes in groundwater dynamics remain under transient hydrodynamic transport conditions.

There is no instantaneous response of transport changes due to hydrodynamic changes because the mass deficit is first replaced by stored water before it becomes substituted by an increased inflow of water from other aquifers. Therefore, monitoring of the changes of isotope and chemical composition of groundwaters in the surroundings of deep exploitation wells has to concentrate on the well itself or the downstream area, need repeated sampling and non-steady state model evaluation of the monitoring results.

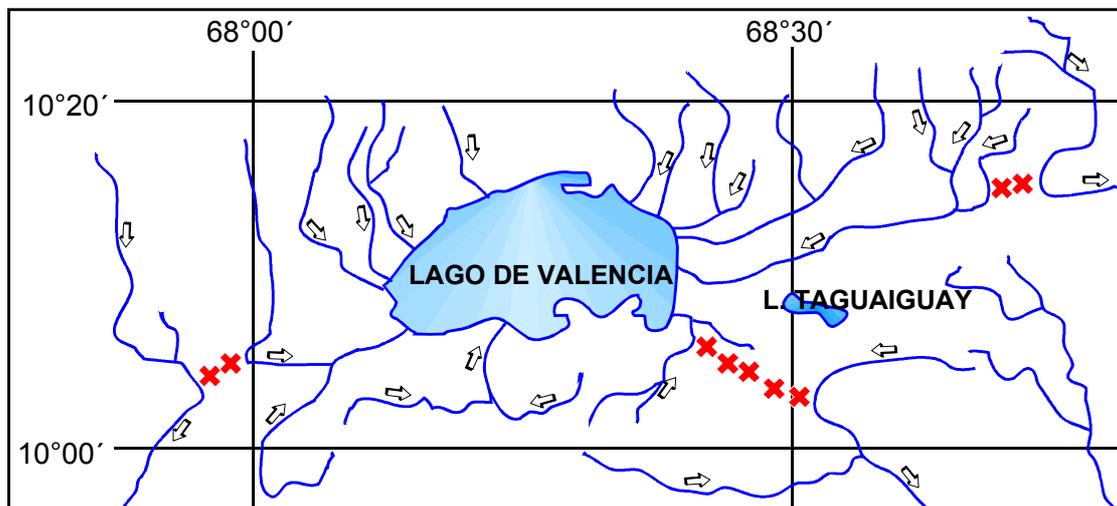


**Fig.2.8** Stream lines representing the geometry and width of the inflow zone to a well extracting from great depth (upper picture). The graph below demonstrates how far the boundary stream lines of the production well move away from the well (point of the ordinate) and how the width increases both with depth and exploitation rate as a percentage of groundwater recharge at the catchment surface. Modelling has been performed for a homogeneous aquifer.

## 2.2 THE ORIGIN OF SALINE GROUNDWATERS IN THE AREA OF THE VALENCIA LAKE, VENEZUELA

### 2.2.1 INTRODUCTION

The catchment area of the Valencia Lake in Venezuela is situated within a tectonic graben in the Coastal Cordillera south of Caracas. Many riverbeds enter the lake but no surface outflow exists (Fig.2.9). However, there is evidence from a morphological (dry valleys) and geological point of view (gypsum), that this catchment discharged superficially in the recent geological past to the Orinoco basin respectively acted in the past also as an evaporation pan. It is supposed that actually surface discharge of the lake is interrupted but subsurface discharge is still active as the electric conductivity of the Valencia Lake is quite low (2000  $\mu\text{S}/\text{cm}$ ) (Sect.2.2.5).



✕ DRY VALLEY

**Fig.2.9** The study area of the Valencia lake in Venezuela and the drainage pattern of the catchment area.

The lake surface covers an area of 360 km<sup>2</sup> within an intermountain plain of 1200 km<sup>2</sup>. The catchment area itself comprises 2600 km<sup>2</sup>; in 1981 it was artificially enlarged to 3200 km<sup>2</sup> by a short cut with a neighbouring catchment that contributes an additional 5 m<sup>3</sup>/s of discharge to the lake.

The water level of the Valencia Lake changed over centuries; from 1700 to 1981 it dropped from 425 m a.s.l. to 402 m a.s.l. Owing to the aggregation of a neighbouring catchment area the lake level rose till 1990 to 406 m a.s.l. The reasons for the decline are not well understood and might be related to climatologically, seismic and more recently to human impact because the groundwater resources in contact with the lake became strongly exploited for irrigation purposes. Similar declining and ascending lake levels are to be met in Guatemala ([Velasques](#)

et al. 1989, Baldison & Seiler 1994), but none of these are simultaneous and all seem to have local meteorological causes in these tropical zones.

Today the Valencia Lake receives the untreated wastewaters of the cities of Maracay and Valencia (each with more than 1 million inhabitants), as well as from wood processing and chemical factories, and from livestock. About 10 ton/year of N and 3 ton/year of S reach the lake. This chemical charge led to a complete eutrophication of the lake; as a consequence, today's fishing and swimming is forbidden.

The intermountain plain is intensively urbanised and irrigated for agriculture. Irrigation waters mostly originate from groundwaters (3000 wells); locally the groundwater table was lowered to below the lake level. Only in the south and southeast of the Valencia lake two surface reservoirs store surface waters for irrigation; in between these the Taguaiguay reservoir is the most important (Fig.2.9).

Since ever groundwater quality was low in the south and southeast; recently it deteriorated also by an increase of sulphur concentrations in both drinking and irrigation waters in the North and East. This recent deterioration may be attributed to

- infiltration of lake waters to groundwaters in areas with a respective hydraulic gradient inland,
- infiltration of deep sulphated groundwaters from beneath the fresh waters of the active groundwater recharge zone or
- return waters from irrigation, having become enriched in agrochemicals.

Using hydrochemical, hydraulic and environmental isotope tools, the origin of sulphate waters and a possible subsurface outflow of the lake was quantified. Based on these data a water balance for the area was elaborated for the first time.

## **2.2.2 HYDROGEOLOGIC OVERVIEW**

The catchment area bordering the intermountain basin is composed of crystalline rocks; its alteration products filled the intermountain plain. The fluvio-lacustrine sediments consist of silts, gravels and sands and in some places also gypsum sediments are exposed from a former evaporation pan.

The storage capacity of crystalline rocks is quite limited and expresses in a quite dense network of rivers; on the contrary, the intermountain plain filled with the weathering products of the adjacent crystalline rocks has a high storage capacity and hydraulic conductivity. Therefore, most of the creeks loose their discharge by bank infiltration hydrogeologically, so that this does not reach the lake as surface discharge.

Groundwater recharge occurs only in the intermountain plain, either by bank infiltration or by aerial infiltration of precipitation. In the southeastern part of the catchment, rivers are scarce and therefore bank infiltration is weaker and water quality is worthier (Sect. 2.2.3.2) than in

the northern part. Actual groundwater abstraction by wells is in the range of 14 m<sup>3</sup>/s; 58% of the extracted waters are applied for irrigation, 32% for domestic and 10% for industrial use. It is estimated that about 10% of irrigation water returns to the groundwater.

### 2.2.3 THE ORIGIN OF GROUNDWATERS

To study the origin and interconnections between ground-, surface and irrigation waters by means of environmental isotopes, repeated sampling took place in selected rivers, springs, wells and in vertical profiles within the Valencia Lake. The stable environmental isotope results are shown in Figs.2.10 and 2.13.

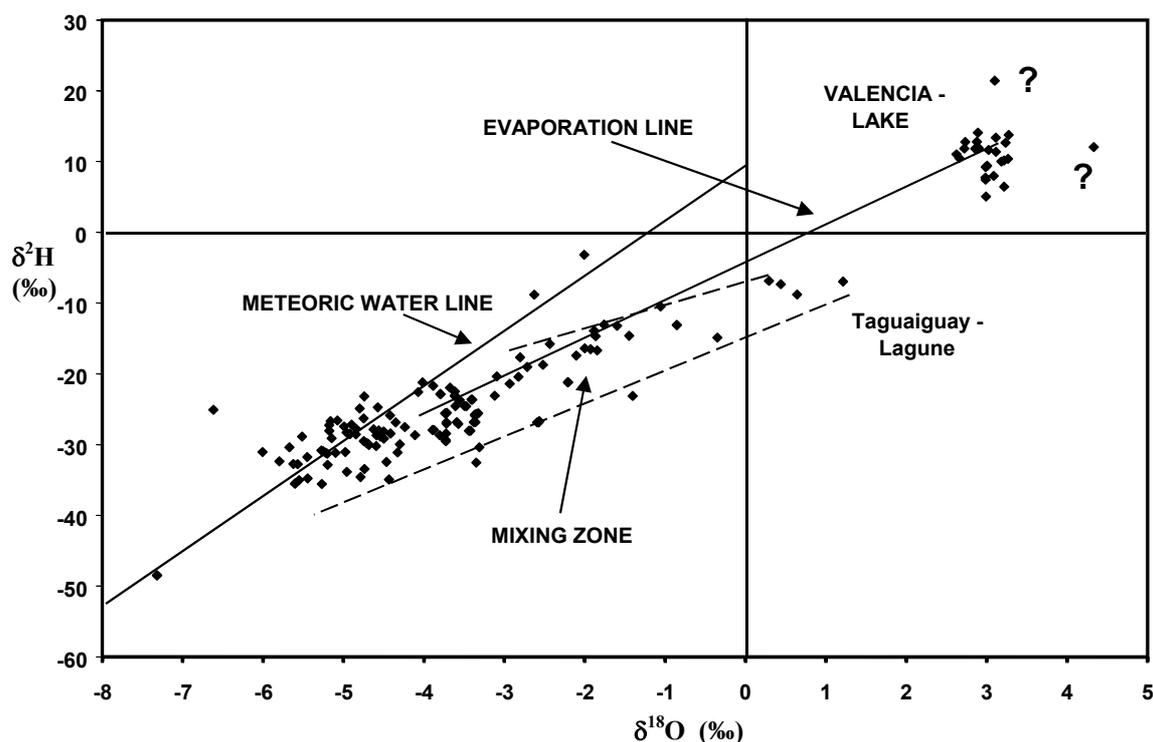


Fig.2.10  $\delta^{18}\text{O} / \delta^2\text{H}$  relation of waters in the area east of the Valencia Lake.

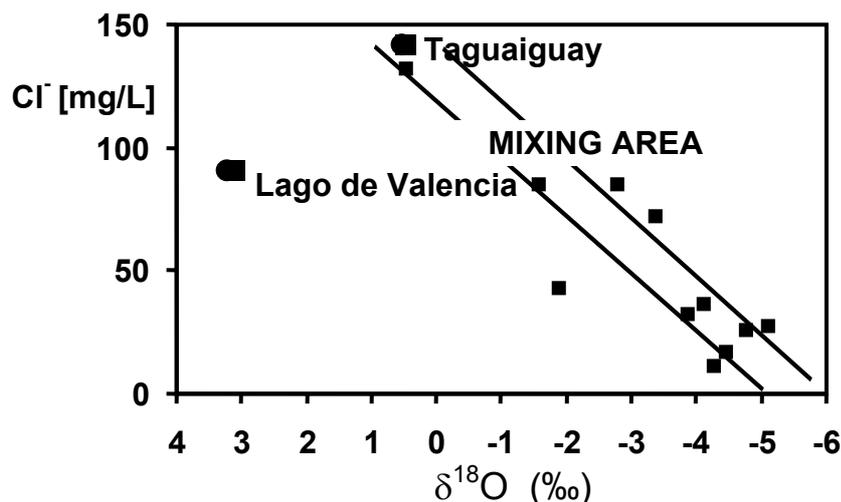
#### 2.2.3.1 HYDROCHEMISTRY AND ISOTOPES EAST AND SOUTH-EAST OF THE LAKE

The stable isotopic composition of ground- and surface waters from this area follows the meteoric water line (Fig.2.10) with a Deuterium Excess of 10‰. The variation of the isotope concentrations along the meteoric water line is attributed to both seasonal variations of direct infiltrating precipitation and to an altitude effect inherent in surface waters infiltrating by means of bank infiltration. Only  $\delta^2\text{H}/\delta^{18}\text{O}$  relations of groundwaters in the south-eastern irrigation area with low groundwater recharge do not group along the meteoric water line; these waters must be influenced by mixing of non-evaporated with evaporated waters either from the lake or from return waters from irrigation waters from surface reservoirs (Fig.2.10).

Since isotopically enriched waters are to be found in areas with a groundwater level above as well as below the lake level, lake infiltration should be completely or partly be ruled out.

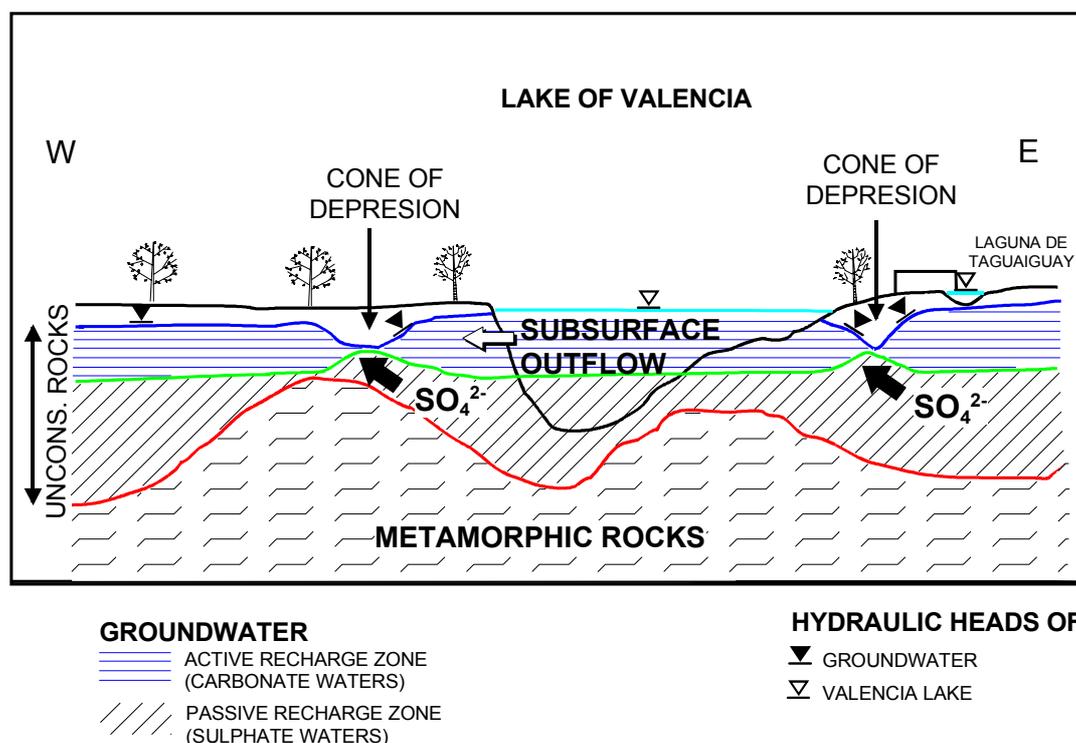
From all water samples also lump parameters (electric conductivity, pH, Eh, O<sub>2</sub>, temperature) have been measured during sampling. In the southeast sulphate (maximum 2000 mg/L) and chloride concentrations (maximum 150 mg/L) are much higher than elsewhere and electric conductivities even may become higher than in the Valencia Lake or the Taguaiguay reservoir. In this region chlorides as well as stable isotopes in groundwater can only originate from precipitation or surface water, because in the fluvio-lacustrine sediments no chloride evaporites exist. Consequently, the fate of both tracers since precipitation must change in parallel, as both became enriched by evaporation. The correlation between <sup>18</sup>O and Cl<sup>-</sup> (Fig.2.11) clearly demonstrates that the chloride enrichments of the Valencia Lake and of the Taguaiguay reservoir are different. The groundwaters from the east mix obviously only with Taguaiguay waters, although in many parts of this area the groundwater table was lowered below the lake level. This indicates that return water from irrigation infiltrated and became mixed with groundwater of this area. Furthermore, the sulphate concentrations in groundwater in this region is locally much higher than ever measured in the Valencia Lake. Since no relations with the lake become obvious and irrigation water has only low sulphate concentration, a sulphate source must exist that is not related to the lake.

<sup>3</sup>H measurements from groundwaters east of the lake (Table 2.1) show that actually at sampling depth below 80 m there is no measurable <sup>3</sup>H. Tamers (1967) showed for this area that <sup>14</sup>C ages for the deep groundwaters are in the range of 10 000 years and thus belong to the passive recharge zone (Seiler & Lindner 1995). On the contrary, in waters between ground surface and 80 m <sup>3</sup>H occurs (Table 2.1).



**Fig.2.11** Correlation between chlorides and <sup>18</sup>O in groundwaters east of the Valencia Lake.

Obviously, groundwater of the active recharge zone was explored and by means of overexploitation hydraulic heads had been lowered to an extent that groundwater with high mean residence times intruded from the passive into the active groundwater recharge zone (Fig.2.12). This water with high mean residence times or low flow velocities has not yet completely leached sedimentary gypsum and thus contributes to the actual deterioration of the groundwater quality through forced hydraulic short cuts.



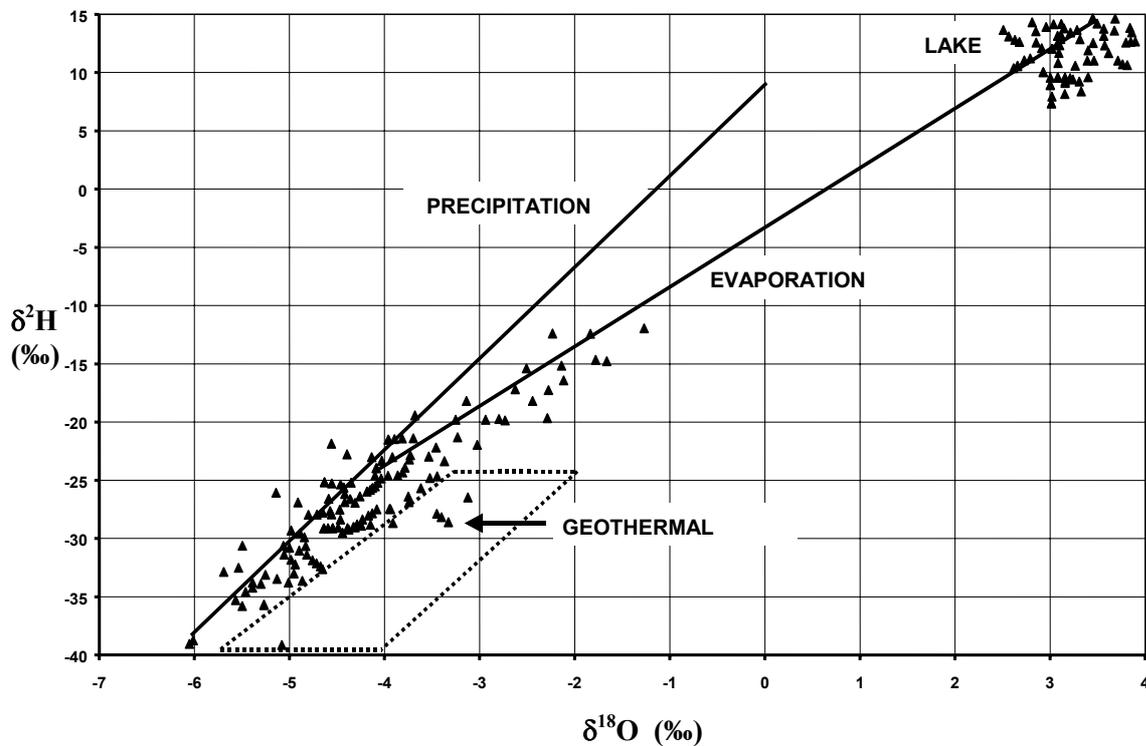
**Fig.2.12** Generalised groundwater flow system in the surroundings of the Valencia Lake and the influence of groundwater abstraction on the interaction between the active and passive groundwater recharge zone.

### 2.2.3.2 GROUNDWATER IN THE WEST AND NORTH OF THE LAKE

This study area is only irrigated with groundwater, and in the north there occur some warm waters. In the  $^2\text{H}/^{18}\text{O}$  diagram water mostly follow the meteoric water line; a few indicate an evaporation impact, whereas individual values show only an enrichment in  $^{18}\text{O}$  but not in  $^2\text{H}$  (Fig.2.13).

As expected, return waters from irrigation by groundwater have no stable isotope enrichment because it mainly underwent transpiration and only very little evaporation. The few stable isotope values showing enrichment occur along a quite narrow zone between La Culebra and Flor Amarilla (Fig.2.14), follow a tectonic fault (La Victoria) and correspond to Lake waters

discharging subsurface to the West. This subsurface outflow explains the low electric conductivity of the Valencia Lake (2000 $\mu$ S/cm).



**Fig.2.13**  $\delta^2\text{H}/\delta^{18}\text{O}$  diagram of groundwaters from the North, West and Southwest of the Valencia Lake.

Some groundwaters in the north of the lake group not along the meteoric water line. These waters were probably not subject to evaporation, because meteoric water in this region near the equator with still lower  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  is unlikely. Since these waters have elevated temperatures, they probably underwent only  $^{18}\text{O}$  enrichment by  $^{18}\text{O}$  exchange with mineral oxides at high temperatures (100 - 150 °C) and sufficient reaction time (Moser & Rauert 1980).

## 2.2.4 WATER BALANCE FOR THE STUDY AREA

Since isotope studies gave clear insights in the subsurface flow and recharge mechanisms, it approximate up a water balance for the study area. Mean annual precipitation (1962-1981) for the watershed is 1110 mm/a and for the Valencia Lake 1000 mm/a. It is obvious from the electric conductivity of the lake (2000  $\mu$ S/cm) and from stable isotopes, that there exists a through flow and subsurface outflow of the Valencia Lake.

This outflow (D) can be estimated from:

$$\begin{aligned}
 D &= (P_{\text{lake}} - EP_{\text{lake}}) A_{\text{lake}} + (P_{\text{catchment}} - ET_{\text{catchment}}) A_{\text{catchment}} \\
 P_{\text{lake}} &= 1.0 \text{ m}^3/\text{m}^2/\text{a} \\
 E_{\text{lake}} &= 2.28 \text{ m}^3/\text{m}^2/\text{a} \quad (\text{measured with an evaporation pan class A}) \\
 A_{\text{lake}} &= 360 \times 10^6 \text{ m}^2 \\
 P_{\text{catchment}} &= 1.11 \text{ m}^3/\text{m}^2/\text{a} \\
 ET_{\text{catchment}} &= ? \\
 A_{\text{catchment}} &= 2200 \times 10^6 \text{ m}^2
 \end{aligned}$$

**Table 2.1**  $^3\text{H}$  concentrations in wells east (AR) and west (CA) of the Valencia Lake.

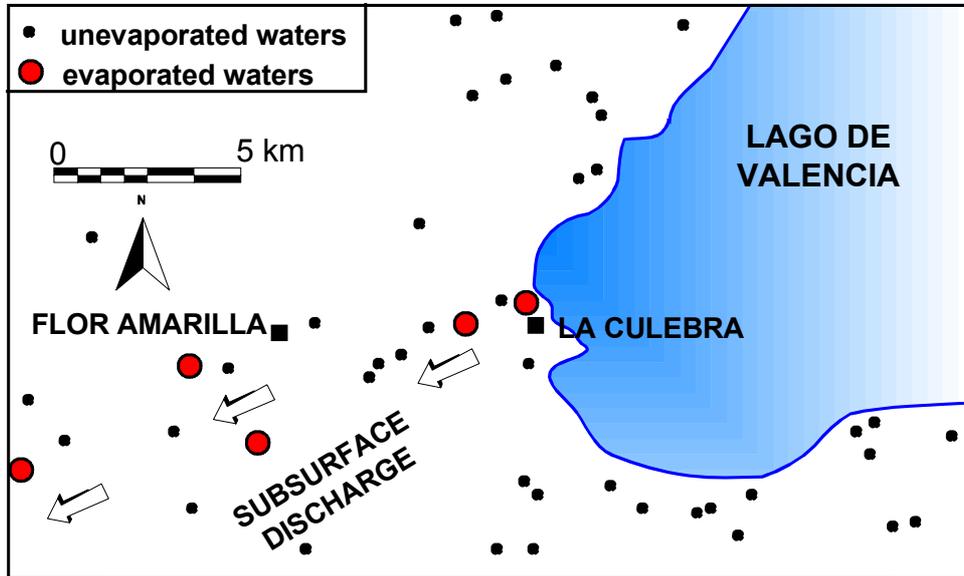
Well	Sampling Date	Sampling Depth (m)	$^3\text{H}$ (TU)
AR 6158 615A	17.03.1993	82	$3.6 \pm 0.7$
AR 6158 616A	16.03.1993	60	$1.8 \pm 0.7$
AR 6258 288A	17.03.1993	80	<1
AR 6258 132A	21.06.1991	80	$0.6 \pm 0.7$
AR 6258 149A	21.06.1991	100	$0.5 \pm 0.7$
AR 6258 SN20	21.06.1991	48	$0.9 \pm 0.7$
CA 6160 029A	18.03.1993	80	<0.7
CA 6160 03 A	18.03.1993	75	$0.9 \pm 0.7$
CA 6160 069A	19.03.1993	105	$0.9 \pm 0.7$
CA 6160 137A	18.03.1993		<0.7
CA 6169 SN 4	19.03.1993	80	<0.7
CA 6161 052A	21.09.1991	60	$3.8 \pm 0.7$
CA 6259 SN01	21.06.1991	60	$0.3 \pm 0.7$
CA 6259 SN02	21.06.1991	16	$0.8 \pm 0.7$
CA 6260 080A	21.06.1991	82	$3.5 \pm 0.7$
CA 6260 097A	21.06.1991	160	$0.6 \pm 0.7$

Assuming the absence of subsurface discharge in the area, the actual evapotranspiration was 892 mm/a. Since subsurface discharge does exist, ET must be lower. According to calculations of ET in the Dominican Republic and Guatemala (Febrillet et al. 1989, Baldison & Seiler 1989, Baldison & Seiler 1994), 850 mm/a might be close to reality in this tropical region. Based on this value the subsurface discharge was

$$D = 3.5 \text{ m}^3/\text{s} \quad \text{or} \quad D = 42 \text{ mm/a.}$$

The exploitation of 14 m<sup>3</sup>/s together with the 3.5 m<sup>3</sup>/s subsurface outflow of the Valencia Lake caused the observed decline of the lake level. However, the recent aggregation of 5 m<sup>3</sup>/s

from a neighbouring catchment area made the lake table rising. Obviously the available groundwater recharge ranges between 12.5 and 17.5 m<sup>3</sup>/s and is very variable in this zone with tropical climate conditions.



**Fig.2.14** Subsurface outflow of lake waters in the West and the geothermal waters in the North of the Valencia Lake.



### 3 IRRIGATION AND THE IMPACT ON GROUNDWATER QUALITY

Irrigation is mostly used in arid to semi-arid zones (Table 3.1), here referred to as dry lands, but is also known from humid areas. Dry lands are poor in precipitation and suffer tremendous climate variability from year to year (Bruins & Lithwick 1998), thus increasing the vulnerability of cultivated ecosystems. Humans may partly govern aridity using rain and discharge harvesting, both stored in the unsaturated zone and not necessarily contributing to groundwater recharge. Due to the special boundary conditions and non-adapted cultivation tools in dry lands, they may often contribute simultaneously to desertification as well.

UNEP (1992) defines different forms of aridity using the precipitation/evapotranspiration ratio and the rainfall variability (Table 3.1).

**Table 3.1** Classification of different forms of aridity according to a proposal of UNEP (1992)

	<b>P/PET ratio</b>	<b>rainfall variability in % of the average</b>
<b>hyper-arid</b>	< 0.05	100
<b>Arid</b>	0.05 - 0.02	50 - 100
<b>semi-arid</b>	0.02 - 0.5	25 - 50
<b>sub-humid</b>	0.5 - 0.65	< 25

Dry conditions negatively affect the two basic requirements of mankind, water and food. Since deserts and 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, irrigation has been developed as an important tool for the production of food and natural raw materials. Since mankind shifted from hunting to farming and systematically since the beginning of the last century irrigation was developed. Today about 17% of the world's croplands are irrigated (about 240 million 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 to 4% and since then dropped to an actual growth of less than 1%. Today all these irrigation areas produce about 1/3 of the food demand in the world.

The actual efficiency of irrigation systems (Thorne & Peterson 1954, Shanan 1992) is mostly low because of significant water losses in surface reservoirs and distribution channels and due to an inefficient use of the water in the fields. These losses cause local increases of groundwater recharge and water logging (rise of groundwater table) and may adversely affect the quality of soils and groundwaters, constructions and public health. Other undesired effects are salinisation and the sedimentation in surface reservoirs reducing reservoir's life time, estimated at 50 to 100 years for the majority. Thus, already within the life-time of reservoirs the availability of irrigation waters decreases significantly.

Irrigation increases primarily transpiration and to a very small extend also evaporation from the effective root zone and soil surfaces, respectively. It has to be applied simultaneously with agrochemicals such as fertilizers and pesticides, which reach the groundwater together with irrigation return water, so affecting the groundwater quality for the public domain. This further imposes limitations of groundwater availability for reasons of water quality.

In most areas with dry and rainy seasons and in most of the arid regions irrigation is based on the use of groundwater. In many desert regions connecting mountain (Himalaya) or rainy areas (Ethiopia) with the ocean, surface waters are being gathered in reservoirs.

Surface water irrigation has natural limitations imposed by a huge variability of yearly precipitation in arid and tropical zones. Groundwater based irrigation is mostly performed by wells penetrating unsystematically to different depth, thus touching unsystematically the active and passive groundwater recharge zone; on the long run this produces a disturbance of the natural flow regimes facilitating the access of contaminants into the depth, that would not occur by natural mixing processes (Sect.1.7).

In many arid and semi-arid regions of the world waste waters are used for irrigation. In the past Israel gave an impressive example of saving water resources through the use of wastewaters for irrigation. Since wastewaters may negatively affect soil properties, crops and groundwaters, pretreatment of wastewaters and a control of wastewater impacts on subsurface systems is recommended. In between the characteristics of waste waters, the content of

- neutral salts,
- heavy metals and organics and
- pathogen organisms

are the most harmful for soil, crops and groundwaters.

Neutral salts ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{Cl}^-$ ) may accumulate in soils according to the intensity of irrigation, causing toxic damage to plants and reducing the availability of water for plants through a high osmotic pressure of the soil solution or through changes in soil structure and texture properties; too high  $\text{Cl}^-$  contents generally affect tissues and plant leaves (Al-Radaideh 1992).

Heavy metals can damage microbial diversity in the effective root zone and disturb enzymatic processes and by that way may adversely influence natural attenuation processes. On the contrary, organics mainly affect groundwater quality if sorption and microbial disintegration are not sufficiently active. Considering the fact that most of the metabolites of organics

- are unknown and in general also not analytically detectable with routine tools,
- may increase in toxicity the smaller the molecular weight is becoming and
- often increase in mobility with decreasing molecular weight,

a detailed knowledge of the behaviour of organics in the unsaturated and saturated zone was needed to assess these dangers for health and life.

Pathogen organisms are quite common in wastewaters (parasites, bacteria, viruses). In fine grained soils and sediments these organisms with sizes between 0.5 and 5 $\mu$ m become mechanically retained. In coarse-grained soils and sediments they may be fixed or transported through bypass- and particle-favored flow, despite their high sorption tendency. This is quite common for parasites and bacteria, but hardly possible for viruses. Thus, mainly parasites and bacteria may cause hygienic and health risks. In this context it is of interest that these organisms survive longest in soils and shortest in crops ([Al-Radaideh 1992](#)).

To prevent the afore mentioned problems at least mechanical wastewater treatment including aeration in open ponds is recommended as a minimum activity. If the mean residence time in treatment ponds is not long enough to significantly reduce micro-organisms by natural UV radiation, a disinfections treatment is needed.

The use of environmental isotopes in irrigation studies can contribute to get a better understanding of

- storage and release of irrigation waters,
- soil salinity ,
- irrigation induced percolation in sediments,
- the contribution of return waters and agrochemicals to groundwaters ,
- the origin of salt waters in groundwater-based irrigation schemes and
- the groundwater flow field.

In most irrigation studies the stable isotopes  $^2\text{H}$ ,  $^{18}\text{O}$  and radioactive  $^3\text{H}$  are used in combination with hydrochemical methods.

### **3.1 THE IMPACT OF IRRIGATION ON PERCOLATION IN DRY LANDS WITH VARIOUS SEDIMENTS**

Irrigation schemes generally focus on fine to medium grained sediments with sufficient water retention capacities that guarantee an equilibrated portion of water and air in the effective root

zone. Mostly flood, often sprinkling and still seldom subsurface drop irrigation is applied; the latter preferentially under greenhouse conditions.

### 3.1.1 EXPERIMENTAL BOUNDARY CONDITIONS AND PERFORMANCE

The two study areas are situated in the Pakistan part of the Punjab (Sajjad et al. 1985, Sajjad et al. 1993) and in the Jordan part of the Rift Valley (Jiries 1991, Jiries & Seiler 1995), respectively. Both regions belong to arid/hyper-arid areas in which irrigation is mainly linked to rivers originating from neighboring areas (Himalayas and Golan/Ajlun, respectively); only in the Jordan Valley some irrigation water is also exploited from groundwaters out of Wadi river cones.

The Punjab plain is still today an active sedimentation area; therefore, it lacks any significant relief. Since sedimentation occurred under marine conditions or in flood plains, sediments are quite homogeneous in their grain- and pore-size distributions and contain syngenetic salt residuals. In the recent geologic past the flatness of the region resulted in frequent changes of the river courses (Nazir 1974). From the beginning of the last century the Punjab area has been covered with many blind ending, unsealed channels (Fig.3.1), importing the irrigation water to the fields.

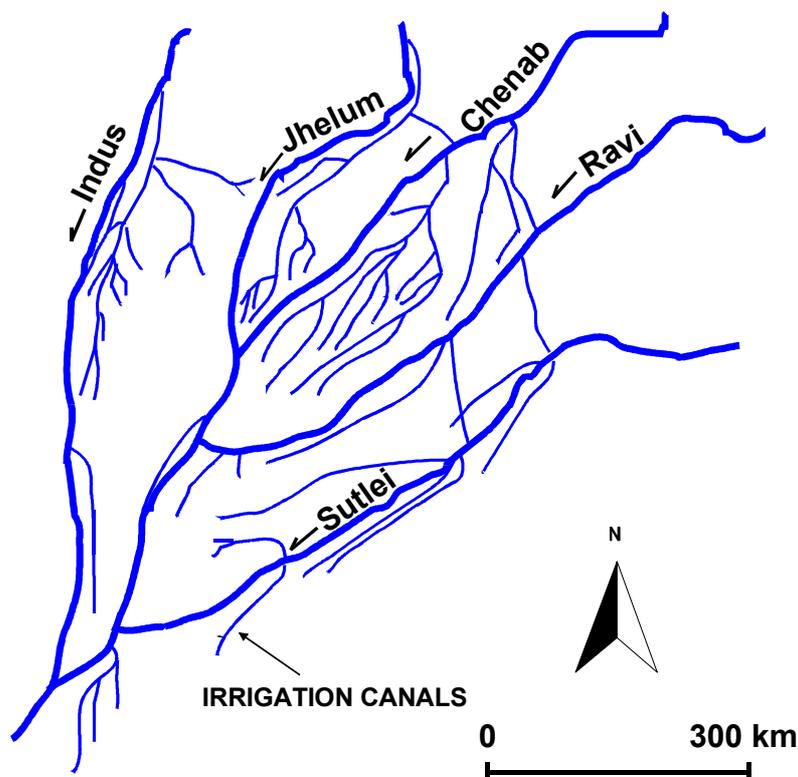
Contrary to the Punjab, the Jordan valley is a young rift area in which erosion prevails on the graben shoulders. Even these days local sedimentation under quite varying river flow velocities creates alluvial cones and sediments with a broad spectrum of grain and pore sizes (Fig.3.2). These alluvial sediments lay on the partially compacted, fine grained and fissured lake sediments of the Lisan formation, which act as the base of perched groundwaters discharging to the Jordan river.

In Pakistan the rivers Indus, Suttley, Ravi and Chenab act as recharge and discharge systems, whereas in the rift valley the Jordan river and the Dead Sea act as discharge base.

In both areas flood irrigation is applied. In both regions its impact on the unsaturated zone has been studied for sediments covering the range from silts to sands with many transitions in between. To execute these studies, fields of 50 x 50 m in size have been dammed in both areas which were irrigated in the Punjab with 75 mm and in the Jordan valley with 150 mm of water. In coarse and fine grained sediments of both regions irrigation waters disappeared quite immediately after irrigation (sands) or within half a day (sandy silt), respectively; in the fissured Lisan Marls waters disappeared surprisingly as fast as in sands (Sect. 3.1.2).

Before and repeatedly after irrigation two to three meter long cores were hand-drilled for soil water extraction in the central part of the experimental sites, to study changes of water contents and of the chemical and isotope composition of soil waters. Soils were sampled at 10 cm intervals and the samples hermetically sealed in plastic tubes (5 cm in diameter and 20 cm in length). Physical, chemical and isotope analysis were performed on extracted waters (Sect.6.4)

Since by nature the Punjab area is not drained by perched groundwaters, contrary to the Jordan area, only in the Punjab also groundwater studies were executed.

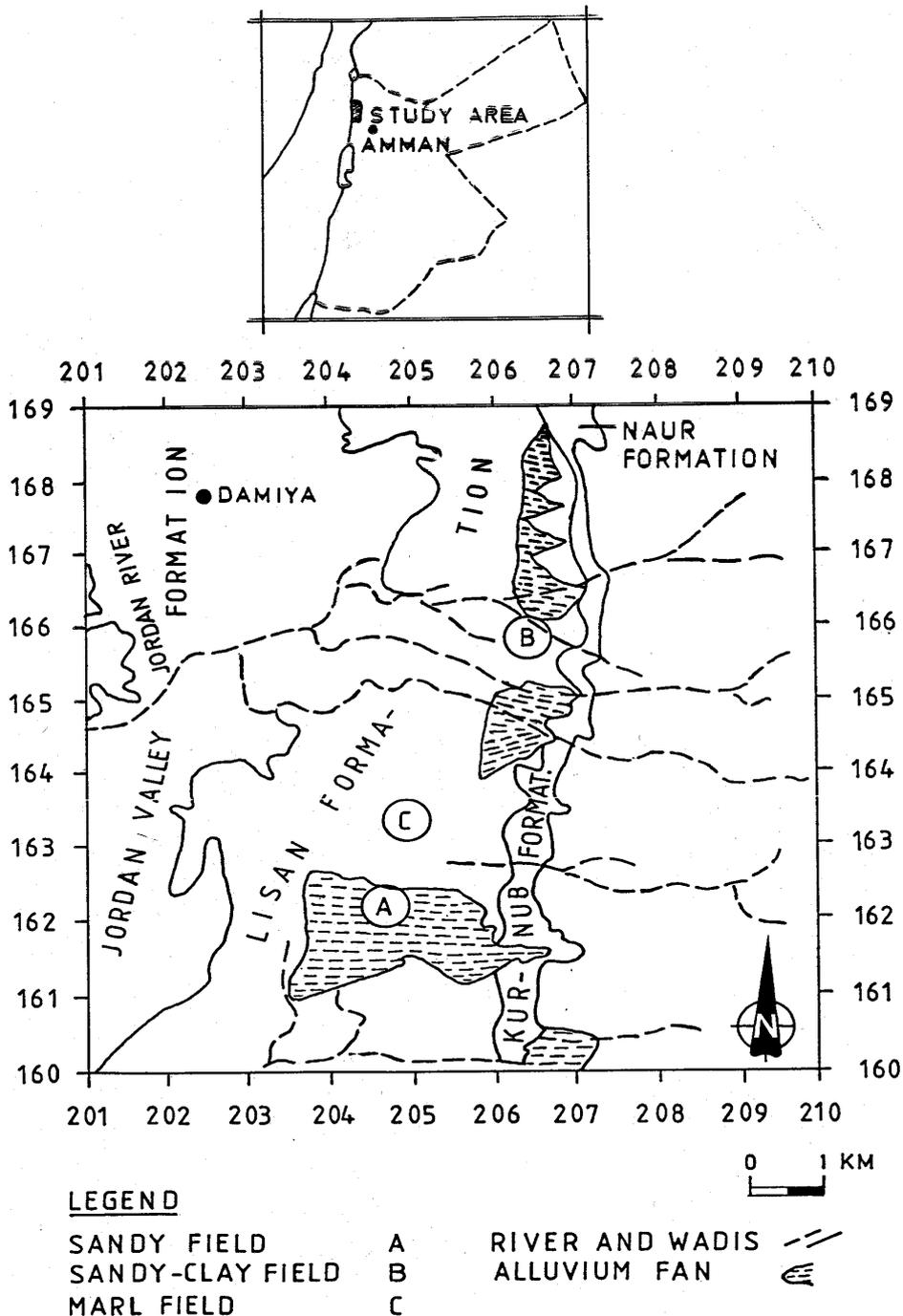


**Fig.3.1** The Punjab study area between the rivers Ravi and Chenab and the existing distribution system of irrigation waters.

### 3.1.2 DISCUSSION OF RESULTS ON PERCOLATION

Based on the natural water content before and one day after irrigation and integrating in profiles the increase of water content due to irrigation, it could be shown for the Punjab (Fig.3.3) that in all sediments the applied irrigation water is stored to 100% within a maximum of three meters below ground level. The more silty the sediment, the less irrigation water penetrates to depth, and conversely. Obviously these sediments have quite homogeneous pore sizes and are not significantly biologically disturbed (roots, worm and mouse holes). Therefore, they produce a homogeneous flux of seepage waters (matrix without by-pass fluxes).

Contrary to the Punjab, in the Jordan valley sediments are quite inhomogeneous either by texture or by structure. Therefore, only a small portion of irrigation water is stored in the matrix, while the rest percolates as bypass-flow (Sect.1.3) to perched groundwaters and discharges subsurface to the Jordan river. As a consequence soil waters are better leached from salts in the Jordan than in the Punjab area.



**Fig.3.2** The Jordan study area with three different experimental sites (1 to 3).

With respect to the behaviour of soil waters after irrigation, in the Punjab region the following observations were made (Figs.3.3 and 3.4):

- 1) At the beginning of the experiment seepage moves continuously downward. Since water contents at the surface reach a lower threshold value of 5-10 vol.%, seepage turns against gravity.

- 2) Irrigation dilutes the pre-existing salt concentration and increases again when evaporation turns seepage from vertical down to vertical up.
- 3) After irrigation soil shrinking starts, while dew dilutes the salt concentration close to the surface of the profile.
- 4) At a groundwater table of 3 to 4 m below ground level irrigation practice in silty sediments does no longer influence groundwater quality (see below). Therefore, low chlorinated groundwater moves from the groundwater table by capillary forces into the unsaturated zone, diluting and narrowing the  $\text{Cl}^-$  peak that was broadened in the unsaturated zone by irrigation. On the contrary, in sandy sediments with a water table close to the ground surface (e.g. 2.5 m) salt is imported by irrigation into the groundwater and becomes reimported into the unsaturated zone as far as seepage changes from downward into an upward direction.
- 5) During the rainy season (monsoon) some through-flow in all types of profiles takes place, causing dilution and leaching of salts that accumulated during the dry season in both irrigated and non irrigated soils. This produced the low chloride concentrations in sandy silts (Fig. 3.4) before the irrigation experiment started.

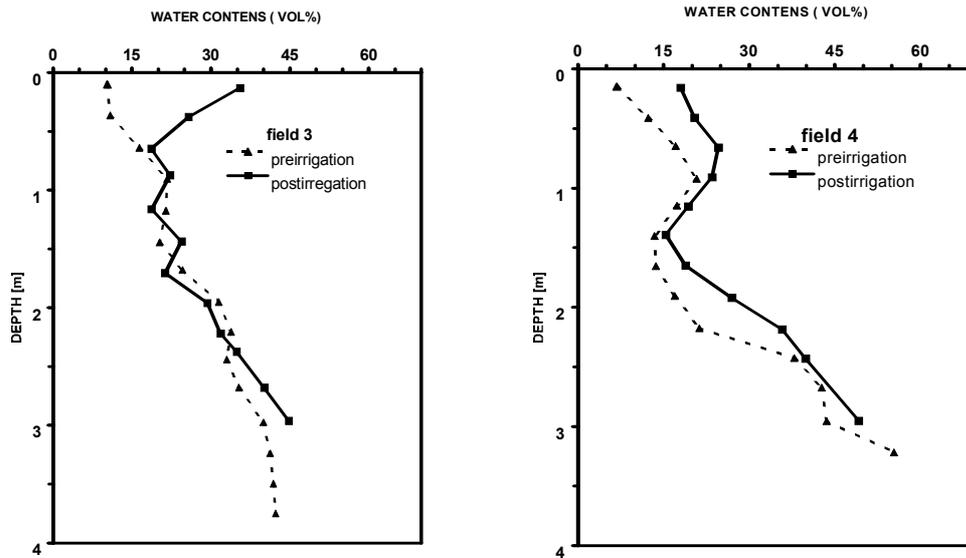
The salinisation of sediments in the unsaturated zone in the Punjab is mostly caused by evaporation:

- salts accumulate permanently in the unsaturated zone if the water table is below 3 m and irrigation is not applied too often; these salts do not reach the water table;
- at least once a year monsoon rains dilute and export salts
- salinisation enhances if the water table nearly reaches the surface (<3 m).

In the Punjab with missing morphology, i.e. the differences in morphologic altitudes are smaller than the differences in hydraulic heads needed for groundwater flow, there is an additional effect enhancing salinisation. To protect the effective root zone and constructions against groundwater, deep drainage channels have been constructed that often do not discharge effectively due to missing topographic gradients. The channels favour evaporation even to deeper than 3 m.

Since the very slow process of water logging can not be avoided due to the existing infiltration of irrigation water, buried drainages or water pumping was recommended to better manage water logging and soil salinisation. Pumped or drained subsurface waters, however, should not be discharged to irrigation channels from where it reinfiltreated to the underground.

On the contrary, in the Jordan valley 150 mm irrigation increased the water content of all profiles under study only partially (Fig.3.5), because most of the water was lost as bypass-flow to the perched groundwater discharging along the alluvial/Lisan marl interface.

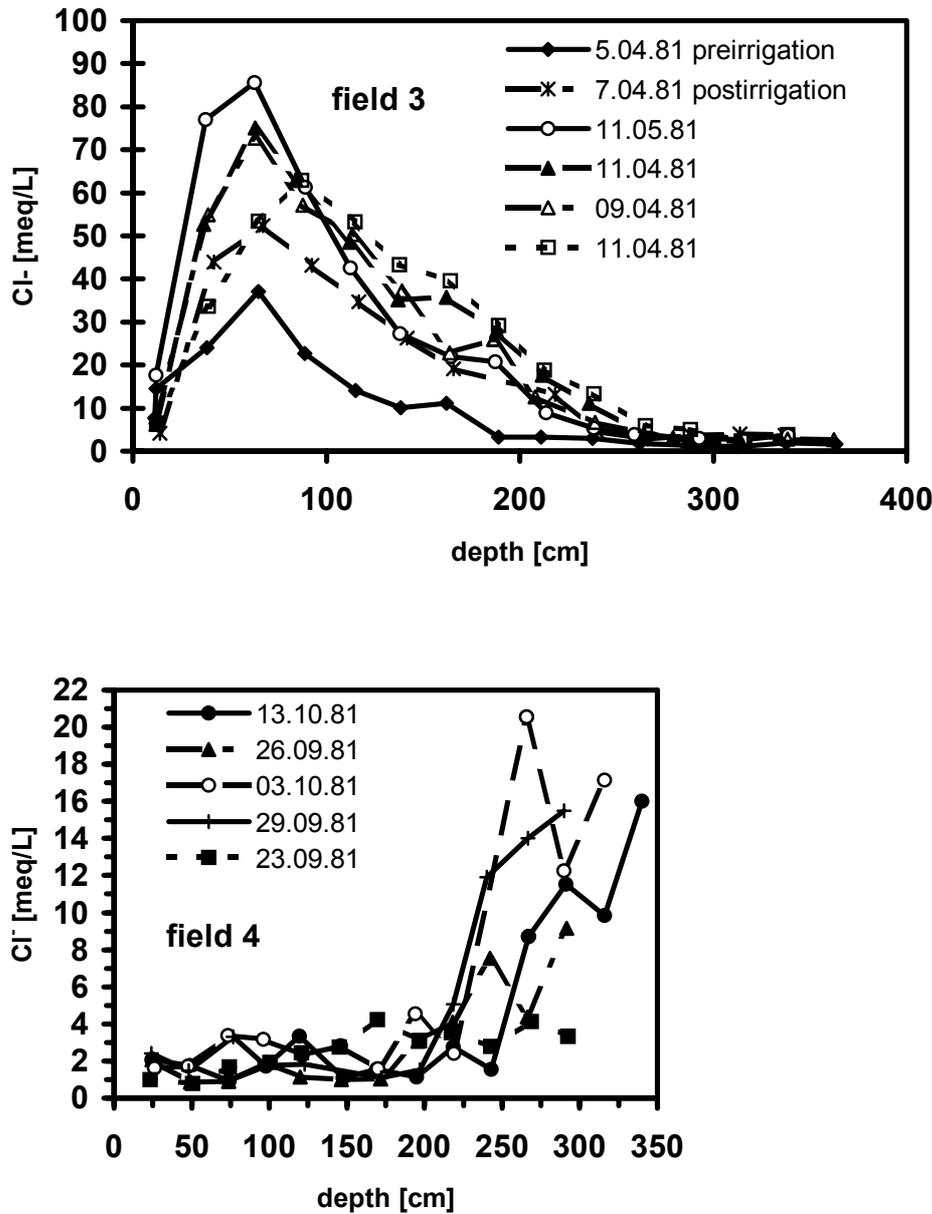


**Fig.3.3** Profiles of changes in water content just before and after irrigation for four typical sediments in the Punjab. The irrigation quantity was 75 mm.

After the wet season only 20% of the applied irrigation water is stored within two meters from the surface, while during the dry season 50 to 60% is stored in the unsaturated zone, because during the dry season the water content did not reach field capacity (Table 3.2). This low storage of water in the unsaturated zone (Table 3.2) is observed in all types of irrigated sediments of this region, even in the Lisan Marls. They are related to bypass-, macropore- or preferential-flow (Sect.1.3, Beven & German 1982), occurring typically

- in fluvial sands and gravels, deposited in areas with high relief energy or
- in cohesive sediments crossed by shrinking or crystallisation cracks.

In the fluvial sediments of the Jordan valley both these peculiarities lead to discontinuous pore size distributions resulting in the coexistence of slow matrix and quick bypass-flow. Bypass-flow moves with apparent velocities of decimetres to meters/day, matrix flow with less than 5 m/year. This contrast primarily has sedimentologic reasons in arid and semiarid areas and may become enhanced by bioturbation and human activities. By experience these two flow systems reach limited depth because capillary gradients increasingly force bypass-flow into the matrix flow system. Penetration depth of bypass-flow reaches to more than 3 m in gravels and more than 2 m below ground floor in sands. Annually bypass-flow may amount to 50% of the infiltrated water.

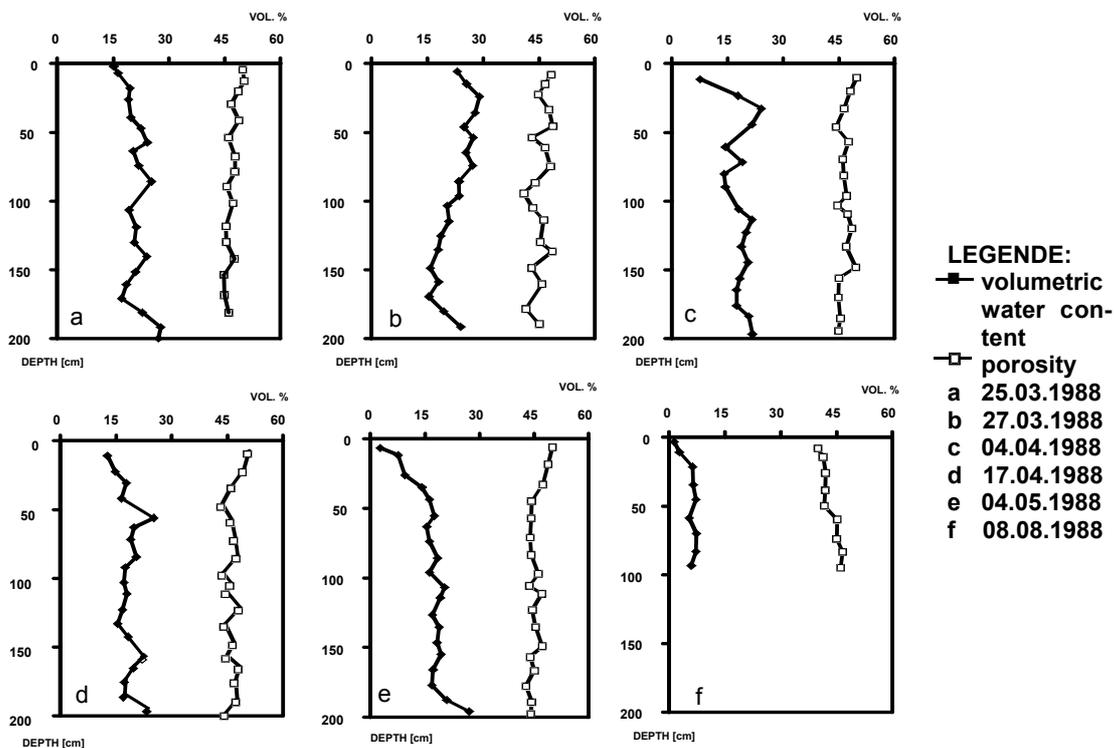


**Fig.3.4** Profiles of changing chloride concentrations in the unsaturated zone of fields 3 (sandy silt) and 4 (sand) (Fig.3.3) after irrigation of 75 mm.

Changes in water content reflect the immediate storage of infiltration events in the percolation zone, whereas the stored waters calculated on the basis of concentration changes of non-reactive tracers (e.g. Cl and <sup>18</sup>O) indicate both immediately stored waters and diffusive tracer exchanges between bypass and matrix flow. Therefore, the calculated values of stored waters using isotope or chemical tracers are systematically higher (Table 3.2 columns 2 and 3 as compared to column 1) and thus document the existence of bypass-flow.

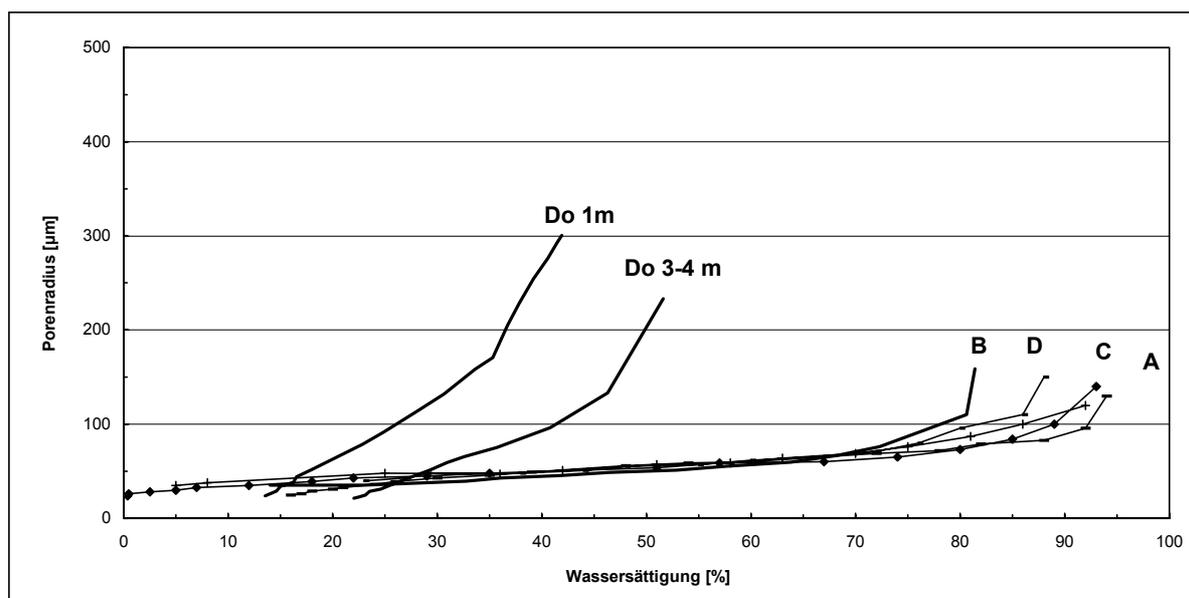
As a result of the experiments in the Jordan valley much water becomes wasted due to bypass-flow when applying flood irrigation.

Some typical pore size distributions of sediments from areas with low and high relief energy are shown in Fig.3.6 as cumulative curves. The more these curves become S-shaped and steep the more the pore sizes in the two flat branches of the S dominate; the more homogeneous the pore sizes the more these curves remain flat.



**Fig. 3.5** Water contents in a sandy-silt sediment of the Jordan valley before (a) and days after irrigation (b to f).

As can be seen from Fig.3.7 the infiltration of irrigation water diminishes the chloride concentration in the sediments of the Jordan Valley. After irrigation, chlorides primarily concentrate at the soil surface and decrease more or less exponentially to a certain depth, since dew occurs in this area only at the soil/air interface, because shrinking cracks are missing (Allison & Hughes 1974). Similar to the results from the Punjab also in the Jordan valley the water table contributes to an upward movement of non-saline waters as far as the water content at the soil surface reaches 5 - 8 vol.% in coarse and fine grained sediments, respectively. Hazardous rains, however, disturb this equilibrium distribution of fluxes and chlorides, in the dry season producing a variety of salt peaks and valleys in the unsaturated zone and again becoming leached during the wet season.



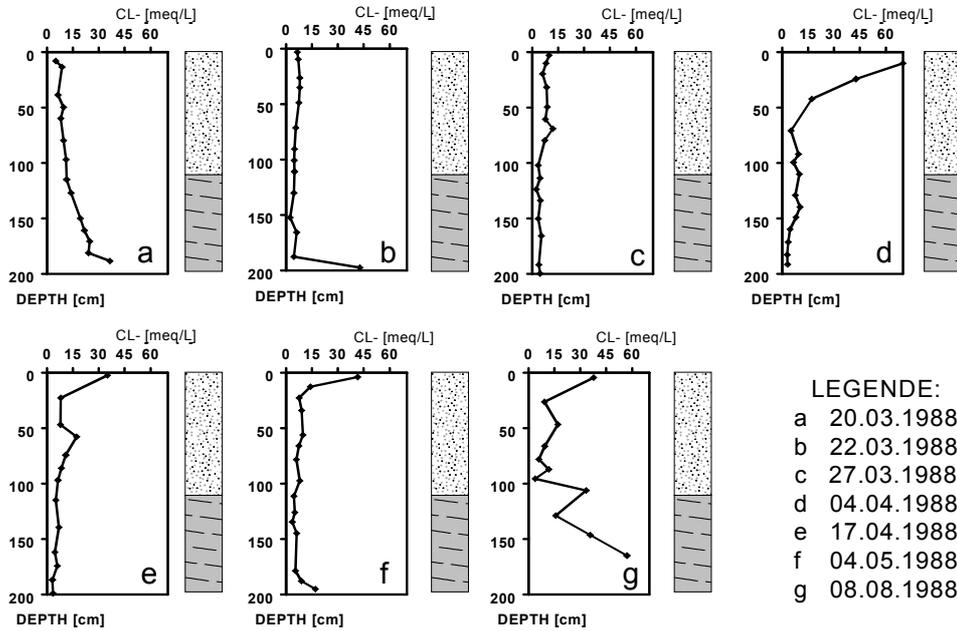
**Fig.3.6** Typical pore size distributions of sediments with prevailing matrix flow (curves A-D) and sediments with matrix and bypass-flow (S-shaped curves Do). Since measuring accuracy is low at very high and low pore radius the S-shape is not too clear to demonstrate.

**Table 3.2** Jordan valley: measured and calculated water contents immediately after irrigation. Light rows: after the wet season (March); shaded rows: during the dry season (August). nc = not calculated.

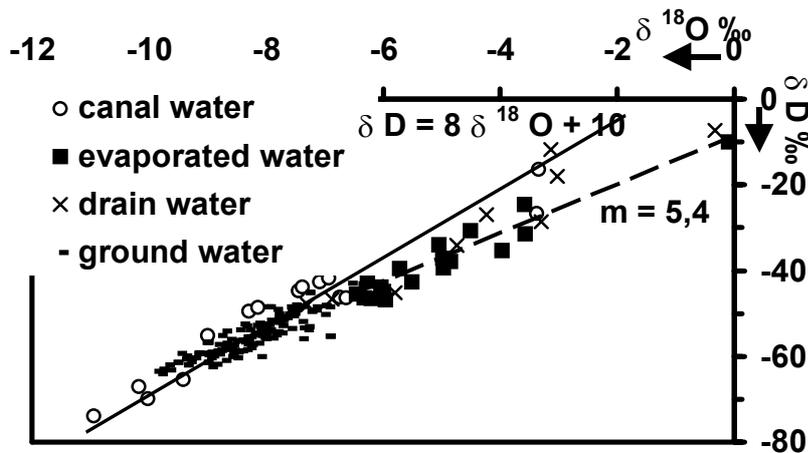
Sediment	Applied irrigation L/m <sup>2</sup>	Initial water content %	Resulting water content %	Stored irrigation water based on calculations of changes of		
				water content	[Cl <sup>-</sup> ]	δ <sup>18</sup> O
Sand	190	10	15	38	53	53
Sand	150	6	12	58	nc	60
Sandy silt	150	22	25	26	30	29
Sandy silt	150	6	12	53	nc	68
Lisan Marls	150	45	50	16	36	nc
Lisan Marls	150	30	37	nc	34	36

Contrary to the Punjab, irrigation does not continuously increase soil salinity in the Jordan valley, because groundwaters in the erosion area of the Jordan valley experience stronger natural recharge and have greater hydraulic gradients than in the Punjab. As a first

approximation groundwaters may be considered as stagnant in the Punjab and as flowing in the Jordan valley.



**Fig.3.7** Changes of chloride concentrations in a sandy silt profile in the Jordan valley after irrigation



**Fig.3.8** Stable isotope concentrations in channel and groundwaters of the study area in Pakistan.

### **3.1.3 THE CONTRIBUTION OF IRRIGATION AND CHANNEL WATERS IN THE AREA BETWEEN CHENAB AND RAVI, PUNJAB, TO GROUNDWATER LOGGING**

In Pakistan almost all irrigation channels are ending blindly and unsealed. Stable isotope sampling of channel and groundwater (Fig.3.8) resulted in the following observations.

- 1) for channel waters no evaporation impact is observed; however, the  $^2\text{H}$  excesses range between 18 (Mediterranean) and 9 (Monsoon),
- 2) groundwaters deeper than 3 m also show no evaporation and also a somewhat lower variability of the  $\delta^2\text{H}/\delta^{18}\text{O}$  ratio than in channel waters; since the groundwater table was much deeper in former times (about 40 m), the actually missing evaporation impact indicates that channel water contributed predominantly to groundwater logging,
- 3) there is a strong evaporation impact as far as groundwaters are drained or become close to the land's surface.



# 4 IMPACT OF URBANISATION ON GROUNDWATER

Urbanisation is increasing worldwide. In 1900 only 10% of the world population lived in cities; for the year 2000 their number is estimated at 50% (UN 1991). The actual ten biggest cities on earth, the so-called mega-cities, have an average population of 17 million.

The three essential infrastructure facilities of towns are water supply, solid waste collection and sewage water collection systems. In both humid and tropical regions the drinking water demand of big cities (> 1 million) usually can not be satisfied by the catchment area of the city itself, because precipitation related discharges are lower than the water demand. Therefore groundwater abstraction for big cities mostly results in overexploitation of the city catchment (Chapter 2) or water for the private and industrial sector is imported from neighbouring catchments. The measures (overexploitation and water import) increase the natural river discharges from the catchment by adding abundantly wastewaters and thus harming the river ecosystem as well as the estuaries and oceans.

Water supply for mega-cities has to cover an average water demand in the range of 20 to 60 m<sup>3</sup>/s. Distribution nets, however, are leaking at a minimum of 5% (e.g. Caracas) up to 50% (e.g. Amman, Mexico City), so increasing the natural groundwater recharge. As a consequence, groundwater levels rise causing hygienic as well as geotechnical problems. The fact is that without groundwater abstraction the rising water level is likely to affect the stability of constructions through increasing buoyancy.

Mega-cities have usually many deeply founded constructions. To protect these against water during and after construction, groundwater abstraction or subsurface drainages are needed on either short or long terms. This may cause adverse geotechnical problems for the neighbourhood.

Finally some mega- or big-cities are allocated near shore or the groundwater resources are underlain by salt waters. In these cases excessive groundwater abstraction may force salt water to move either laterally or vertically into the freshwater, so deteriorating groundwater quality (Sect.2.2).

As far as groundwater abstraction below cities is linked with drinking water supply, groundwater protection measures are required that are difficult to handle and to supervise in town areas. Therefore with respect to increasing urbanisation, adequate subsurface management and control is needed to contribute to solutions for groundwater related

geotechnic, hygienic and protection problems of urban areas. The Caracas study (Sect.4.1) aims to contribute to reach sustainable drinking water supply by groundwater abstraction.

Environmental isotope and artificial tracer methods may significantly contribute to solve questions of groundwater exploitation, mixing and origin in urban areas.

- 1) Radioactive environmental isotopes may support
  - in differentiating the groundwater flow field by means of mean residence times or groundwater "ages" (Chapter 2 and Sect.1.7; Volume IV)
  - in setting up an early warning system to control sustainable groundwater protection (Sect.2.1).
- 2) Stable environmental isotopes may contribute
  - to quantify mixing ratios of waters from different origin
  - to map losses from the distribution and collection systems, and to monitor sewage water losses
  - to recognise the origin e.g. of contaminants ([Hiscock et al. 1997](#)).
- 3) Artificial tracer methods can be used to control
  - efficient groundwater abstraction measures for construction purposes (Chapter 2)
  - the efficiency of protection measures for constructions.

It should be emphasised that tracer tools become more efficient when combined with traditional methods.

## **4.1 GROUNDWATER MANAGEMENT BELOW THE CITY OF CARACAS, VENEZUELA**

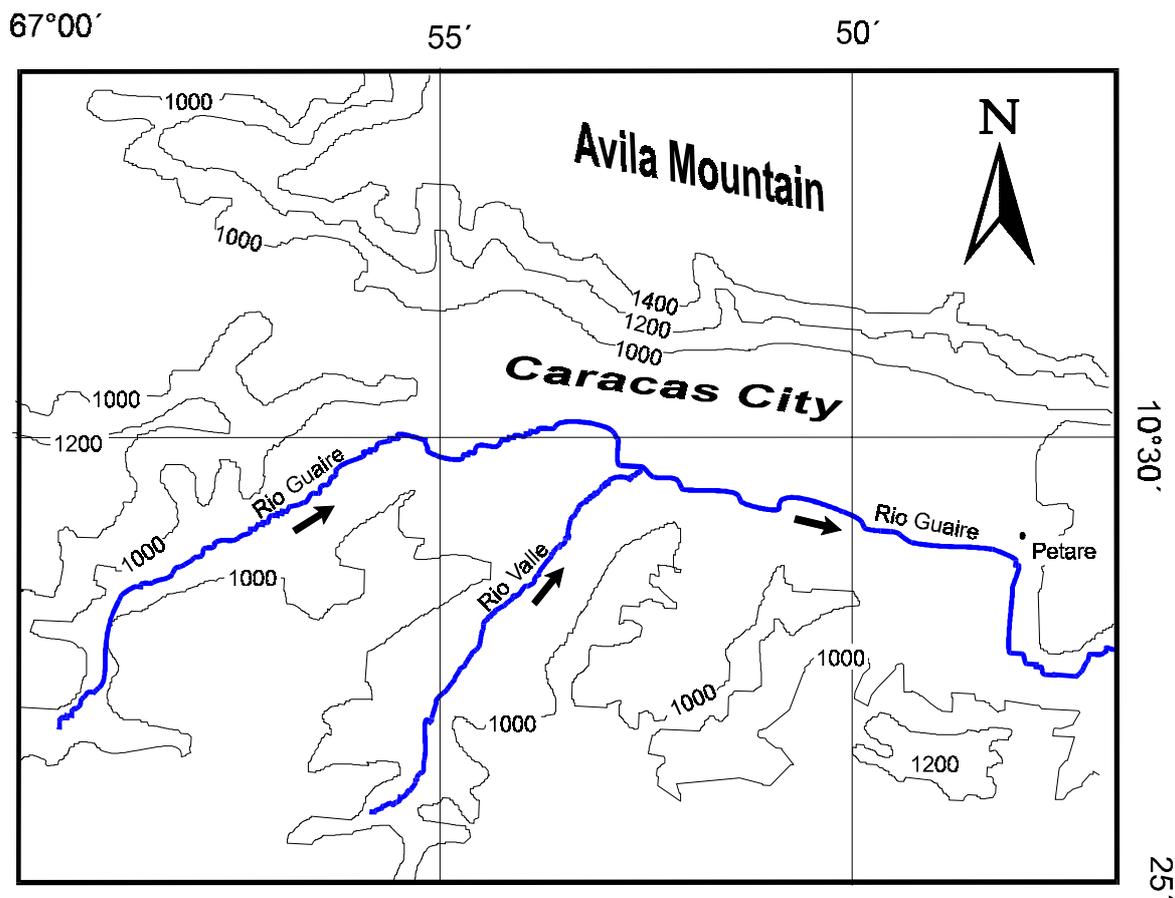
The population of the town has exploded within the last 150 years from approximately 40 000 to 4 000 000 and is still growing.

About 17.4 m<sup>3</sup>/s of drinking water is provided to the city from surface reservoirs in neighbouring catchments; further resources for water supply have to be developed for this further growing city. One potential additional source is the aquifer beneath the city, which was developed stepwise during the last few years. To assess chances and limits to further exploit this aquifer in a sustainable manner, a water balance had to be set up, the state of groundwater quality must be registered and possible groundwater protection measures must be discussed.

#### 4.1.1 GEOLOGY OF THE CARACAS VALLEY

The Caracas valley, surrounded by crystalline rocks, was filled up to 300 m with weathered materials. The Caracas aquifer consists of fluvial gravels, sands, interbedded by clays and silts from a former lake. All these sediments intercalate in a very irregular manner as is typical for narrow lakes in an environment with high relief energy.

The two rivers Guaire and Valle (Fig.4.1) discharge overland flow, interflow and groundwater from the catchment. Today both rivers are canalised in the town area and exchanges between



**Fig.4.1** The catchment area of the Guaire river from the sources to Petare and the city of Caracas on the valley floor (below 1000 m a.s.l.). Left hand of the confluence of the Valle and Guaire rivers stretches the old (DF), right hand the new city (MI).

ground- and surface-waters are hindered, except in the area of Petare (Fig.4.1) where the Caracas aquifer ends and the Guaire enters a canyon in crystalline rocks.

The catchment area as far as Petare covers 564 km<sup>2</sup>, of which the city takes 65.4 km<sup>2</sup>. In the Caracas valley some hundred wells exist, of which only few are installed as production wells. These have not been positioned systematically; they were filtered according to the hydraulic

conductivities (Chapter 2) of the aquifers encountered and penetrate a few ten to about 120 m into the valley. No well is known to perforate the whole aquifer system of maximum 300 m.

#### 4.1.2 WATER BALANCE AND THE ORIGIN OF GROUNDWATERS BENEATH THE CITY

Precipitation in the Guaire catchment area averages 925 mm/a. It causes outside the city overland and subsurface discharges, within the city mainly overland discharge. In the past most of the creeks entering the valley from crystalline rocks infiltrated partly or completely into the unconsolidated Caracas aquifer. Today they are canalised within the town and thus contribute only to surface discharge. This contribution is estimated at about 105 mm/a, producing about 1.7 m<sup>3</sup>/s to the Guaire River. Infiltration around the town has been calculated using chloride concentrations in precipitation (1.5 mg/L) and in anthropogenic uninfluenced groundwater (15 mg/L) (Fig.4.4). Since no chloride evaporites occur both in the valley fill and the surrounding metamorphic rocks, infiltration (R) is calculated on the basis of the mass conservation equation, resulting in:

$$P \cdot Cl_{\text{precipitation}} = R \cdot Cl_{\text{groundwater}}$$

$$R = (925 - 105) \times 1.5/15 = 82 \text{ mm/a} \equiv 2.7 \text{ L/(s} \cdot \text{km}^2)$$

Similar infiltration rates are known from other crystalline areas (Seiler & Müller 1996). The lateral subsurface recharge from the catchment outside the city area consequently amounts to

$$(564 - 65.4) \times 2.7 = 1.3 \text{ m}^3/\text{s}.$$

and the no more occurring recharge in the city area to

$$65.4 \times 2.7 = 0.18 \text{ m}^3/\text{s}$$

As a result of surface and subsurface discharges the actual evapotranspiration (ET) amounts to

$$ET = 925 - 105 - 82 = 738 \text{ mm/a}$$

which is in fairly good agreement with the actual evapotranspiration calculated for neighbouring tropical zones (Seiler et al. 1992, Baldison et al. 1995).

#### 4.1.3 STABLE ISOTOPE CONCENTRATIONS IN THE GROUNDWATER

Stable isotope concentrations ( $\delta^2\text{H}$ ,  $\delta^{18}\text{O}$ ) in precipitation, rivers and springs at the border of the city follow the meteoric water line (Fig.4.2)

$$\delta^2\text{H} = 8 \delta^{18}\text{O} + 12\text{‰}$$

Groundwater below the city is isotopically enriched (Fig.4.2) by evaporation processes. These waters underwent evaporation in surface reservoirs, where they were collected and stored, and in the open treatment plants of the water supply. Some of these waters are being lost by the distribution and collector systems below the town area. These mix with non-evaporated groundwaters from lateral inflow, so contributing much longer to the groundwaters under the old city (DF) than under the new city (MI) that grew during the last 40 years. Taking the mean value of evaporated drinking waters ( $c_1$ ), of unevaporated groundwaters on the meteoric water line ( $c_2$ ) and of groundwaters beneath the city ( $c_3$ ) the fraction of losses ( $n$ ) from the distribution and collector net can be calculated from the mixing equation (Box 4.1).

$$n = \frac{c_3 - c_2}{c_1 - c_2}$$

This calculation shows losses of 5.2% of the distributed and collected water. With respect to an amount of 17.4 m<sup>3</sup>/s of imported water, the losses are then 0.9 m<sup>3</sup>/s, correspondingly added to the groundwater recharge under the city.

The spatial pattern of groundwater affected by evaporation can be used to map the approximate sources and loss intensities from the distribution and collector systems.

Together with losses from the drinking water distribution net of 0.9 m<sup>3</sup>/s and the lateral subsurface inflow of groundwater (1.3 m<sup>3</sup>/s), a total of 2.2 m<sup>3</sup>/s is recharged to the Caracas aquifer and about 2 m<sup>3</sup>/s is actually abstracted from wells of different depths.

All the surface (1.7 + 0.18 m<sup>3</sup>/s), subsurface (1.3 m<sup>3</sup>/s) and imported waters (17.4 m<sup>3</sup>/s) produce a total discharge of the catchment of 20.6 m<sup>3</sup>/s which is in good agreement with discharge measurements in the Guaire river at Petare that have been executed repeatedly with fluorescent dyes.

#### 4.1.4 DYNAMICS OF THE GROUNDWATER

A plot of <sup>3</sup>H versus depth (Fig.4.3) shows that <sup>3</sup>H concentrations of groundwater drop abruptly at 40 to 50 m depth to non-measurable concentrations. This depth is by definition the interface between the active and passive recharge zone (Sect.1.7; Seiler & Lindner 1995). Starting from this interface to greater depth, <sup>14</sup>C concentrations drop to less than 40 pMC, electric conductivities rise and stable isotope concentrations show that admixture of evaporated waters is no more detectable. Obviously the impact of water losses from the distribution and collector systems of waters did not significantly penetrate to the passive recharge zone, although this infiltration lasts already many decades. Thus the losses from the city's distribution and collector net represent isotopically and chemically a long-term tracer record, enabling us to recognise qualitatively the susceptibility of different zones of the aquifer system to pollution. The conclusion is that the active and the passive recharge zone have a different importance for the availability (Seiler & Lindner 1995) and long-term quality of the groundwater exploited from beneath an urban area. This result applies to other areas

with high pollution risk as well, and will be used as a new approach for sustainable drinking water exploitation e.g. in an urban area.

**BOX 4.1**  
**MIXING EQUATION**

Components 1 and 2 are mixed resulting in component 3. The calculation is based on the load ( $F = CQ$  in mass/time) of the contributing and resultant components.

$$C_1Q_1 + C_2Q_2 = C_3(Q_1 + Q_2) \quad (4.1)$$

Define:

$$n = \frac{Q_1}{Q_2 + Q_1} \quad (4.2)$$

Then

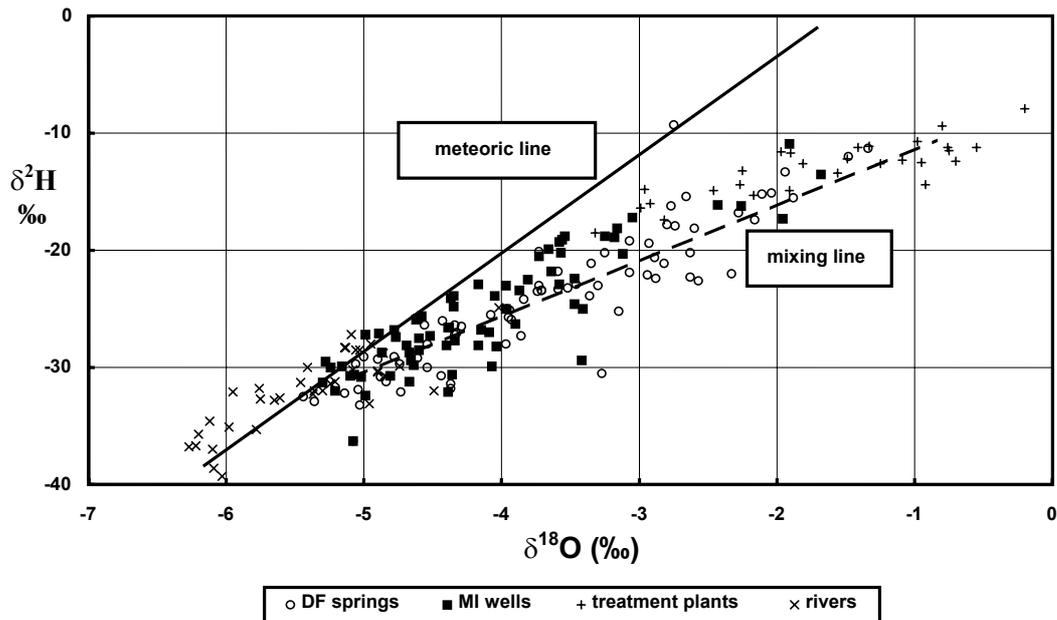
$$1 - n = \frac{Q_2}{Q_2 + Q_1} \quad (4.3)$$

Inserting Eq.4.2 and Eq.4.3 in Eq.4.1 we have:

$$nC_1 + (1 - n)C_2 = C_3$$

or 
$$n = \frac{C_3 - C_2}{C_1 - C_2} \quad (4.4)$$

Mathematical modelling on the average fraction of groundwater recharge reaching the passive recharge zone showed that as an average less than 15 to 20% penetrates to this zone (Sect.1.7, Seiler & Lindner 1995). This is the effectively available recharge at below 50 m of depth that can be exploited without significantly changing the natural groundwater flow field. Higher fractions will create hydraulic short cuts mainly to overlaying aquifers, in order to compensate the missing water quantities (Fig.1.10). By experience and by modelling it becomes evident, that this is a long-term transient process. Any contribution of contaminated waters to the groundwater in the underground of Caracas will initially and preferentially affect the active recharge zone as indicated by  $^{18}\text{O}$  and  $^3\text{H}$  (Figs.4.2 and 4.3).

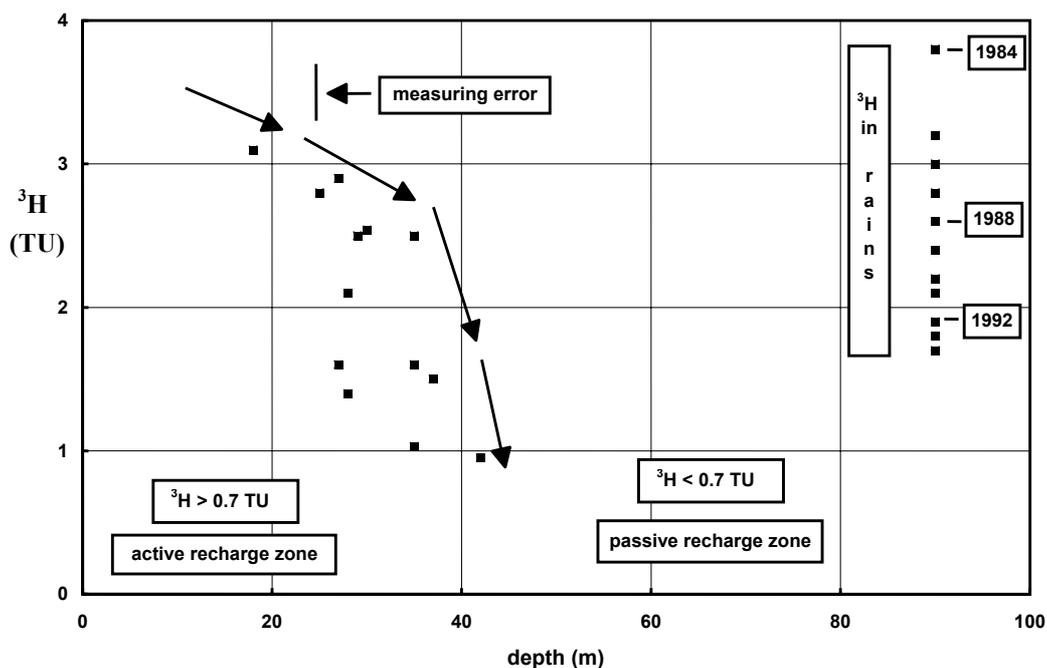


**Fig.4.2**  $^2\text{H}/^{18}\text{O}$ -diagram of groundwaters from the Caracas area. Most waters beneath the city represent a mixture between naturally occurring groundwaters allocated at the meteoric water line and waters of treatment plants.

#### 4.1.5 CONTAMINANTS IN THE GROUNDWATER

Point sources of groundwater contamination have been detected during the construction of the Caracas subway. They influence only very locally groundwater quality, still seem to occur scarcely beneath the town and are restricted to highly industrialised areas of the city. In contrast, diffuse source contaminations, especially losses from the wastewater collector systems, influence groundwater quality to some extent.

Chloride and  $^{18}\text{O}$  are both conservative tracers in the water cycle. In the active recharge zone of the Caracas region they originate either from precipitation, chlorides from treatment plants or waste waters. Thus, in a chloride/ $^{18}\text{O}$  diagram all chloride concentrations exceeding the mixing stretch between natural variations of  $^{18}\text{O}$  concentrations and the output concentration of chloride from treatment plants must point to pollutions (Fig.4.4). This figure shows also that chloride concentrations in groundwater beneath the old city (DF) are on average higher than under the new city (MI).



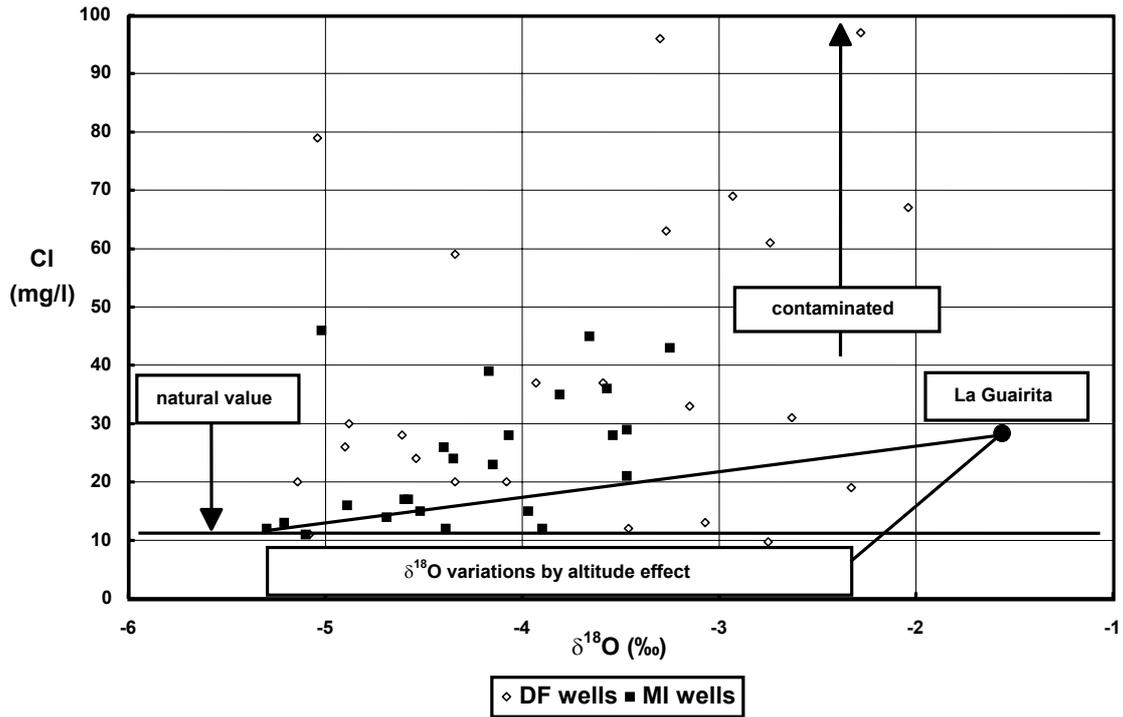
**Fig.4.3** The change of  $^3\text{H}$  with mean groundwater depth. The interface between the active and passive recharge zone is coincident with just no more measurable Tritium concentrations (TNT).

The natural nitrate concentrations have been calculated to be on average 10 mg/L. From the nitrate/depth diagram, however, it becomes obvious (Fig.4.5) that below the old city (DF) groundwaters in the active recharge zone may have even lower nitrate concentrations than natural, coupled with the occurrence of nitrite and ammonia. On the contrary, below the new city the nitrates never reach lower concentrations than natural.

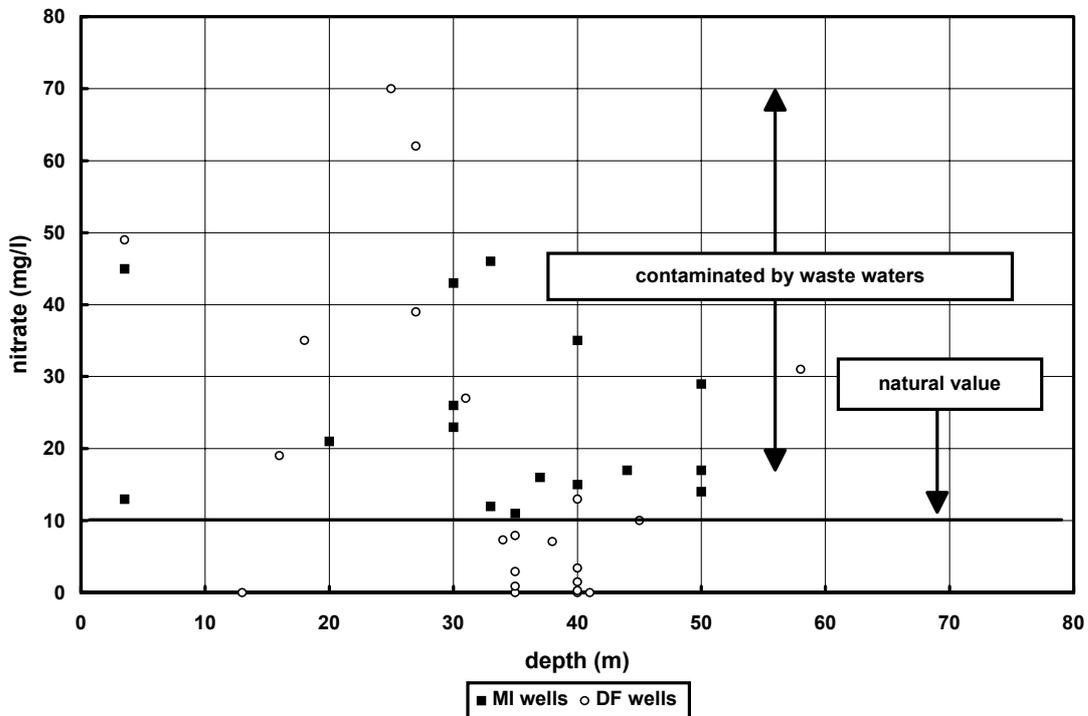
The  $\text{NO}_2^-$  and  $\text{NH}_4^+$  occurrences in groundwater below the old city, not present under the new city, are interpreted as the result of microbial activities in the active recharge zone below the DF, still absent below the new city. As a consequence of changes in land use microbial activities may become stimulated after certain incubation times (Barringer et al. 1990). Since the new city is less than 40 years old, this microbial activity is still developing, as is also known from other parts of the world (Seiler et al. 1997).

Analyses of heavy metals and metalloids in groundwater beneath Caracas City show either non- or just-measurable concentrations, not exceeding permissible limits; organics have not yet been measured. With respect to pathogenic micro-organisms, the mechanical filtering capacity of the alluvials in the Caracas valley as well as the preferential fixation of micro-organisms on solid surfaces provide a high mechanical retention capacity (Alexander & Seiler 1983), being even stronger in the unsaturated than in the saturated zone of the aquifer due to low water contents (Schaefer et al. 1998).

## Impact of Urbanisation



**Fig.4.4** Chloride/ $\delta^{18}\text{O}$  diagram for groundwaters out of wells within the old (DF) and the new city (MI) and the treatment plant La Guairita.



**Fig.4.5** Nitrate concentrations in waters out of wells within the old (DF) and the new city (MI) as a function of mean sampling depth.

A further advantage in exploiting deep groundwaters in potentially endangered areas is shown by the geometry of the inflow area to the wells (Sect.2.1.3, Fig.2.8). Since the Caracas valley is small and several kilometres long and groundwater recharge occurs mainly laterally to the town area, most of the inflow areas to the deeply screened wells will stretch to the border of the valley. The contaminants potentially accessing the groundwater beneath the town than would overflow wells as long as exploitation will not exceed about 0.9 m<sup>3</sup>/s.

The mean residence time (T) within the active recharge zone was calculated from aquifer and recharge data by applying:

$$T = \frac{pM}{Q} \quad (4.4)$$

With a porosity of  $p = 0.25$ , an aquifer thickness of  $M = 50$  m, a surface area of the Caracas aquifer of  $A = 65.4 \times 10^6$  m<sup>2</sup>, and a subsurface discharge of  $Q = 2.2$  m<sup>3</sup>/s the resulting residence time came to 12.3 years. Tritium data (Fig.4.3) point to a value of about 15 years, using simple piston flow assumptions. Consequently, only inorganic pollutants with high or even missing disintegration half-life, or pollutants without or with a very small sorption rate may potentially endanger this groundwater resource.

# 5 IMPACT OF LAND USE ON GROUNDWATER QUALITY

The land surface is exposed to different contaminant sources (air, household, dump sites, industry, traffic and agriculture). Contamination may reach subsurface waters enhanced by special surface receptors (e.g. interception evaporation) and become transported by overland flow, interflow and infiltration (Sect.1.4) to surface and groundwater.

The emission of contaminants is partly produced by combustion processes, introducing  $\text{H}_3\text{O}^+$ ,  $\text{NO}_x$ ,  $\text{SO}_x$ ,  $\text{CO}_2$ , heavy metals and organics into the atmosphere. They subsequently reach the land cover either by interception (dry and wet) or directly by precipitation (wash out). Usually the contaminant concentration in interception deposition and in air are equal. The former may even be larger because of evaporation at the interceptor surfaces (tree leaves). In rainy deposition, on the contrary, the contaminant content is mostly diluted.

A contaminants in the air have been accumulated over a long period of time and can not be regulated, that is, at this scale there is no possibility to clean the atmosphere by technical means on a short term. Their presence is most prominent close to the emitting source, and in forest areas, especially at the regional air moisture condensation level where moisture condensation may contribute as much to precipitation as rain itself. The pollution is usually higher in air moisture than in precipitation, so that the pollution deposition is much stronger than by rain alone. The deposition is lowest on bare soils.

Another contamination source for land surfaces is the excessive distribution of agrochemicals (organic and inorganic), used to support and enhance soil fertility and to protect plants. Its impact on subsurface resources can to some extent be governed as far as the application is not too excessive and the time of application with respect to meteorological conditions is carefully selected.

Groundwater is not completely exposed to all contaminants, as some of them become sorbed on soils or are being exported in dissolved condition or particle bound by interflow (Sect.1.3). In the unsaturated zone the contaminants may undergo chemical or microbial disintegration as far as the habitat and flow conditions favor microbial activities.

Artificial tracer and natural isotope methods may be applied to trace the history of elements, to recognize the efficiency of chemical or microbial environments like biofilms, and time spans for disintegration processes. They can also contribute to developing long-term strategies of groundwater protection (Seiler et al. 1992). In this respect an interesting field of applications are the biporous media to which belong most of the Mesozoic hard rocks

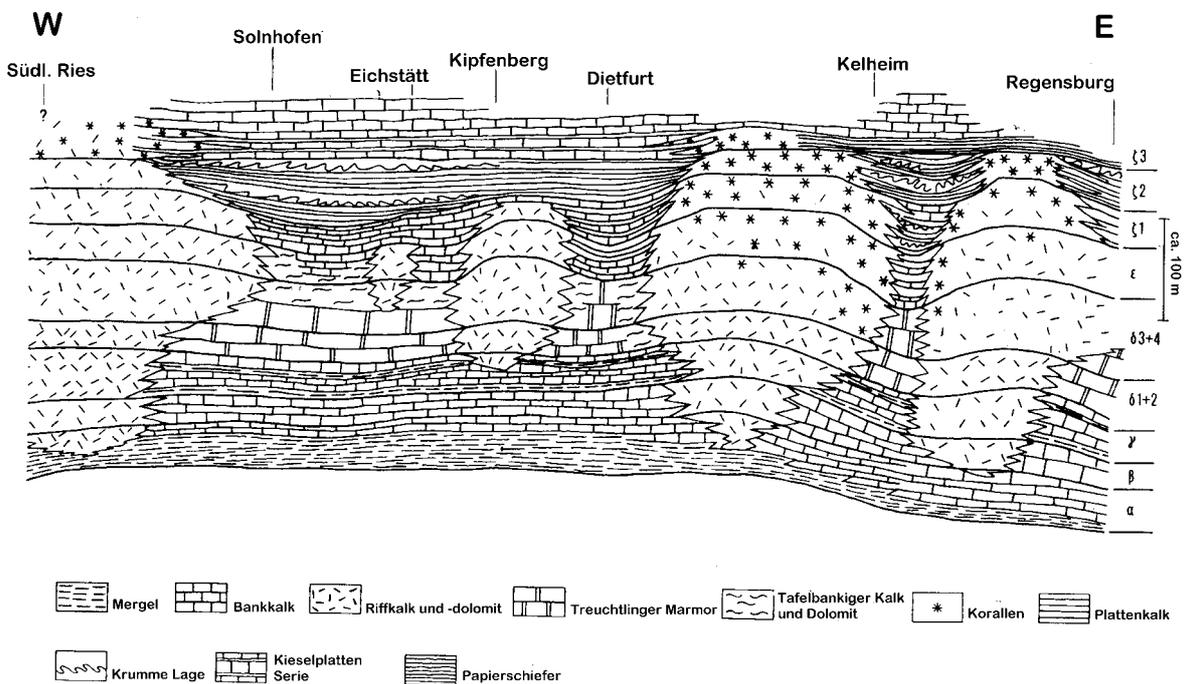
explored for groundwater abstraction. Such media offer simultaneously high storage, considerable dilution and efficient drainage capacities.

## 5.1 THE ROLE OF SEDIMENT FACIES IN STORAGE AND DISINTEGRATION OF AGROCHEMICALS IN THE KARST OF SOUTH GERMANY

### 5.1.1 INTRODUCTION

Bedrock aquifers are commonly highly heterogeneous. The frequency distribution of individual flow velocities in these aquifers covers a wide and discontinuous range, so creating storage and drainage conditions for seepage and groundwater flow. However, this cannot be recognised from average hydraulic parameters obtained by traditional methods, which may lead to problems in assessing natural attenuation processes, groundwater exploration and short- and long-term aspects of groundwater protection.

Hydraulic tests are based on pressure equilibration as well as on mass transport. Tracer tests, on the contrary, provide information exclusively about mass transport, which is a particularly important consideration for the above-mentioned processes.



**Fig.5.1** General stratigraphic section of the carbonates of the Franconian Alb, starting from the Dogger/Malm interface (Meyer & Schmidt-Kaler 1989).

### 5.1.2 THE MALM CARBONATES OF THE FRANCONIAN ALB

The carbonates of the Franconian Alb, Germany, belong to two consecutive cycles of sedimentation, each of which starts with a marl facies and changes gradually into bedded limestones. In the upper cycle, however, reefs replace bedded limestones over significant stratigraphic intervals (Fig.5.1).

Bedded limestones typically lack syngenetic porosity, but are characterised by narrow or open fissures and solution channels. Unlike the bedded limestones, the reef dolomites commonly have porosities (Weiss 1987)

- of sedimentary and early diagenetic age,
- due to weathering of dolomites,
- from fissures and
- solution processes.

These porosities of different origins in the reef facies lead to a broader spectrum of individual hydraulic conductivities than in the bedded facies. As a result, flow velocities in the reef facies range from a few meters per year to kilometres per day, whereas velocities in the bedded facies range from few hundred meters to kilometres per day.

### 5.1.3 RESULTS OF TRACER EXPERIMENTS

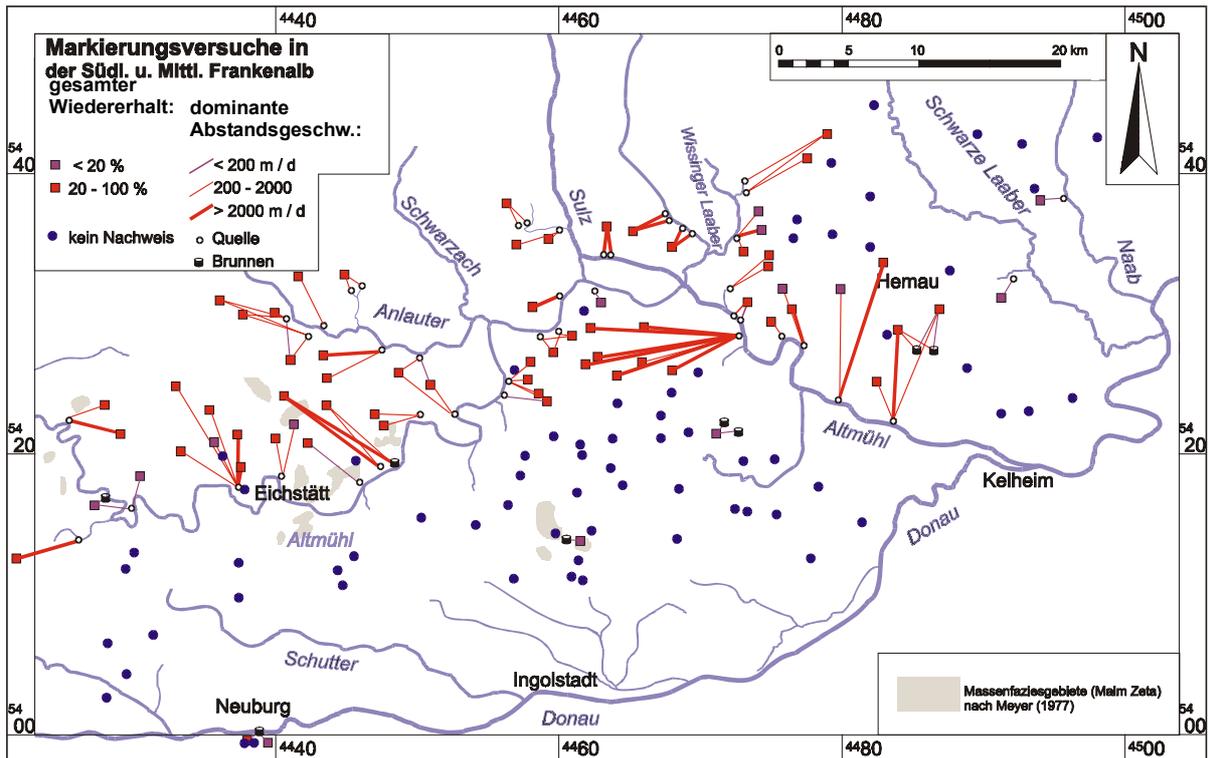
The research area covers about 1000 km<sup>2</sup> within the Upper Jurassic. More than 150 tracer tests have been executed with fluorescent dyes that behave conservatively with respect to flow velocities (Behrens 1971).

About half of the tracer tests (Fig.5.2) have been performed in the bedded facies: tracer recovery and flow velocities were mostly high. During an observation time of more than 7 years, tracer tests in the reef facies ended as a rule at distances exceeding 1.5 to 2 km without recovery.

Statistical evaluation of measured flow velocities leads to the following classification:

- group I    610 ± 330 m/d
- group II  2135 ± 533 m/d
- group III  4190 ± 925 m/d.

Flow velocities of group I result in an average hydraulic conductivity of about  $5 \times 10^{-3}$  m/s, which agrees well with results from pumping tests (Seiler et al. 1992). Flow velocities exceeding 1000 m/d likely reflect the existence of preferential flow path. On the other hand, low hydraulic conductivities that do not appear to be consistent with tracer experiments are also known from pumping tests. This could be attributed to a more pronounced dilution of tracers.



**Fig.5.2** Results of tracer experiments with (■) and without (●) recovery in the Karst of the Franconian Alb (Glaser 1998).

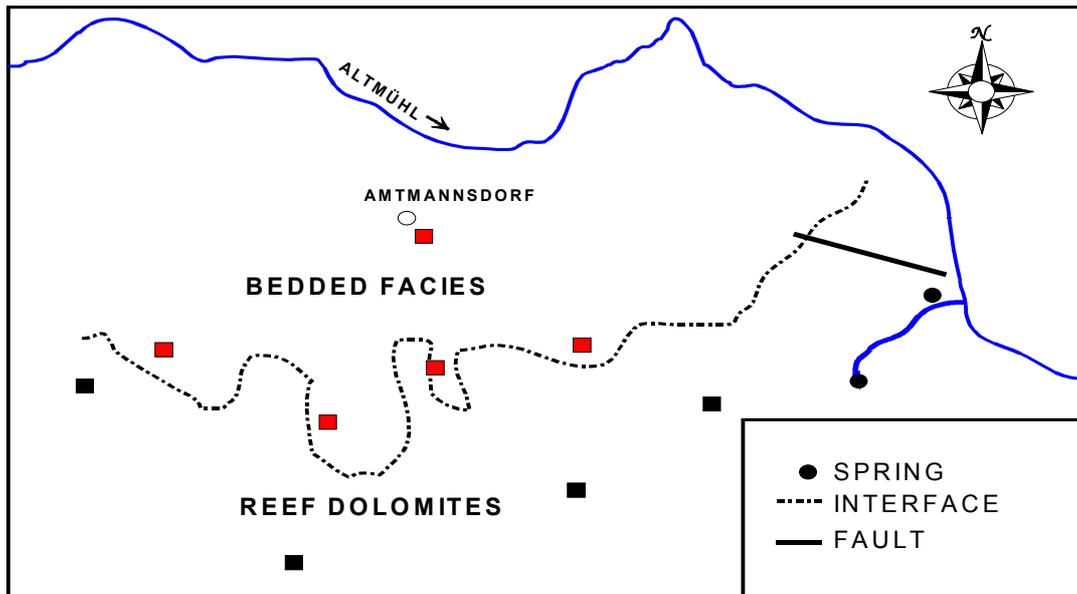
In one area the catchment is crossed by a steep, vertical boundary between the bedded and reef facies of non-tectonic origin (Fig.5.3). All tracer tests in the bedded facies have been recovered. In the reef facies, however, recovery did not occur at distances in excess of 2 km.

These must be attributed to a virtual retardation of the conservative tracer, due to diffusive and convective tracer exchanges between fissures and matrix porosity. A comparison of fissures in both areas revealed that high fissure intensities and low fissure apertures characterise the bedded facies. In contrast, fissuring in the reef facies is less intensive and fissures have larger openings (Seiler et al. 1992). Hydraulic conductivities in the reef facies should thus exceed those of the bedded facies, but flow velocities measured by tracer experiments are even lower in the reef than in the bedded facies. This again is linked to diffusive tracer exchanges between fissures and the porous matrix in the reef facies.

#### 5.1.4 THE DILUTION OF DYE TRACERS

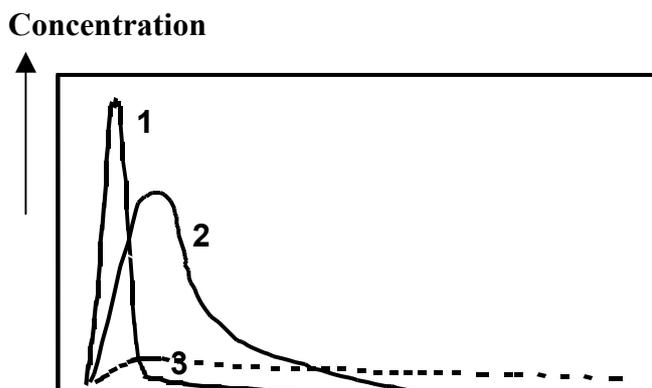
The concentration-time curves for tracer tests in the study area can be subdivided into three categories (Fig.5.4):

- 1) high concentration maxima and narrow geometry (curve 1 in Fig.5.4) point to high flow velocities ( $> 1.5$  km/d) and low dispersivities; such results are attributed to flow in solution channels



**Fig.5.3** Results of tracer tests along a vertical, non-tectonic interface between bedded and reef facies. Tracer recovery was high in the bedded facies; in the reef facies no tracers were recovered.

- 2) lower concentration maxima than before mentioned and a less narrow geometry (curve 2 in Fig.5.4) point to flow in fissures with some diffusive tracer exchange between large and narrow fissures
- 3) very low concentration or undetectable tracer maximum over 1.5 km (the detection limit of fluorescent dyes is 2 to 20 ng/L) and a pronounced tailing (curve 3 in Fig.5.4) is produced by a diffusive and convective tracer exchange between the small volume of water in fissures (< 2 vol.%) and the huge volume of water in a low hydraulic conductivity matrix (3 to 20 vol.%).



**Fig.5.4** Concentration versus time curves from the Malm carbonates of the Franconian Alb. Results from tracer propagation in 1 = solution channels, 2 = fissures of the bedded facies; 3 = reef facies; note that for curve 3 the time scale is 100 times larger than in cases 1 and 2.

### 5.1.5 TRITIUM IN GROUNDWATERS FROM BEDDED AND REEF FACIES

Tracer tests provide sectorial information about groundwater flow. In contrast, environmental isotopes like  $^3\text{H}$  can be used to add aerial information on the groundwater flow field. During the dry season, for example, a clear difference exists in  $^3\text{H}$  concentrations of groundwaters from bedded and reef facies:

- in the bedded facies  $^3\text{H}$  concentrations are close to the mean of precipitation of the last few years (Seiler et al. 1995) (Fig.5.5),
- in areas with less than 1% of tracer recovery  $^3\text{H}$  concentrations are significantly lower and stand for mean residence times exceeding 100 years (Fig.5.6).

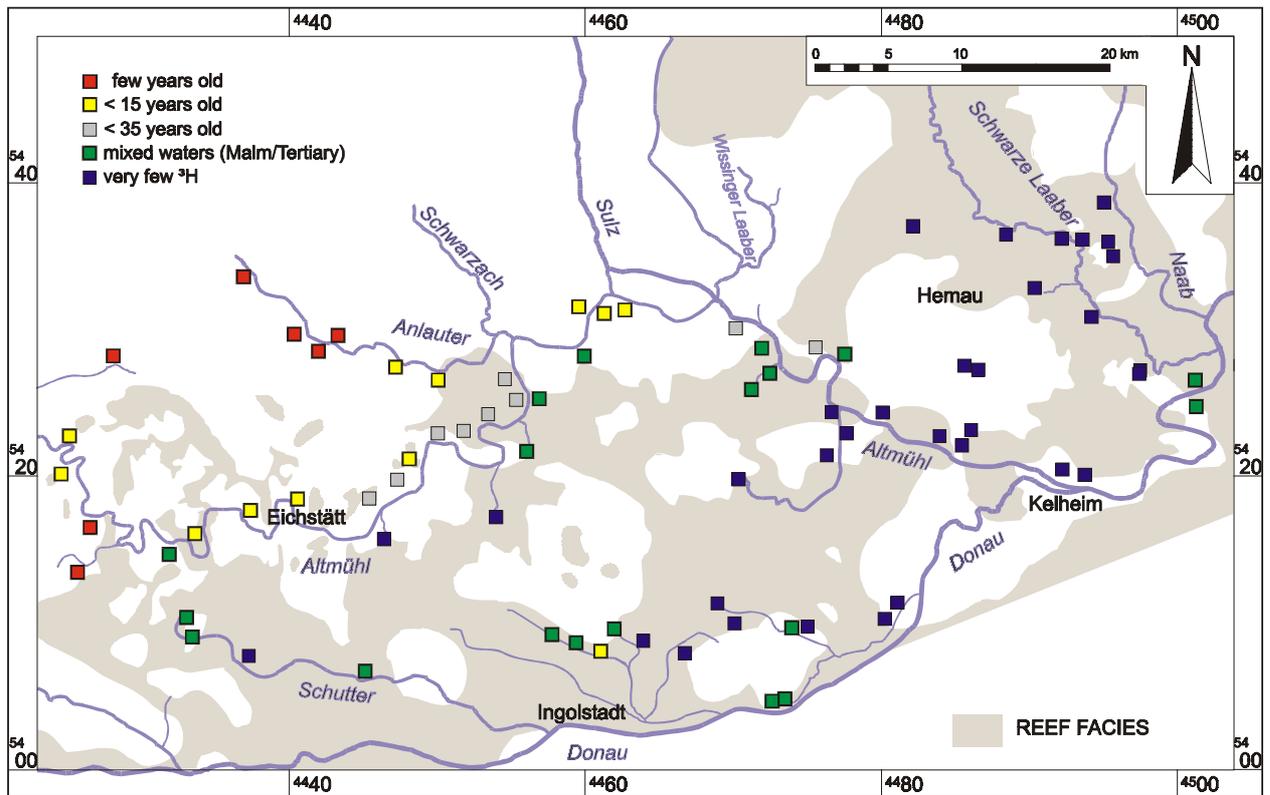
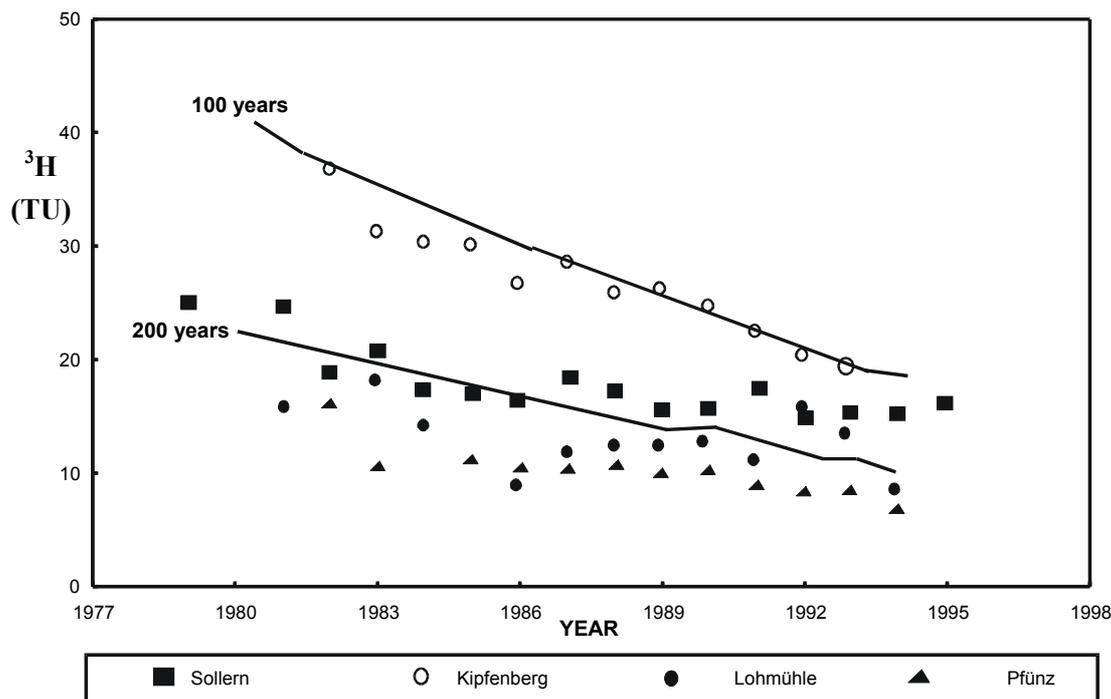


Fig.5.5 Water ages in the reef and bedded facies based on  $^3\text{H}$  data.

Some springs have been sampled during 10 years, once a year at the end of the dry season.  $^3\text{H}$  evaluation of this sampling shows mean residence times exceeding 50 to 200 years (Fig.5.6). This is based on an exponential age distribution, referring to dry weather discharge conditions. The high mean residence times do not mean that the artificial tracers in these springs could not be recovered. The results of the tracer experiments, however, point to very low recoveries over short distances as well as low flow velocities, both characteristic for fissured rocks with high matrix porosities.



Chp.III 1.1  
Fig. 12

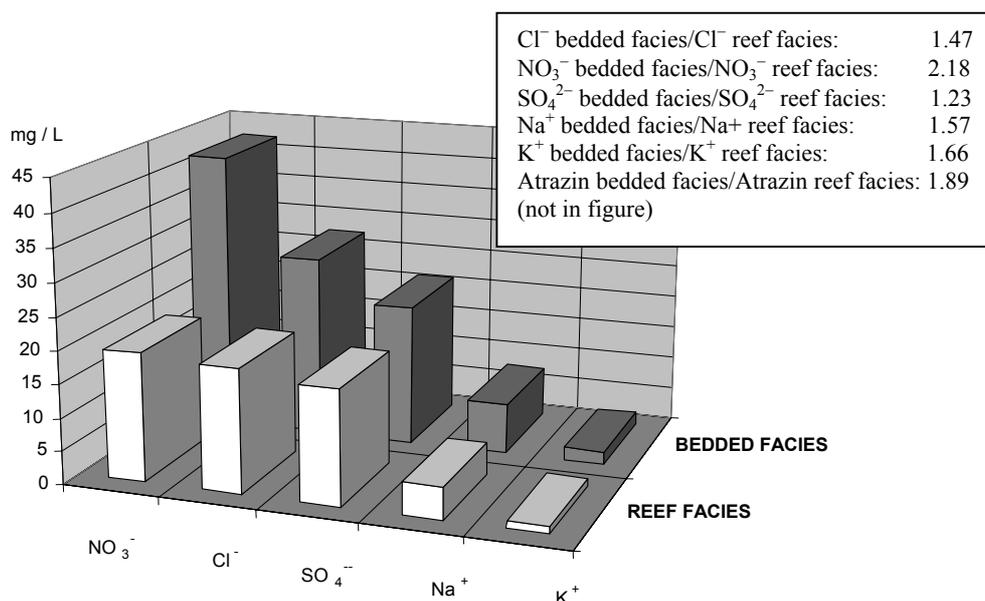
**Fig.5.6**  $^3\text{H}$  concentrations in springs from the reef facies at the end of the yearly dry period.

### 5.1.6 FATE OF NITRATES IN THE REEF FACIES

The huge water storage capacity of the reef facies could lead to long-term problems in groundwater quality, as far as no biologic disintegration exists. In the research area nitrogen excess amounts to 60 kg/ha per year, while the groundwater recharge is about 255 mm/a. From these numbers a concentration of 24 mg N/L or 100 mg  $\text{NO}_3/\text{L}$  is expected in the Karst groundwater. In the bedded facies the real concentrations indeed range from 60 to a maximum of 80 mg/L. In the reef facies, however, the values are below 20 mg/L (Fig.5.7). The aquifer without matrix porosity shows the current pollution situation, whereas the aquifer without is either not yet fully charged with pollutants, or the pollutant concentration is decreased by microbial processes in the rock matrix (Seiler 1997).

### 5.1.7 BACTERIAL POPULATIONS IN THE UNDERGROUND

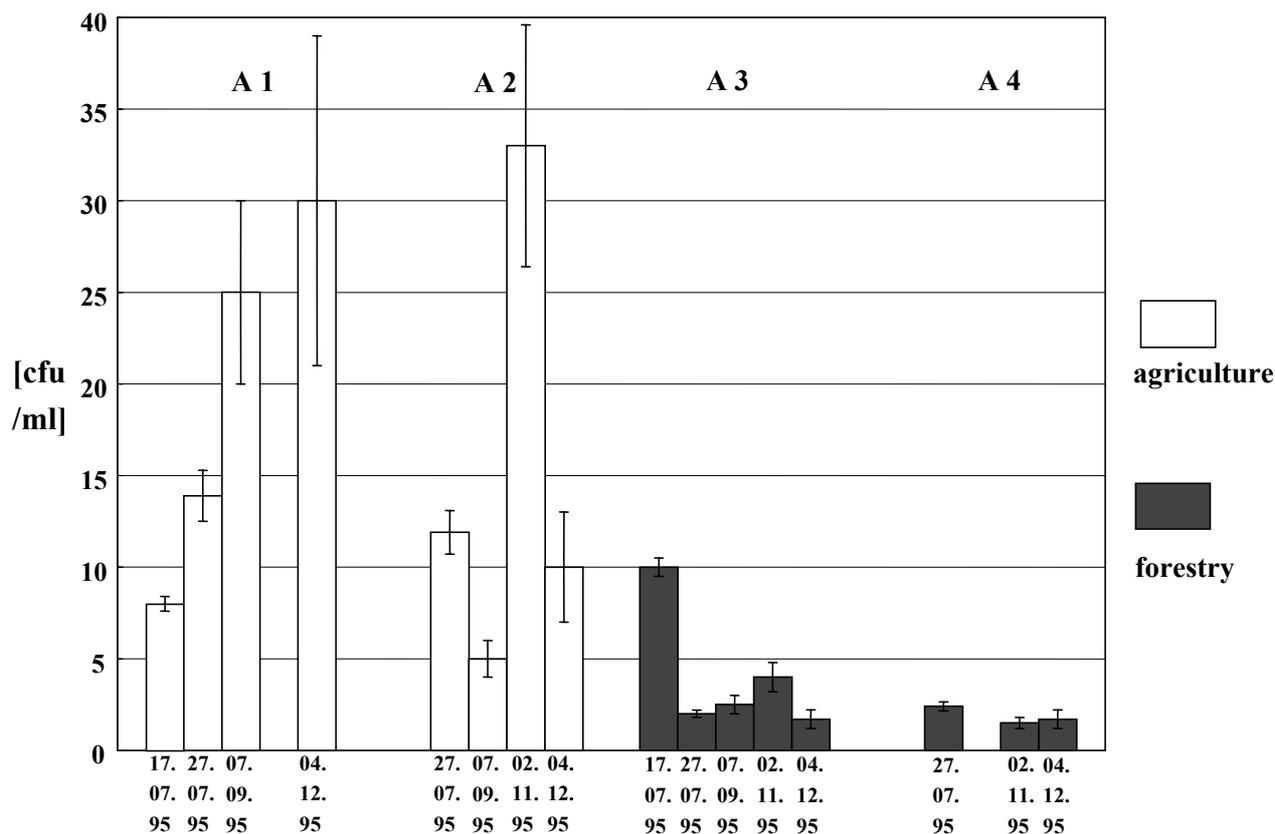
Water samples of springs and wells from areas with different land use (agriculture: A1-A2, forestry: A3-A4) were analysed microbially. The rocks of these areas consist of reef. The total bacterial numbers (DAPI-stain) and colony forming units (cfu) were quantified on  $\text{R}_2\text{A}$  agar (aerobic incubation, 22°C) and on a denitrification agar ( $\text{R}_2\text{A}$  agar + 0,5%  $\text{KNO}_3$ , anaerobic incubation, 22°C). In addition, of some bacterial isolates the denitrifying activity was analysed.



**Fig.5.7** Average concentration of agrochemicals in groundwater from aquifers without (bedded facies) and with matrix porosity (reef rocks) in the Franconian Alb, Germany (Glaser 1998).

The groundwater samples from agricultural and forest areas had total bacterial counts of  $2 \times 10^5$  to  $9 \times 10^5$ /mL and  $5 \times 10^4$  to  $1 \times 10^5$ /mL, respectively. As compared to the total counts, only less than one percent could be cultivated on R<sub>2</sub>A agar. Colony forming units were 100 to 700/mL (A1, A2) and 30 to 200/mL (A3-A4). The cfu's did not show significant seasonal differences from July to December. Under anaerobic conditions only 1 to 10% of the cfu's were growing. The water samples of reef facies from the agricultural (A1-A2) or forest areas (A3-A4) have anaerobic cfu's between 7 and 30/mL or between 1 and 4/mL, respectively. In the samples of the agricultural areas there are a higher numbers of total and viable counts as compared to those of the forest areas.

Some bacterial colonies, which were growing under anaerobic conditions, were isolated and analysed for denitrifying activity. The physiological tests showed that all of these bacteria reduce nitrate to nitrite, only some produce gas in an anaerobic atmosphere in nitrate containing media.

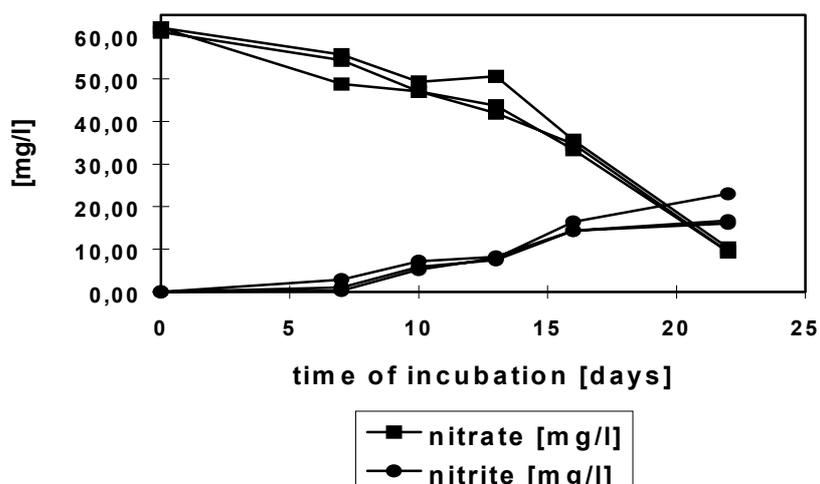


**Fig.5.8** Colony forming units (cfu) on denitrification agar (R2A agar + 0,5% KNO<sub>3</sub>) under anaerobic conditions.

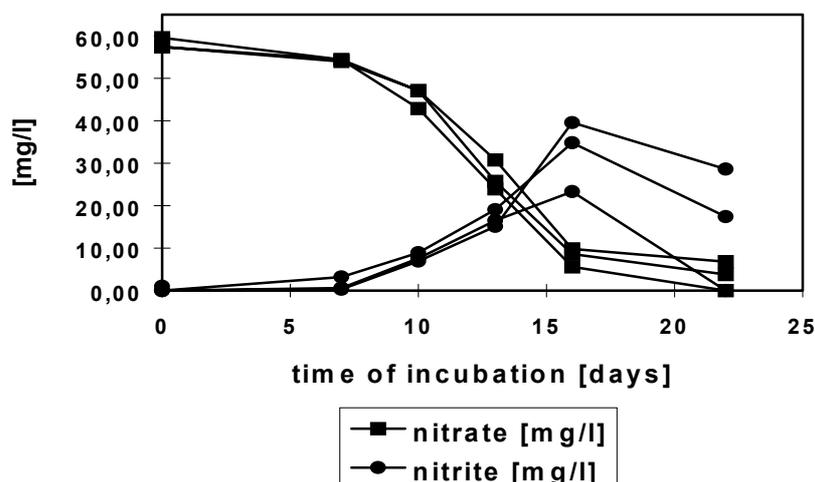
### 5.1.8 LABORATORY DENITRIFICATION EXPERIMENTS

It is important not only to study microbial activity of cultivated bacteria, but also to analyse the denitrifying potential of groundwater in comparison with biofilms. Groundwater samples (300 mL) were incubated for 3 weeks under anaerobic conditions. 50 mg NO<sub>3</sub><sup>-</sup>/L and no supplementary carbon source were added to the water samples. The DOC content of the groundwater samples of both areas was about 2 mg/L and the natural nitrate concentration of 9 to 12 mg NO<sub>3</sub><sup>-</sup>/mL. The NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> concentrations in the water samples were measured during an anaerobic incubation (Fig.5.9 A and B). Clearly, a decrease in NO<sub>3</sub><sup>-</sup> and a concomitant increase in NO<sub>2</sub><sup>-</sup> were observed in the incubated water samples. In the water samples from the agricultural area NO<sub>3</sub><sup>-</sup> loss and NO<sub>2</sub><sup>-</sup> production started after 7 days. After 16 days a decrease of NO<sub>2</sub><sup>-</sup> was observed. This higher activity in NO<sub>3</sub><sup>-</sup> disintegration in samples A1 as compared to A3 could be explained by the higher anaerobic cfu's of sample A1 (Fig.5.8). In addition to the NO<sub>2</sub><sup>-</sup> production, the N<sub>2</sub>O development was measured. In sterile controls no denitrifying activity was found. These results demonstrate, that the

## a) Water samples from reef facies with agricultural lan use (A1)



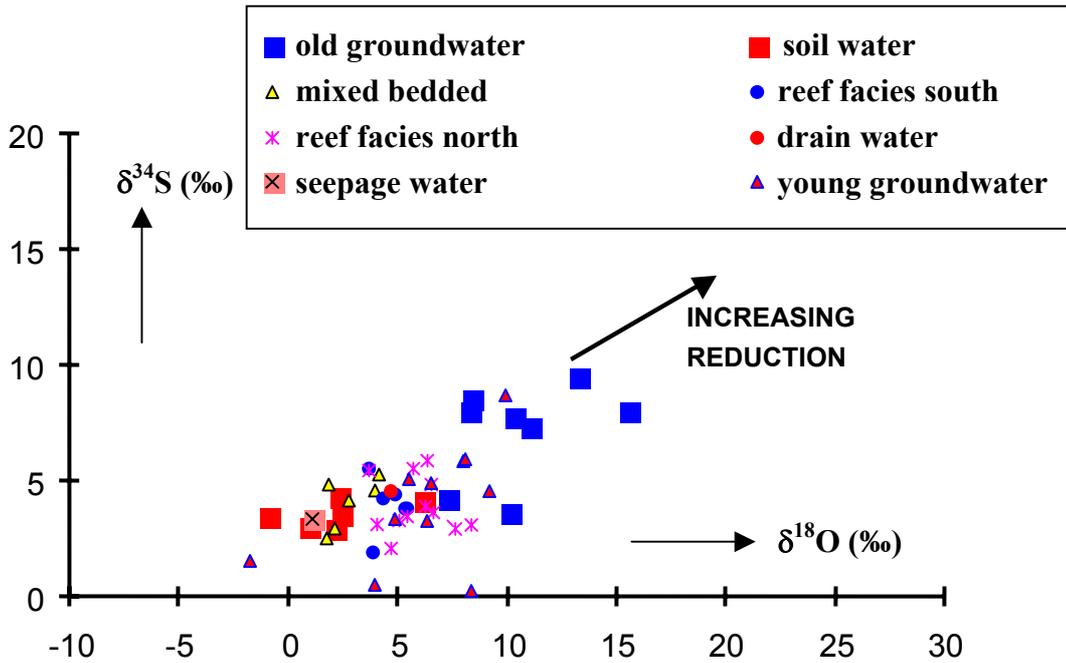
## b) Water samples from reef facies with forestland use (A2)



**Fig.5.9** Concentration changes of nitrate and nitrite in anaerobically incubated water samples from agriculture (a) and forest areas (b); 50 mg  $\text{NO}_3^-/\text{L}$  and no additional carbon source was added. This proposal with a and by here is accepted

groundwaters of two of the Karst areas exhibit a substantial denitrifying activity, despite of very low organic carbon supply. It is hypothesised, that some autolithotrophic activity exists in these water samples that are very rich in dissolved carbonate (370-390  $\text{HCO}_3^-$  mg/L). Since most of the micro-organisms, living in a kind of quick sorption and slow desorption equilibrium, are settled on surfaces, sterilised rock pieces were inserted in wells and springs to harvest micro-organisms in biofilms at the rock surface. The same denitrification test as shown in Fig.5.8 has been executed with biofilm micro-organisms. As a result, from all tests this denitrification process was much faster.

Since denitrification needs anaerobic conditions, while the redox potential of groundwater is in the range of +400 mV, it was supposed that the denitrification process is focused on biofilms. If so, in this reducing environment an isotope shift in  $^{34}\text{S}$  or  $^{15}\text{N}$  was expected, leading to respective isotope enrichment in the low energetic phase (Fig.5.10). First results indeed demonstrate that in groundwater these isotope concentrations increase. This is not as spectacular as it primarily was in biofilms, because the isotope concentrations decrease after release from biofilms.



**Fig.5.10**  $^{34}\text{S}$  and  $^{18}\text{O}$  concentrations in groundwaters with high redox potential (+400 mV).



# 6 SAMPLING OF WATER – QUANTITIES, METHODS, POINTS OF ATTENTION

Water sampling intends to provide information on water quality and quantity, and on hydrodynamic properties of systems under observation. To achieve appropriate information the following conditions should be fulfilled:

- Problem oriented sampling devices are required to safeguard the original information on qualitative and quantitative properties of subsurface waters.
- At the sampling point the water collected should reflect groundwater at the same depth in the aquifer system and the flow should not be disturbed by the well construction.
- In aquifer systems with strong time dependent characteristics, sampling must be adapted to the actual representative information of the system by adequate pumping before sampling.

A survey of water sampling is given in Volume I of this series, by [Clark & Fritz \(1997\)](#) and [Mazor \(1997\)](#), and by various Web sites of isotope laboratories.

All isotopic, hydrogeologic, hydrochemical and hydrodynamic interpretations have to be space and time related. Therefore, not only the above-mentioned sampling conditions must be satisfied but also an adequate number of sampling locations and a proper sampling frequency is required. To achieve a proper selection of locations and time series of information, sufficient data about the well design as well as a conceptual working hypothesis on the hydrodynamics of the subsurface waters are needed; this conceptual working hypotheses must usually be adjusted to the progress of the investigations. A common time related practice is to sample just before and at the end of the season of main groundwater recharge.

## 6.1 WELL CONSTRUCTIONS AND SAMPLING

In aquifers without wells groundwater flow is commonly horizontal, but may experience a slight vertical flow component

- according to the depth of the aquifers,
- beneath subsurface water divides or
- beneath groundwater discharge zones like rivers and springs.

Drilled wells commonly disturb this natural flow pattern by connecting aquifers with different hydraulic heads or by introducing a homogeneous filter pack in the well within an aquifer with varying hydraulic conductivities. Both effects induce hydraulic short cuts along the well axis and consequently vertical flow. Thus often a mixing of waters of different chemical or isotope information is obtained that does not exist naturally. A typical example of a vertical short cut is shown in [Fig.6.1](#); it clearly demonstrates that only at the source of the hydraulic short cut (upper part of [Fig.6.1](#)) unmixed information about water composition is available. Such short cuts may occur in an individual well manifold producing quick and slow up- and downward movement of waters.

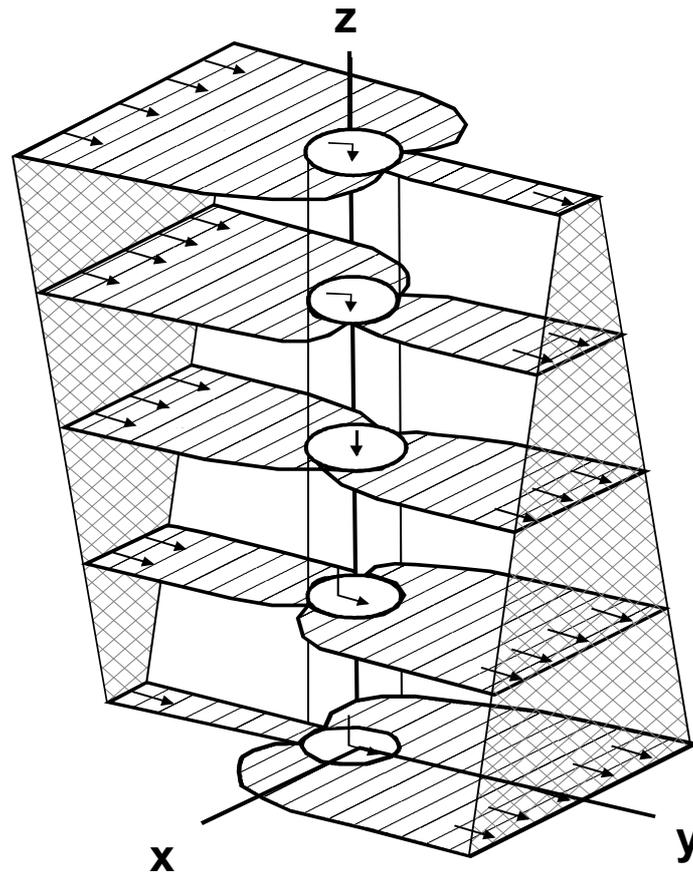
For the detection of vertical flow in wells, profiles of temperatures and electric conductivities often offer a good first approximation. A detailed insight in the velocity and direction of vertical flow of wells is obtained by injecting a non-reactive tracer (e.g. dye tracers or gamma emitting tracers) and registering concentration changes through a chain of detectors in the water column of the well ([Drost et al. 1973](#)).

Commonly groundwater sampling is performed by pumping from production wells. As a result a weighted information ( $F$ ) along the screened well is obtained.

Since the detailed distribution of hydraulic conductivities is often unknown, also  $Q_i$  is unknown and the information about sampling can only be related to mean screened groundwater depth explored by the well. This may be misleading in some interpretations and should be compensated for by a respective high number of sampling locations. As a result an approximation of parameter changes with depth is obtained (e.g. [Fig.4.2](#)). In observation wells depth-related sampling can be performed either by a special well construction or by special probes.

Optimal sampling is guaranteed by multi-level wells, in which sampling tubes are installed at fixed and hydraulically separated depths. These do not experience groundwater contributions from horizons above or beneath the sampling depth. Such wells are often used for special investigations. However, the well construction is expensive and requires specialist handling; sampling is generally time-consuming because discharges are usually below 0.1 L/s.

Good alternatives to multi-level wells are drilled wells with many individual screens, separated by clay sealings, that allow sampling of groundwater at specific depth.



**Fig.6.1** Flow field around and in a well with differences in hydraulic heads along the well axis

For sampling, the screened sector must be packered to eliminate vertical water exchanges along the well axis between the screened sectors above and beneath.

$$F = \frac{\sum C_i Q_i A_i}{A} \quad [\text{weight/time}] \quad (6.1)$$

## 6.2 SAMPLING DEVICES

Sampling of water can be performed with mechanic, electric or pneumatic devices, and by sucking in the case of water levels till 7 to 8 m below ground level.

There are low price pumps on the market that can be used in wells with minimum filter diameter of 40 mm and that may push a water column to a maximum height of 60 m. Most of these low price pumps are of plastic material, abuse rather quickly and produce discharges of less than 0.5 L/s at high water table, the deeper the water table, the smaller the discharge.

Mechanic devices have mechanic valves, at the top and bottom of a tube, opening up during quickly lowering the sampler and staying closed during the upwards movement of the water sample by means of the water pressure in- and outside the sampler. Groundwater with a high

fraction of suspended matter, however, may negatively affect this kind of sampling, because particles may hinder the hermetic closure of the valves. Then water from other horizons may become admixed to the sampled water when the sample is lifted to the surface.

In principle electric and mechanic devices function similarly. In case of using only one valve, the device should become evacuated before lowering. The disadvantage of single-valve samplers is that sampling may cause degassing of the water. The reliability also suffers from suspended matter in the water column.

A very efficient and simple pneumatic sampler consists of a valve at the bottom of a collector tube and two tubes inside connected to the land surface; one of these internal tubes ends at the top and the other at the bottom of the sampler. The one ending at the top is connected to a foot pump and serves for increasing the pressure at the sampling depth, closing the valve at the bottom of the sampling tube and forcing water to evade from the internal tube ending at the bottom. Increasing and decreasing the pressure in the sampling tube can be repeated according to the quantity of water desired. This device may become useless in water with suspended matter (see above), while sampling depth is limited due to buoyancy.

Sampling of water vapour is performed by using a cooling trap with liquid nitrogen, covering a U-shaped tube, which is flushed by air from a pump at the one end of the tube. By experience it takes 3 to 4 hours to collect about 20 mL of air water.

### 6.3 SAMPLE QUANTITIES AND WATER STORAGE

For the analysis of the classical anions and cations 500 mL of water is needed using traditional titration methods, and about 150 mL using ion chromatography coupled with carbonate titration (a minimum of 100 mL of it is requested for carbonate titration). Water for traditional analysis should not be pre-treated; the sample bottles should be tightly closed and stored at 4° C. It is important that the analytical work is executed immediately or as soon as possible after sampling, in order to prevent changes in the chemical composition of the water due to degassing, photolytic or microbial reactions.

Pre-treatment of sampled waters is requested for special gas (e.g. H<sub>2</sub>S) and heavy metal analysis. In these cases H<sub>2</sub>S should be fixed to prevent volatilisation. To prevent concentration changes of dissolved heavy metals, water samples should be acidified.

Sampling for isotopic analysis depends on the analytical accuracy required for the analytical method concerned (see for detailed discussion on the laboratory procedures Volume I).

<sup>2</sup>H and <sup>18</sup>O analyses are usually executed both. 20 mL of water is sufficient. Samples should be stored in dry glass or PVC bottles that become tightly closed to avoid evaporation.

<sup>3</sup>H analyses usually need electrolytic enrichment. For liquid scintillation counting a minimum of 500 mL of waters is needed to obtain an accuracy of about ± 0.5 TU. Using gas scintillation counting only 20 to 30 mL of water is needed to produce an analytical

accuracy of about  $\pm 0.4$  TU. Better analytical accuracies (mTU) are obtained in counting the  $^3\text{He}$  production of decaying  $^3\text{H}$ . This method is time consuming and needs special equipment.

$^{14}\text{C}$  of DIC (dissolved inorganic carbon) need about 3 g of carbon when applying traditional beta counting methods, or 1 mg of C applying AMS (accelerator mass spectrometry). For routine  $^{13}\text{C}$  measurement a few mg of carbon is needed. According to the total DIC of the investigated water a respective water volume must be sampled. For large  $^{14}\text{C}$  samples tens of litres of water are required from which the inorganic carbon (dissolved  $\text{HCO}_3^-$  and  $\text{CO}_2$ ) is precipitated at the well site as  $\text{SrCO}_3$  or  $\text{BaCO}_3$  by adding  $\text{Sr}(\text{OH})_2$  or  $\text{Ba}(\text{OH})_2$ . Another method is the extraction of  $\text{CO}_2$  in the field after acidifying about 50 L of water by adding hydrochloric acid, and dissolving the  $\text{CO}_2$  in 50 mL of an alkaline solution. This can be shipped to the laboratory.

$^{15}\text{N}$  analyses for hydrogeologic purpose are applied to 100  $\mu\text{M}$  of N from waters. This quantity allows also  $^{18}\text{O}$  determination in the nitrate. The respective volumes of water sample required can be calculated on the basis of a chemical analysis. It is also possible to concentrate  $\text{NO}_3^-$  or  $\text{NH}_4^+$  on anion or cation exchange resins, respectively (Garten 1992).

$^{34}\text{S}$  analyses need about 100 mg of S. Also here an  $^{18}\text{O}$  determination in the sulphate is recommended. The necessary quantity of water to be sampled can be calculated after a chemical analysis of the water. In this case the water should be filtered before becoming stored in the bottle. It is also possible to concentrate  $\text{SO}_4^{2-}$  on anion resins; this method is preferable to precipitation as  $\text{BaSO}_4$ .

$^{39}\text{Ar}$  measurements need about 2000 mL of Ar gas that is to be extracted from groundwater in the field.  $^{39}\text{Ar}$  samples should reach the isotope laboratory immediately after sampling to measure  $^{37}\text{Ar}$  as well.

$^{85}\text{Kr}$  measurement needs about 20  $\mu\text{L}$  of Kr gas from the water sample.

Water and precipitate of all these samples should be stored in glass or PVC bottles with stopcocks hermetically sealed. They should be stored at  $4^\circ\text{C}$  to keep any disintegration, degassing and evaporation at minimum.

## 6.4 SAMPLING OF SEEPAGE WATERS

Water samples from the unsaturated zone may be collected either by using suction cups, or by extraction water from sediments by replacement, heating or dilution. The suction cups mostly are permanently installed in the unsaturated zone. The suction efficiency of these cups is restricted to between a few and about 800 hPa. In dryer materials typical for sediments and soils close to the land's surface, for instance during the vegetation period or in dry lands, the water has to be extracted either by dilution or by heating of the core material.

Suction cups should consist of inert materials like ceramics or sinter materials. The pore sizes of it are to be adapted to the main pore sizes of the sediment. As an example, suction cups with 20 $\mu\text{m}$  pore size are well adapted to most sediments in the vadose zone. Before the implantation of the cups they should become conditioned with water similar to that encountered in the unsaturated zone. This is especially true for the chemical analyses. The underpressure employed should not differ too much from the prevailing one, in order to avoid degassing of the water causing disturbance of gas related components like carbonates. Since flow and water content in the unsaturated zone are mostly low, sampling of water will always cover a longer time span.

Since the unsaturated zone is very inhomogeneous as compared to the spherical space influenced by the suction cup, it is emphasised to have samples collected by more than one cup at the same level. Fig.6.2 demonstrates differences in the results of a tracer experiment, in which samples were collected with three cups at the same depth, at a mutual distance of about two meters.

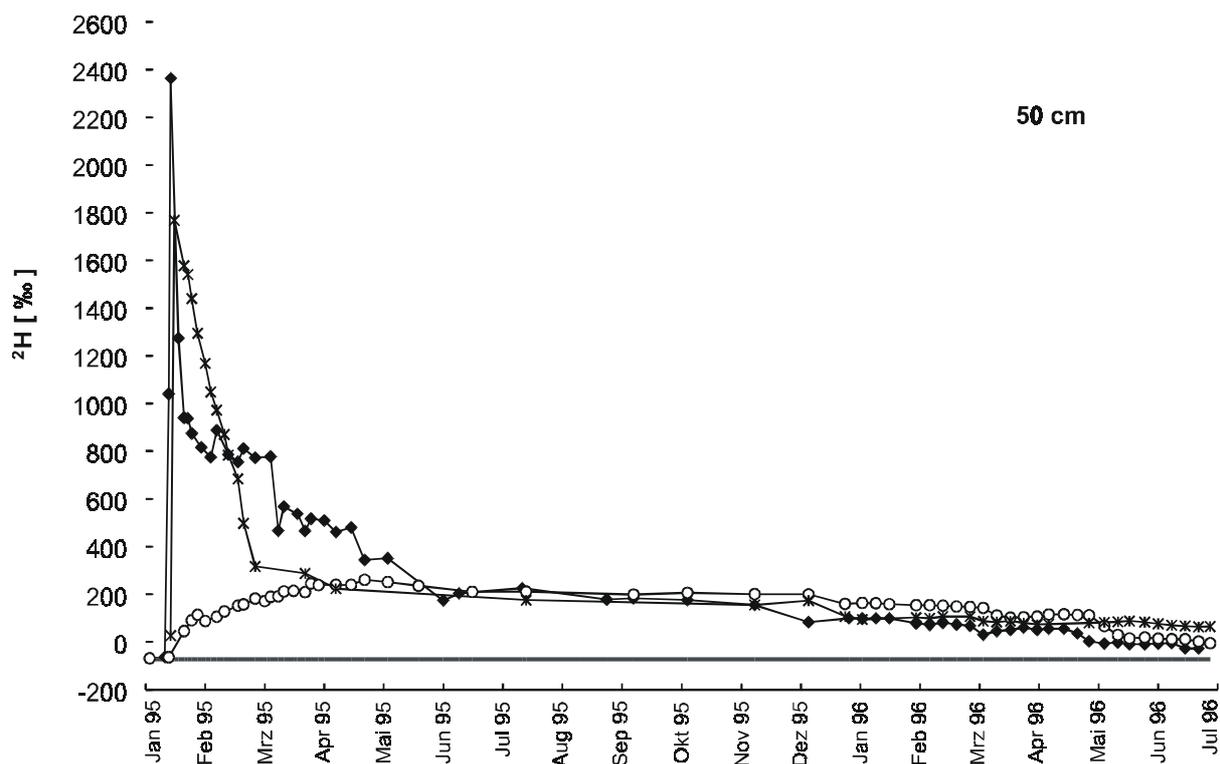
Determination of the quantity of pore water by chemical or isotopic dilution analysis aims in the first instance at saturating the sediment to some extent to make water easier extractable. This *dilution* should be combined with a homogenisation of the two waters. In the second step homogenised water is extracted by centrifugation or with suction cups. For the dilution analysis extreme compositions of waters are used like distilled water for chemical analysis or Antarctic waters with strongly deviating  $\delta^{18}\text{O}$  values for stable isotopic analysis. The water content of the sample ( $Q_s$ ), the added quantity of water ( $Q_a$ ) and its isotopic or chemical composition ( $C_a$ ) and the resulting composition of mixed waters ( $C_m$ ) can easily be determined (cf. Sect.4.3 in Volume I). From the mass balance:

$$C_s Q_s + C_a Q_a = C_m Q_m = C_m (Q_s + Q_a)$$

follows:

$$C_s = \frac{C_m (Q_s + Q_a) - C_a Q_a}{Q_s} \quad (6.2)$$

In this way the isotopic or chemical composition of the water from the unsaturated zone ( $C_s$ ) is determined from the mixing equation (Box 4.1)



**Fig.6.2** Results of a tracer experiment performed in the unsaturated zone and sampled by three individual cups at 50 cm depth.

Distillation of waters from sediments (Araguas-Araguas et al. 1995, Ingraham & Shadel 1992) must be performed in closed systems and till the point of complete dryness of the sediment. Only under these conditions isotope fractionation does not play any more any role and an even distribution of isotope concentration in the pore water has no more influence on the analytic result.

In some special cases also replacing methods (Ingraham & Shadel 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.



# 7 OUTLOOK TO FURTHER APPLICATIONS

This volume refers to results demonstrating the necessity of a combined use of isotopic, hydrochemical and hydrogeologic methods to understand the dynamics of groundwater systems and to assess man's impact on water fluxes and quality. This field is expanding and isotopic tools are developing to conquer new fields of applications.

Microbial activities in groundwater are more pronounced than recognised till now. They contribute to self-purification or natural attenuation processes quite efficiently and may help to assess the resilience or elastic response of subsurface waters to pollution. They thus play an important role in defining sustainable measures of groundwater protection.

Microbial disintegration processes also lead to isotope fractionation, as is well known from the reduction of nitrogen or sulphur. In some cases isotopic investigations may play a significant role in recognising the reaction space in an aquifer where reduction reactions take place as, for instance, in biofilms or in the matrix pores with very low hydraulic conductivities. In these cases measurement of the redox potential in the groundwater suggests oxidative conditions while the N and S isotopes point to reduction processes taking place in a turnover space with low water quantities.

A quite similar field of application of stable environmental isotopes has been started recently by using  $^{13}\text{C}$ ,  $^{14}\text{C}$ , by [Vengosh et al. \(1991, 1994\)](#) and [Eisenhut & Heumann \(1997\)](#) using  $^{11}\text{B}$ , by [Hiscock et al. \(1997\)](#) using  $^{15}\text{N}$ -isotopes, and by [Hallas & Trembaczowski \(1998\)](#) using  $^{34}\text{S}$ -isotopes, as finger prints of either synthetic or natural chemicals applied near groundwater resources. As far as they do not undergo coupled fractionation and microbial disintegration, they can be utilised to localise their access to and behaviour in the subsurface. It is evident that such investigations should be linked to species related chemical analysis.

Recent investigations ([Rau 1999](#)) also proved that the combined evaluation of stable isotope results might lead to a better understanding, if conceptual hydrogeologic models are appropriate or need modification. This should not only control isotope-based model concepts but should also become introduced in numerical hydraulic modelling.

There are many types of mathematical models to simulate and predict water flow and the related behaviour of pollutants in the unsaturated and saturated zone. Some of these are little parameterised and allow lump assessments, others are highly parameterised and mostly suffer from a lack of direct field data. Instead the missing field data must be provided by statistical extrapolation. First attempts to link isotopic data to numerical models ([Andres & Egger 1983](#)) are promising. The advantage of introducing environmental isotope results in numerical models is illustrated by the following. Most hydraulic data represent both instantaneous

information on the spot. Since advanced hydraulic models on flow and pollutant transport are multi-parameterised, the calibration of such models can be fitted in different ways by respective parameter variation. In case of extrapolation of these calibrated models to other boundary conditions they may fail, because parameters have not been adequately used to calibrate the model. Therefore, environmental isotope results may be used for model calibration and add time- and space- integrative views to the evaluation.

Groundwaters have an isotopic and chemical stratification, that originates from (i) the type of groundwater flow, (ii) the half-life of radioactive environmental isotopes used, (iii) the impact of climate changes on the isotopic and chemical input functions, or (iv) the time-related exchange processes (e.g. ion exchange). Under certain conditions such changes may not be documented in water level changes but expressed in chemical and isotopic changes (Sect.2.1.3). In systems with small turnover times this stratification has usually no significance; in slowly moving systems, however, strategies of groundwater management will change the flow regime over a long period of time. The rate and direction of such changes can be monitored by changes in the isotopic or chemical composition of the water, and be evaluated by appropriate mathematical models. Especially the combination of monitoring of non-reactive tracers and mathematical modelling leads to an early-warning assessment, supporting measures to avoid access of pollutants or arising soil/rock mechanical problems (subsidence) which are mostly irreversible.

# REFERENCES

- Alexander, I. & K.-P. Seiler 1983. Lebensdauer und Transport von Bakterien in typischen Grundwasserleitern - Münchener Schotterebene. DVGW-Schriftenreihe 35: 113-125.
- Al-Radaideh, I. 1992. Die Nutzung von Abwasser zur Trinkwasserversorgung und in der Landwirtschaft in ariden Gebieten. - Schriftenreihe GWA 128, Aachen.
- Allison, G. B., Hughes, M.W. 1974. Environmental Tritium in the unsaturated zone: Estimation of recharge to an unconfined aquifer. Proc. on Isotope Techniques in Groundwater Hydrology Vol. 1, IAEA Vienna: 57-69.
- Alvarado, J., Seiler, K.-P. & Trimborn, P. 1996. Investigación hidrogeológica, isotópica e hidroquímica de la cuenca del Lago de Valencia, Venezuela. Proc. on Isot. in Water Res. Management, Vol. 2, IAEA Vienna: 281-299
- Andres, G., Egger, R. 1982. Untersuchung zum Grundwasserhaushalt des Tiefenwassers der Oberen Suesswassermolasse durch Grundwasseraltersbestimmungen. - Informationsber. Bayer. Landesamt Wasserwirt. 8, Muenchen: 201 pp.
- Andres, G., Egger, R. 1985. A new Tritium interface method for determining the recharge rate of deep groundwater in the Bavarian Molasse Basin. J. Hydrol. 82: 27-38.
- Araguas-Araguas, L., Rozanski, K., Gonfiantini, R., Luvatt, D. 1995. Isotope effects accompanying vacuum extraction of soil water for stable isotope analysis. J. Hydrol. 168: 159-171.
- Baldison, R. & Seiler, K.-P. 1989. Estudio Isotópico e Hidrogeológico en la Cuenca del Río Samalá, Guatemala. - Report, unpublished, IAEA Vienna.
- Baldison, R., Seiler, K.-P., Trimborn, P. 1994. Investigaciones isotópicas ambientales, químicas and hidrogeológicas en la Cuenca del Lago Atitlán, Guatemala. - IAEA-TECDOC-835, IAEA, Vienna: 225-236.
- Barringer, T., Dunn, D., Battagliu, W., Vowinkel, E. 1990. Problems and methods in relating land use to groundwater quality. - Water Res. Bulletin 26: 1-9.
- Behrens, H., 1971. Untersuchungen zum quantitativen Nachweis von Fluoreszenzfarbstoffen bei ihrer Anwendung als hydrologische Markierungsstoffe. Geologica Bavarica 64: 120-131.
- Beven, K., German, P. 1982. Macropores and water flow in soils. Water Resour. Res. 18, 1311-1325.
- Bruins, H.J., Lithwick, H. 1998. The arid frontier. Kluwer Acad. Publishers, Dordrecht, Boston, London.
- Chilton, P.J., Stuart, M.E., Darling, W.G. 1998. Use of stable isotopes in the investigation of the effect of waste water reuse on groundwater in Mexico. IAEA-TECHDOC-1046, IAEA Vienna: 209-225.

- Clark, I.D., Fritz, P. 1997. Environmental isotopes in Hydrogeology, CRC Press: 328 pp.
- Drost, W., Moser, H., Neumaier, F., Rauert, W. 1973. Methodes isotopiques en Hydrogeologie. Eurisotope Monographie 16: 186 pp.
- DVWK 1983. Beiträge zu tiefen Grundwässern. DVWK-Schriften 61: 1-107.
- DVWK 1987. Erkundung tiefer Grundwasserzirkulationssysteme. DVWK-Schriften 81, 1-223.
- DVWK 1995. Speicher-Durchfluß-Modelle zur Bewertung des Stoffein- und Stoffaustrags in unterschiedlichen Grundwasser-Zirkulationssystemen. DVWK-Schriften 109: 118.
- Egger, R. 1978. Das Grundwasser in der Oberen Suesswassermolasse im Raum München und Augsburg. PhD thesis (unpublished), Univ. of Munich, 110S.
- Eisenhut, S., Heumann, K.G. 1997. Identification of groundwater contaminations by landfills using boron isotope measurements with negative thermal ionisation mass spectrometry. - Fresenius J. Analy. Chem. 359, 375-377.
- Engelhardt v., W. 1960. Der Porenraum der Sedimente. Springer, Berlin: 207 pp.
- Evin, J., Vuillaume, Y. 1970. Etude par le radiocarbon de la nappe captive de l'Alnien du Basin de Paris. Proc. Isotope Hydrology, IAEA Vienna: 315-331.
- Febrillet, J., Bueno, E., Seiler, K.-P. & Stichler, W. 1989. Estudio Isotópicos e Hidrogeológicos en la Región Suroeste de la República Dominicana. IAEA-TECDOC-502, IAEA Vienna: 237 - 290
- Feddes, R.A., Kadat, P., van Bakel, P.J.T., Bronswyk, J.J.B., Halbertzma, J. 1988. Modeling Soil Water Dynamics in the Unsaturated Zone - State of the Art. J. Hydrol. 100: 69-111.
- Foster, S.S.D. 1975. The chalk groundwater anomaly - a possible explanation. J. Hydrol. 25: 159-165.
- Freeze, R.A. & Cherry, J.A. 1979. Groundwater. Prentice-Hall, Englewood Cliffs N.Y.: 604 pp.
- Freeze, R.A. & Witherspoon, P.A. 1967. Theoretical analysis of regional groundwater flow: 2. Effect of water table configuration and subsurface permeability variations. Water Resources Res.3: 623-634.
- Garten, C.T. 1992. Nitrogen isotope composition of ammonium and nitrate in bulk precipitation and forest throughfall. - Int. J. Anal. Chem. 47, 33-45.
- Genuchten van, M. Th. 1994. New Issues and Challenges in Soil Physics Research. - 15<sup>th</sup> World Congress of Soil Science, Vol. 1: Inaugural and State of the Art Conferences, Acapulco Mexiko: 5-27.
- Germann, P. F. 1990. Preferential flow and the generation of runoff. 1. Boundary layer flow theory. Water Resources Research 26: 3055-3063.
- Glaser, St. 1998. Der Grundwasserhaushalt in verschiedenen Faziesbereichen des Malms der Südlichen und Mittleren Frankenalb. GSF-Ber., Neuherberg 2/98: 135 pp.

- Hallas, S., Trembaczowski, A. 1998. The influence of brown coal exploitation in Poland on the groundwater pollution as determined by isotopic analysis of sulphate. IAEA TECHDOC-1046, IAEA Vienna:81-93.
- Hillel, D. 1971. Soil and Water. Acad. Press, New York, London.
- Hiscock, K.M., Dennis, P.F., Feast, N.A., Fairbairn, J.D. 1997. Experience in the use of stable isotopes to distinguish groundwater contamination from leaking sewers in urban areas. In: Chilton et al (eds.): Groundwater in the urban area, Proc. Of the XXVI IAH Congres, Vol. 1, Balkema, Rotterdam, Brookfield:427-432.
- IAEA 1975. Environmental Isotope Data No. 5: World survey of isotope concentration in precipitation (1970-1971). - Tech. Rep. 165, IAEA Vienna: 307 pp.
- Ingraham, N.L., Shachel, C. 1992. A comparison of the toluen distillation and vacuum/heat methods for extraction soil water for stable isotope analysis. J. Hydrol. 140: 371-387.
- Jiries, A. 1991. Investigation of unsaturated water movement in irrigated fields with typical sediments in the Jordan Valley, Jordan. PhD thesis, Ludwig-Maximilians-University, Munich.
- Jiries, A., Seiler, K.-P. 1995. Water movement in typical soils in the Jordan valley, Jordan. Mesopotamia J. Agric. 27: 5-12.
- Kaess, W. 1998. Tracing Technique in Geohydrology. Balkema, Rotterdam, Brookfield: 581 pp.
- Kendal, C., McDonnell, J.J. 1998. Isotope tracers in catchemnt hydrology. Elsevier, Amsterdam, Lausanne, New York, Oxford, Singapore, Tokyo: 839 pp.
- Kim, J.I., Delakowitz, B., Zeh, P., Klotz, D. & Lazik, D. 1994. A column experiment for the study of colloidal radionuclide migration in Gorleben aquifer systems. Radiochimica Acta 66/67: 173 pp.
- Klotz, D. 1977. Berechnete Durchlä#ssigkeiten handelüblicher Brunnenfilterrohre. GSF-Ber. R 133, München: 56pp.
- Lallemand-Barres, A. & Peaudecerf, P. 1978. Recherche des relations entre les valeurs de la dispersivité macroscopique d'un milieu aquifère, ses caractéristiques et les conditions de mesures. Etude bibliographique. Hydrogéologie et Géologie de l'ingénieur: 277-284.
- Linsley, R.K., Kohler, KmA., Paulhus, J.H.L. 1949. Applied Hydrology. McGraw-Hill, New York, Toronto, London: 689 pp.
- Luckner, L. 1994. Zustand und Schutz des Grundwassers in den neuen Bundesländern. DVGW Schriftenreihe Wasser 84, 135-148.
- Magara, K. 1978. Compaction and Fluid Migration, Practical Petroleum Geology. Elsevier, Amsterdam, Oxford, New York: 319 pp.
- Maloszewski, P., Zuber, A. 1982. Determing the turnover time of groundwater systems with the aid of environmental tracers. J. Hydrol. 57: 207-231.

- Maloszewski, P., Zuber, A. 1985. On the theory of tracer experiments in fissured rocks with a porous matrix. *J. Hydrol.* 79: 333-358.
- Maloszewski, P., Zuber, A. 1993. Tracer experiments in fractured rock: matrix diffusion and the validity of models. *Water Resources Res.* 29: 2723-2735.
- Matthess, G. 1970. Beziehungen zwischen geologischem Bau und Grundwasserbewegung in Festgesteinen. *Abh. hess. LA Boden* 58: 105 S.
- Matthess, G., Bedbur, E., Gundermann, K.-O. Löff, M. & Peters, D. 1991. Vergleichende Untersuchungen zum Filtrationsverhalten von Bakterien und organischen Partikeln in Porengrundwasserleitern. *Zentralbl. Hygiene und Umweltmedizin* 191: 53 pp.
- Mazor, E. 1997. *Chemical and isotope groundwater hydrology: The applied approach 2*. Edit. Decker New York: 413 pp.
- McLaughlan, R.G., Knight, M.J., Stuetz, R.M. 1993. Fouling and corrosion of groundwater wells. *Res. Public.* 1/93, Nat. Centre for Groundwater Management, Sydney: 42 pp.
- Meyer, R.K.F., Schmidt-Kaler, H. 1989. Paläogeographischer Atlas des Süddeutschen Oberjuras. *Geol Jb. A* 115: 77 pp.
- Moser, H., Rauert, W. 1980. *Tracermethoden in der Hydrologie*. Schweizerbart, Stuttgart: 400 pp.
- Müller, H.E. 1999. Die Funktion der Mikroorganismen bei der Neubildung von Grundwasser. *Zbl. Geol. Paläont. Teil I*: 27-39.
- Nazir, A. 1974. *Groundwater resources of Pakistan*. Ripon Printing Press, Lahore: 295 pp.
- Nemecek, E.P. 1961. Horizontalfilterbrunnen zur Grundwassergewinnung. *Wasserwirtschaft Wassertechnik* 11: 99-107.
- Nemecek, E.P. 1964. Die Berechnung des Horizontalfilterbrunnens. *Österreichische Wasserwirtschaft ÖWW* 16: 20-32.
- Oeschger, H., Siegenthaler, U. 1972. Umgebungsisotope im Dienst der Hydrologie und Ausblick auf neue Methoden. *GWF, Wasser Abwasser* 113: 501-508.
- Petrov, M.P. 1976. *Deserts of the world..* Eiley & Sons, New York: 447 pp.
- Rau, I. 1999. Untersuchungen zur langzeitigen Speicherung von persistenten Schadstoffen in heterogen porösen Medien mit Umwelttracern. Unpubl. Diss. LMU, München.
- Rauert, W., Wolf, M., Weise, S.M., Andres, G., Egger, R. 1993. Isotope-hydrological case study on the penetration of pollution into the deep Tertiary aquifer in the area of Munich, Germany. *J. Cont. Hydrology* 14: 15-3
- Richter, W. & Lillich, W. 1975. *Abriß der Hydrogeologie*. Schweizerbart, Stuttgart: 281 pp.
- Rietti-Shati, M., Ronnen, D. & Mandelbaum, R. 1996. Atrazin degradation by *Pseudomonas* strain ADP entrapped in sol-gel glass. *J. Sol-Gel Sc. and Technol.* 23: 77-79.
- Sajjad, M.I., Tasneem, M.A., Hussain, S.D., Seiler, K.-P. , Saiyid-Ud-Zafar, M. 1993. Estimation of flow velocities and salt movements in unsaturated zone using

- isotopic and conventional techniques. *The Science of the Total Environment* 138: 235-247.
- Sajjad, M.I., Waheed, R., Hussain, S.D., Seiler, K.-P., Stichler, W. & Tasneen, M.A. 1985. Study of downward movement of soil moisture in the unsaturated zone. IAEA-TECDOC-357, IAEA Vienna: 89-120.
- Scanlon, B.R. 1992. Evaluation of liquid and vapour flow in desert soils based on chlorine-36 and Tritium tracers and non-isotherme flow simulation. *Water Resources Res.* 28: 285.
- Schaefer, A., Usthal, P., Harms, H., Staufer, F., Dracos, T., Zehnder, A.J.B. 1998. Transport of bacteria in unsaturated porous media. *J. Contam. Hydrol.* 33: 149-169.
- Seiler, K.-P. & Alvarado Rivas, J. 1997. Recharge and Discharge of the Caracas Aquifer, Venezuela. *Proc. IAH Congr. on Groundwater in the urban environment*: 5 pp. (in print).
- Seiler, K.-P. & Müller 1996. Grundwasserneubildung und Grundwasserumsätze im Kristallin des Bayerischen Waldes. *Dt. geol. Mitt.* 36: 194-199.
- Seiler, K.-P. & Lindner, W. 1995. Near surface and deep groundwater. *J. Hydrol.* 165: 33-44.
- Seiler, K.-P. 1969. Kluft- und Porenwasser im Mittleren Buntsandstein des südlichen Saarlandes. *Geol. Mitt.* 9: 75-96.
- Seiler, K.-P. 1985. Results of field experiments on hydrodynamic dispersion in Quaternary gravels of Southern Germany. *Sc. Base for Water Res. Management, IAHS Publ. No. 153*: 351-360.
- Seiler, K.-P. 1997. Microbial activities in Karst aquifers with matrix porosity and consequences for groundwater protection in the Franconian Alb. In E. KRANJC: *Tracer Hydrology*. Balkema, Rotterdam, Brookfield: 339-346.
- Seiler, K.-P. 1998. Isotope Study of the hydrological impact of large scale agriculture. *Int. Symp. on Isotope Techn. in the Study of Past and Current Environmental Changes in the Hydrosphere and Atmosphere, IAEA Vienna*: 339-352.
- Seiler, K.-P., Behrens, H., Wolf, M. 1995. Use of artificial and environmental tracers to study storage and drainage of groundwater in the Franconian Alb, Germany, and the consequences for groundwater protection. *Proc. Isotopes in Water Resources Management Vol. 2, IAEA Vienna*: 135-146.
- Seiler, K.-P., Behrens, H. & Hartmann, H.-W. 1991. Das Grundwasser im Malm der Südlichen Frankenalb und Aspekte seiner Gefährdung durch anthropogene Einflüsse. - *Deutsche Gewässerkr. Mitteilungen* 35, 171-179.
- Seiler, K.-P., Behrens, H., Hartmann, H.-W. 1992. Das Grundwasser im Malm der Südlichen Frankenalb und Aspekte seiner Gefährdung durch anthropogene Einflüsse. *Deutsche Gewässerkr. Mitteilungen* 35: 171-179.
- Seiler, K.-P., Maloszewski, P. & Behrens, H. 1989. Hydrodynamic dispersion in karstified limestones and dolomites in the Upper Jurassic of the Franconian Alb. *J. Hydrol.* 108: 235-247.

## References

- Seiler, K.-P., Müller, E. & Hartmann, A. 1996. Diffusive Tracer exchanges and Denitrification in the Karst of Southern Germany. Proc. Int. Symp. on the Geochem. of the Earth Surface: 644-651.
- Seiler, K.-P., Müller, E., Hartmann, A. 1997. Matrix Porosities and Microbial Activities in Karst Aquifers and Consequences for Groundwater Protection Measures in the Franconian Alb, Germany. Proc. 6<sup>th</sup> Conference on Limestone Hydrology and Fissured Media, Neuchatel: 239-242.
- Seiler, K.-P., P., Trimborn, J. & Alvarado 1992. Das Grundwasser im Umfeld des Lago de Valencia, Venezuela und seine anthropogene und geogene, nachteilige Beeinflussung. Z. dt. geol. Ges. 143: 398-403.
- Shanan, L. 1992. Planing and management of irrigation systems in developing countries. Agric. Water Management Journ.: 22.
- Sklash, M.G., Farvolden, R.N. & Fritz, P. 1976. A conceptual model of watershed response to rainfall, developed through the use of oxygen-18 as a natural tracer. Can. J. Earth Sc. 13: 271-283.
- Sklash, M.G., Farvolden, R.N. 1979. The role of groundwater in storm runoff. J. Hydrol. 43: 45-65.
- Stille, H. 1903. Geologisch-hydrologische Verhältnisse im Ursprungsgebiet des Paderquellen zu Paderborn. Abh. kgl. preuß. L.A. u. Bergakad. 38: 129 S.
- Sudicky, E.A. & Frind, E.O. 1981. Carbon-14 dating of groundwater in confined aquifers: Implication of aquitard diffusion. Water Resources. Res. 17: 1060-1064.
- Tamers, M.A. 1967. Surfacewater infiltration and groundwater movement in arid zones of Venezuela. Proc. Isotopes in Hydrology, IAEA Vienna: 339-351.
- Thorne, D.W., Peterson, H.B. 1954. Irrigated soils, their fertility and management. The Blakiston Comp., New York, Toronto: 392 pp.
- Toth, J. 1963. A theoretical analysis of groundwater flow in small drainage basins. J. Geophys. Res. 68: 4795-4812.
- Toth, J. 1995. Hydraulic continuity in large sedimentary basins. Hydrogeol. J. 3: 4-16.
- UN 1991. World urbanisation prospects. New York.
- UNEP 1992. World atlas of desertification. E.Arnold, London.
- Velasques, E., Arragon, V.R., Seiler, K.-P., Stichler, W. 1989. Investigaciones hidrogeológicas e isotópicas en el sistema del Lago Peten Itza, en el norte de Guatemala. Isotope Hydrology Invest. in Latin America. IAEA-TECDOC-502, IAEA Vienna: 319-336.
- Vengosh, A., Chivas, A.R., McCulloch, M.T., Starinsky, A., Kolodny, Y. 1991: Boron isotope geochemistry of Australian salt lakes. Geochim. Cosmochim. Acta 55: 2591-2600.
- Vengosh, A., Heumann, K.G., Juraske, S., Kasher, R. 1994. Boron isotope application for tracing sources of contamination in groundwater. Envi. Sci. Tech. 28: 1968-1974.

## References

- Verhagen, B.T., Geyh, M.A., Froehlich, K., Wirth, K. 1991. Isotope hydrological methods for the quantitative evaluation of groundwater resources in arid and semiarid areas. Development of a methodology. Federal Ministry of Economic Cooperation. Fed. Rep. of Germany: 164 pp.
- Verhagen, B.T., Mazor, E., Sellschop, J.P.F. 1973. Radiocarbon and tritium evidence for direct rain recharge to groundwaters in the Northern Kalahari. *Nature* 249: 643-644.
- Wang, J.S.Y. 1991. Flow and transport in fractured rocks. *Rev. Geophys.* 29: 254-262.
- Weiss, E.G. 1987. Porositäten, Hydraulic conductivitäten und Verkarstungserscheinungen im Mittleren und Oberen Malm der Südlichen Frankenalb. PhD-thesis, University of Erlangen, 211pp.
- White, R.E. 1985. The influence of macropores on the transport of dissolved and suspended matter through soil. *Adv. in Soil Sci.* 3: 95-119.
- WHO 1997. Guidelines for drinking water quality; health criteria and other supporting Information. Vol. 2, WHO Geneva: 973 pp.

## References

# LITERATURE

- |  |  |   |
|--|--|---|
| <b>H.Moser</b><br><b>W.Rauert</b>        | <b>Isotopenmethoden in der Hydrologie</b> (1980)<br>(in German language) ISBN 3-443-01012-1  | Gebr. Borntraeger<br>Berlin, Stuttgart  |
| <b>P.Fritz</b><br><b>J.Ch.Fontes</b>     | <b>Handbook of Environmental Isotope<br/>Geochemistry</b> ISBN 0-444-41781-8<br><br>Vol.1. The Terrestrial Environment A (1980)<br>Vol.2. The Terrestrial Environment B (1986)<br>Vol.3. The Marine Environment A (1989) | Elsevier SciencePubl.<br>Amsterdam, Oxford<br>New York, Tokyo<br>ISBN 0-444-41780-X<br>ISBN 0-444-42225-0<br>ISBN 0-444-42764-3 |
| <b>F.J.Pearson</b><br>e.a.               | <b>Applied Isotope Hydrogeology</b> , a case study<br>in Northern Switzerland (1991)<br>ISBN 0-444-88983-3   | Elsevier Science Publ.<br>Amsterdam, Oxford,<br>New York, Tokyo   |
| <b>I.Clark</b><br><b>P.Fritz</b>         | <b>Environmental Isotopes in Hydrogeology</b><br>(1997)<br>ISBN 1-56670-249-6  | Lewis Publishers<br>Boca Raton,<br>New York   |
| <b>F.Gasse</b><br><b>Ch.Causse</b>       | <b>Hydrology and Isotope Geochemistry</b><br>ISBN 2-7099-1377-1  | Editions de l'Orstom<br>Paris   |
| <b>W.Kaess</b>                           | <b>Tracing in Hydrogeology</b> (1998)<br>ISBN 3-443-01013-X  | Balkema   |
| <b>C.Kendall</b><br><b>J.J.McDonnell</b> | <b>Isotopes in Catchment Hydrology</b> (1998)<br>ISBN 0-444-50155-X  | Elsevier/North<br>Holland Publ.Comp.<br>Amsterdam   |

- E.Mazor**      **Chemical and Isotopic Groundwater Hydrology – The applied approach (1998)**      Marcel Dekker Inc.  
ISBN 0-8247-9803-1
- P.G.Cook**      **Environmental Tracers in Subsurface Hydrology (2000)**      Kluwer Acad. Publ.  
**A.L.Herczeg**  
**(ed.)**      ISBN 0-7923-7707-9
- G.Friedlander**      **Nuclear and Radiochemistry (1981)**      John Wiley & Sons  
**J.W.Kennedy**      New York, Chichester,  
**E.S.Macias**      Brisbane, Toronto  
**J.M.Miller**      ISBN 0-471-86255-X
- G.Faure**      **Principles of Isotope Geology (1986)**      John Wiley & Sons

# IAEA PUBLICATIONS

## IAEA CONFERENCE PROCEEDINGS

- 1963 **Radioisotopes in Hydrology**, Tokyo, 5-9 March 1963, IAEA, Vienna, 459 pp. (STI/PUB/71) (out of print)
- 1967 **Isotopes in Hydrology**, Vienna, 14-18 November 1966, IAEA, Vienna, (in co-operation with IUGG), 740 pp. (STI/PUB/141) (out of print)
- 1970 **Isotope Hydrology**, Vienna, 6-13 March 1970, IAEA, Vienna, (in co-operation with UNESCO), 918 pp. (STI/PUB/255) (out of print)
- 1974 **Isotope Techniques in Groundwater Hydrology**, Vienna, 11-15 March 1974, IAEA, Vienna, 2 volumes: 504 and 500 pp. (STI/PUB/373) (out of print)
- 1979 **Isotope Hydrology** (in 2 volumes), Neuherberg, Germany, 19-23 June 1978, IAEA, Vienna, (in co-operation with UNESCO), 2 volumes of 984 pp. (STI/PUB/493) ISBN 92-0-040079-5 and ISBN 92-0-040179-1
- 1983 **Isotope Hydrology**, Vienna, 12-16 September 1983, IAEA, Vienna, (in co-operation with UNESCO), 873 pp. (STI/PUB/650) ISBN 92-0-040084-1
- 1987 **Isotope Techniques in Water Resources Development**, Vienna, 30 March-3 April 1987, IAEA, Vienna, (in co-operation with UNESCO), 815 pp. (STI/PUB/757) ISBN 92-0-040087-6
- 1992 **Isotope Techniques in Water Resources Development**, Vienna, 11-15 March 1991, IAEA, Vienna, (in co-operation with UNESCO), 790 pp. (STI/PUB/875) ISBN 92-0-000192-0
- 1993 **Isotope Techniques in the Study of Past and Current Environmental Changes in the Hydrosphere and the Atmosphere**, Vienna, 19-23 April 1993, IAEA, Vienna, 624 pp. (STI/PUB/908) ISBN 92-0-103293-5
- 1995 **Isotopes in Water Resources Management** (in 2 volumes), IAEA, Vienna, 20-24 March 1995, IAEA, Vienna, 2 volumes: 530 and 463 pp. (STI/PUB/970) ISBN 92-0-105595-1 and 92-0-100796-5
- 1998 **Isotope Techniques in the Study of Environmental Change**, Vienna, 14-18 April 1997, IAEA, Vienna, 932 pp. (STI/PUB/1024) ISBN 92-0-100598-9
- 1999 **Isotope Techniques in Water Resources Development and Management**, 10-14 May 1999, IAEA, Vienna, CD Rom (IAEA-CSP-2/C) ISSN 1562-4153

## **SPECIAL IAEA SYMPOSIA**

- 1967 **Radioactive Dating and Methods in Low-Level Counting**, Monaco, 2-10 March 1967, IAEA, Vienna, 744 pp. (STI/PUB/152) (out of print)
- 1979 **Behaviour of Tritium in the Environment**, San Fransisco, USA, 16-20 October 1978, 711 pp. (STI/PUB/498) ISBN 92-0-020079-6
- 1981 **Methods of Low-Level Counting and Spectrometry**, Berlin, Germany, 6-10 April 1981, IAEA, Vienna, 558 pp. (STI/PUB/592) (out of print)

## **IAEA REPORTS AND TECHNICAL DOCUMENTS (TECDOCS)**

- Environmental Isotope Data no.1 – no.10: World Survey of Isotope Concentration in Precipitation**, Data from network of IAEA and WMO over period 1953-1991, published 1969-1994.
- Interpretation of Environmental Isotope and Hydrochemical Data in Groundwater Hydrology**, Proc. Adv. Group Meeting, Vienna, 27-31 January 1975, IAEA, Vienna, 1976, 230 pp. (STI/PUB/429) ISBN 92-0-141076-X
- Isotopes in Lake Studies**, Proc. Adv. Group Meeting, Vienna, 29 August-2 September 1977, IAEA, Vienna, 1979, 290 pp. ISBN 92-0-141179-0 (out of print)
- Arid Zone Hydrology: Investigations with Isotope Techniques**, Proc. Adv. Group Meeting, Vienna, 6-9 November 1978, IAEA, Vienna, 1980, 265 pp. (STI/PUB/547) ISBN 92-0-141180-4
- Stable Isotope Standards and Intercalibration on Hydrology and Geochemistry**, (R. Gonfiantini ed.), Report on Consultants' Meeting, Vienna, 8-10 September 1976, IAEA, Vienna, 1977.
- Stable Isotope Hydrology Deuterium and Oxygen-18 in the Water Cycle**, (J.R.Gat and R.Gonfiantini eds.), Monograph by Working Group, IAEA, Vienna, 1981, 340 pp. (STI/DOC/10/210)
- Palaeoclimates and Palaeowaters: A Collection of Environmental Isotope Studies**, Proc. Adv. Group Meeting, Vienna, 25-28 November 1980, IAEA, Vienna, 1981, 207 pp. (STI/PUB/621) ISBN 92-0-141083-2

- Guidebook on Nuclear Techniques in Hydrology**, by Working Group IAEA, Vienna, 1983, 439 pp. (STI/DOC/10/91/2)
- Stable Isotope Reference Samples for Geochemical and Hydrological Investigations**, (R. Gonfiantini ed.), Report by Advisory Group's Meeting, Vienna, 19-21 September 1983, IAEA, Vienna, 1984.
- Stable and Radioactive Isotopes in the Study of the Unsaturated Soil Zone**, Proc. Meeting on IAEA/GSF Progr., Vienna, 10-14 September 1984, IAEA, Vienna, 1985, 184 pp. (TECDOC-357)
- Isotope Techniques in the Study of the Hydrology of Fractured and Fissured Rocks**, Proc. Adv. Group Meeting, Vienna, 17-21 November 1986, IAEA, Vienna, 1989, 306 pp. (STI/PUB/790)
- Stable Isotope Reference Samples for Geochemical and Hydrological Investigations**, Report on Consultants' Meeting, Vienna, 16-18 September 1985, edited by G. Hut, IAEA, Vienna, 1987.
- Use of Artificial Tracers in Hydrology**, Proc. Adv. Group Meeting, Vienna, 19-22 March 1990, IAEA, Vienna, 1990, 230 pp. (TECDOC-601)
- C-14 Reference Materials for Radiocarbon Laboratories**, (K. Rozanski, ed), Report on Consultants' Meeting, Vienna, 18-20 February 1981, IAEA, Vienna 1991.
- Guidelines for Isotope Hydrology**, Manuel for Operation of an Isotope Hydrology Laboratory IAEA, Vienna, 1999 (in prep.)
- Isotopes of Noble Gases as Tracers in Environmental Studies**, Report by Consultants' Meeting, Vienna, 29 May-2 June, 1989, IAEA, Vienna, 305 pp. (STU/PUB/859) (out of print) ISBN 92-0-100592-X
- Statistical Treatment of Data on Environmental Isotopes in Precipitation**, IAEA, Vienna, 1992, 781 pp. (STI/DOC/10/331)
- Isotope and Geochemical Techniques applied to Geothermal Investigations**, Proc. Res. Coord. Meeting, Vienna, 12-15 October 1993, IAEA, Vienna, 1995, 258 pp. (TECDOC-788)
- Reference and Intercomparison Materials for Stable Isotopes of Light Elements**, Proc. Cons. Meeting, Vienna, 1-3 December 1993, IAEA, Vienna, 1995. (TECDOC-825)
- Manual on Mathematical Models in Hydrogeology**, IAEA, Vienna, 1996, 107 pp. (TECDOC-910)

# CONSTANTS

a	year = $3.1558 \times 10^7$ s
amu	atomic mass unit = $1.660\ 54 \times 10^{-27}$ kg
c	velocity of light (in vacuum) = $2.997\ 925 \times 10^8$ m·s <sup>-1</sup>
cal	calorie = 4.184 J
e	elementary/electron/proton charge = $1.602\ 18 \times 10^{-19}$ C
eV	electronvolt = $1.602\ 18 \times 10^{-19}$ J
g	acceleration of free fall = $9.806\ 65$ m·s <sup>-2</sup>
h	Planck constant = $6.626\ 08 \times 10^{-34}$ J·s
J	Joule = 0.2390 cal
k	Boltzmann constant = $1.380\ 54 \times 10^{-23}$ J/K
m <sub>e</sub>	electron mass = $9.109\ 39 \times 10^{-31}$ kg
m <sub>n</sub>	neutron mass = $1.674\ 93 \times 10^{-27}$ kg
m <sub>p</sub>	proton mass = $1.672\ 62 \times 10^{-27}$ kg
M/E eq.	mass/energy equivalence: 1 amu ≡ 931.5 MeV
N <sub>A</sub>	Avogadro constant = $6.022\ 14 \times 10^{23}$ mol <sup>-1</sup>
π	= 3.141 592 6535
R	gas constant = $8.314\ 51$ J·K <sup>-1</sup> ·mol <sup>-1</sup>
T	thermodynamic temperature = t (°C) + 273.15 K
V <sub>m</sub>	molar volume (= 22.41 L·mole <sup>-1</sup> at STP)

# SYMBOLS AND UNITS

A	area	[m <sup>2</sup> ]
B	width of the flow field contributing to a well	[m]
C	concentration	[mg/L] or L/(s km <sup>2</sup> )
D	specific discharge	[mm/a] or L/(s km <sup>2</sup> )
EP	potential evapotranspiration	[mm/a] or L/(s km <sup>2</sup> )
ET	evapotranspiration	[mm/a] or L/(s km <sup>2</sup> )
F	freight	[mg/times] or [kg/(ha year)]
H	High	[m]
K	permeability	[m <sup>2</sup> ]
k <sub>1</sub>	hydraulic conductivity of the filter tube	[m/s]
k <sub>2</sub>	hydraulic conductivity of the filter pack	[m/s]
k <sub>3</sub>	hydraulic conductivity of the aquifer	[m/s]
k <sub>f</sub>	hydraulic conductivity	[m/s]
M	thickness	[m]
n	relative portion	[-]
P	precipitation	[mm/a] or L/(s km <sup>2</sup> )
Q	discharge	[m <sup>3</sup> /s]
R	groundwater recharge	[mm/a] or L/(s km <sup>2</sup> ) 1 L/(s km <sup>2</sup> )≅31.5 mm/a
R <sub>f</sub>	retardation factor	[-]
r <sub>1</sub>	inner radius of the filter tube	[m]
r <sub>2</sub>	outer radius of the filter tube	[m]
r <sub>3</sub>	radius of the borehole	[m]
t	time	[sec]
T	mean residence time	[years]
TU	Tritium Unit	≅ <sup>3</sup> H/ <sup>1</sup> H = 10 <sup>-18</sup> 1 TU = 0.11 Bq/L
v	velocity	[m/d]
v <sub>b</sub>	borehole velocity	[m/d]
v <sub>f</sub>	filter velocity	[m/d]
p	porosity	[-]
pMC	percent modern <sup>14</sup> C	[%]
v <sub>a</sub>	distance velocity	[m/d]

$v_b$	borehole velocity	[m/d]
$r$	radius	[m]
$t$	time	[d]
$\alpha$	geometric factor	[-]
$\gamma$	unit weight of rocks	[g/cm <sup>3</sup> ]
$\delta$	relative abundance ratio of stable isotopes	[‰], as a relative deviation from a standard

# SUBJECT INDEX

xxf = page xx and following pages

## a

---

Active recharge zone 13, 16f, 24f, 31f, 39, 64f  
Agriculture 6, 33, 35, 70, 76, 81  
Aluminium mixed oxides 10  
Ammonia 67  
Aquifer, consolidated 5, 7, 13, 24, 28  
Aquifer, unconsolidated 5, 7, 13, 25, 28, 63  
Argon-39 (<sup>39</sup>Ar) 20, 24, 27, 87  
Arid zones 12, 45f, 48, 53  
Artificial groundwater recharge 12  
Artificial tracers 21, 23, 61, 70

## b

---

Bacteria 10f, 47, 76f  
Bank filtration 12  
Biofilm 12, 71, 77f, 90  
Boron-11 (<sup>11</sup>B) 90  
Brome-82 (<sup>82</sup>Br) 30  
Bypass-flow 6, 11f, 49, 52f, 57

## c

---

Capillary fringe 11  
Carbon-14 (<sup>14</sup>C) 16f, 24, 27f, 39, 64, 87, 90  
Catchment area 7, 25, 27, 31, 34f, 41, 60f, 73  
Cation exchange 87  
Chemical environment 10  
Chalk 7, 11  
Chloride 30, 38f, 52, 54f, 58, 63, 66f  
Clay 10, 25, 31, 62, 83  
Concentration-time curve 74  
Conceptual model 7  
Cone of depression 25  
Consolidated aquifer *see aquifer*  
Connate water

## d

---

Deep groundwater 13f, 16, 33, 39, 69  
Denitrification 76f, 80  
Desert 13, 24, 45f

Desertification 6, 45  
Desorption 78  
Deuterium (<sup>2</sup>H) 9, 20, 27, 37f, 56, 58, 64f, 87  
Dew 50, 55  
Diagenesis 8  
Discharge 13f, 23, 29, 35, 37, 43, 45,  
48f, 52, 60, 62f, 69, 76, 83  
Distribution coefficient 10  
Dissolved organic carbon (DOC) *see DOC*  
DOC 6, 24, 26, 53, 77  
Drop irrigation 48  
Dry land 13, 48, 88  
Dye Tracers 74, 83

## e

---

Early warning system 19, 21, 61, 91  
Electric conductivity 35, 38, 41, 63, 83  
Environmental tracers 7, 21, 23  
Evaporation pan 35, 37, 41  
Evaporites 38, 63  
Evapotranspiration 43, 45, 63  
Exploration 24, 34, 71  
Exploitation 3, 14, 18f, 39, 43, 60f, 65, 69

## f

---

Facies 31, 72, 73f  
Fertilisers 46  
Field capacity 52  
Filtering 11, 69  
Filter velocity 28f  
Fissured rock 24, 76  
Flood irrigation 49, 53  
Flow direction 27f  
Fluorescent tracers 73, 75  
Formation water 14  
Freshwater 1, 16, 60

## g

---

Geothermal water 42  
Geotechnics 25, 60f  
Groundwater exploitation *see exploitation*  
Groundwater exploration *see exploration*  
Groundwater mining 13, 25f, 28  
Groundwater mixing 7f, 37, 46, 61, 64f,  
67, 83, 89  
Groundwater modelling 2, 10, 14, 20, 27,  
33f, 65f, 90f  
Groundwater protection 2, 6, 33, 60f, 70f, 90

Groundwater quality 3f, 10, 13, 19f, 26, 33,  
36f, 39, 46f, 52, 60,  
62, 65f, 70, 76, 90  
Groundwater recharge *see recharge*

## h

---

Heterogeneous-porous media 7f, 70  
Humid zones 13, 24, 45, 60  
Hydraulic conductivity 7f, 13f, 18, 24,  
37, 73, 75  
Hydraulic head 25f, 39, 83f  
Hydraulic short cut 16, 19, 26, 35, 39, 66, 83  
Hydrodynamic dispersion 7f, 24  
Hygiene 25, 47, 60f

## i

---

Infiltration 1, 3, 5f, 12, 24, 36f, 52f, 55,  
63, 65, 70  
Interflow 2, 5f, 12, 14, 62, 70  
Ion exchange water 7, 16, 91  
Ion exclusion 10  
Iron mixed oxides 10  
Irrigation 20, 35f, 45f, 52f, 54f, 58  
Irrigation return water 36f, 46f  
Isochrones 16, 34

## k

---

Karst 11, 71, 73, 76, 78  
Krypton-85 (<sup>85</sup>Kr) 23f, 87

## l

---

Land use 12, 20, 67, 70, 76, 80  
Lateral flow 8, 60, 63f, 69  
Leaching 5f, 19, 52, 57

## m

---

Macro pores flow *see bypass-flow*  
Manganese mixed oxides 10  
Matrix flow 53  
Mean residence time 6f, 23f, 39, 47, 60, 69,  
76  
Metamorphic rocks 7, 10, 63  
Meteoric Water Line (MWL) 37, 39f, 64, 66  
Microbial disintegration 11f, 23, 47, 69f,  
76, 78, 87, 90  
Model calibration 91

Molecular diffusion 8, 10, 29

## n

---

N<sub>2</sub>O 78  
Natural attenuation 47, 66, 71, 90  
N-15 (<sup>15</sup>N) 12, 20, 78, 87, 90  
Nitrates 67f, 76f, 81, 87  
Nitrites 67, 77, 81  
Non-reactive tracers 8, 9, 20, 27,  
29f, 53, 83, 91  
Non-reactive pollutants 9

## o

---

Overexploitation 20, 23, 25f, 39, 60  
Overland flow 2, 5f, 62, 70  
Oxygen-18 (<sup>18</sup>O) 12, 20, 23, 27f, 37, 39f, 42,  
48, 53, 56, 58, 64, 66f, 81, 87  
<sup>18</sup>O in nitrates 12, 20  
<sup>18</sup>O in sulphates 12, 20

## p

---

Passive recharge zone 5, 13f, 16f, 19, 24, 31,  
32f, 39f, 46, 64f, 67  
Permafrost 13  
Pore size distribution 7, 48f, 53, 55, 57, 88  
Preferential flow *see bypass-flow*

## r

---

Reactive tracers 7  
Reactive pollutants 7, 9, 10  
Reefs 7, 9, 71f, 73f  
Recharge 2, 5, 7, 10, 12f, 19, 24f, 31f, 36f,  
39f, 43, 45f, 53, 55, 60, 63f, 69, 76, 82  
Reduction process 12, 90  
Retardation factor 10, 73  
Residence times *see mean residence times*

## s

---

Saline water 8, 20, 26, 35, 55  
Salinisation 3, 46, 52  
Saltwater intrusion 16  
Sampling (of water) 27, 32, 35, 37f, 41,  
56, 68, 76, 82f  
Sandstone 7, 11  
Saturated zone 7, 47, 69, 82, 90  
Screening of wells 24  
Sedimentary rock 5, 7f, 25, 28, 52f,

55f, 62, 71, 88f  
 Semiarid zones 12, 45f, 30f, 36f 46f, 53  
 Shrinking cracks 50, 53, 55  
 Single well technique 28f, 31  
 Soil water 6, 49  
 Soluble rocks 1, 7  
 Solution cavities 7, 9  
 Sorption 5, 10f, 47, 69, 78  
 Sulphate 36, 38, 87  
 Sprinkling irrigation 48  
 Steady state flow 6, 35  
 Subsidence 25, 28, 91  
 Sulphur-34 ( $^{34}\text{S}$ ) 12, 20, 27, 78, 81, 87, 90  
 Surfacewater 2f, 11f

## **t**

---

Temperature 28, 38, 40, 83  
 Transient flow 14, 19, 25f, 34, 66  
 Tritium nought line (TNL) 15f, 28  
 Turnover time of groundwater 2, 13, 90f  
 Tritium ( $^3\text{H}$ ) 9, 16f, 20, 23f, 32f, 39, 41, 48,  
 64, 66f, 69, 75f, 78, 87

## **u**

---

Unconsolidated aquifer *see aquifer*  
 Unsaturated zone 6f, 9, 11, 24, 45, 47, 49,  
 52, 54, 69f, 82, 88f

## **v**

---

Vadose zone 89  
 Vertical flow (in wells) 28, 82f

## **w**

---

Waste disposal 5, 20f  
 Water age 7, 16f, 76f, 98  
 Water balance 36, 40, 61, 63  
 Water cycle 2f, 17, 66  
 Water quality *see groundwater quality*  
 Water use 3, 6

