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.

<table>
<thead>
<tr>
<th>Water Form</th>
<th>Percentage</th>
<th>Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Groundwater</td>
<td>96.3 %</td>
<td>8 000 000 km³</td>
</tr>
<tr>
<td>Lake water</td>
<td>2.7 %</td>
<td>226 000 km³</td>
</tr>
<tr>
<td>Soil Moisture</td>
<td>0.8 %</td>
<td>62 000 km³</td>
</tr>
<tr>
<td>Air Humidity</td>
<td>0.2 %</td>
<td>15 000 km³</td>
</tr>
<tr>
<td>River water</td>
<td>0.01 %</td>
<td>1 000 km³</td>
</tr>
<tr>
<td>Annual average discharge from continents</td>
<td>45 000 km³</td>
<td></td>
</tr>
</tbody>
</table>

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 km³/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 km³ corresponding to a total water demand per capita of 1000 m³/year. As compared to this number the individual water demand for households is about 55 m³/year and the demand for drinking and food processing about 5 m³/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 extend 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$^3$ (Global 2000).

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

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
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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 extend.

![Diagram of a landscape with the four most important discharge components.](image)

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

![Graph showing DOC concentrations and discharge over time.](image)

**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 extend 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 extend 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
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reefs, or Cretaceous chalks (Stille 1903, Seiler 1969, Matthess 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 (Lallemand-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).
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 ($^2$H, $^3$H, $^{18}$O), belong to this group.

![Fig.1.4](image-url) 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 fare 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.

![Typical isotherms to describe instantaneous sorption.](image)

**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 µm; 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
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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 $^{34}$S, $^{15}$N and $^{18}$O in SO$_4^{2-}$ and 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).

Microbrial 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 = 400m, x =15000m). 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.
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.
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 $^3$H, $^{14}$C and ion exchange waters (Ca$^{2+}$ replaced by 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 $^3$H. To do this, the TNL (Tritium-Null-Line, Tritium nought line) is defined as an interface below which the $^3$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.
Contrary to salts or the mineralisation of groundwaters, $^3$H 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 solved 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.