GENESIS
groundwater and dependent ecosystems

Guidelines on flowpath characterization, dynamics and GW renewal

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Summary (publishable) for policy uptake	Aim of this work is to present conceptual framework and operational tools for characterisation of flow in groundwater systems as related to surface waters and dependent ecosystems within the context of assessing and preventing threats to groundwater quantity and quality. The coherence of this integrative, multidisciplinary effort is achieved by placing different processes and parts of groundwater systems in the framework of conceptual models development and putting emphasis on the tracer-based techniques. These Guidelines are meant to be an aid to groundwater managers, researchers and educators but also to policy makers and stakeholders concerned with understanding and quantitative characterisation of groundwater systems. After presenting an overview of conceptual models the Guidelines consider issues that need to be addressed for a comprehensive characterization of groundwater flow system. They are related to spatially complex and transient patterns of water flow and contaminant transport that are expressed at a wide range of scales.		

SEVENTH FRAMEWORK PROGRAMME

Environmental and artificial tracers are presented as tools in integrated characterization of groundwater systems. Tracers methods provide information integrated over different spatial and temporal scales and are well suited for development of the conceptual models. Use of tracers in quantification of timescales of contaminant transport is demonstrated.

Following chapters provide conceptual framework and present methods for characterization of groundwater flow through the linked compartments of groundwater systems, from infiltration to surface waters. Groundwater renewal and its importance for sustainability of groundwater resources is treated in a separate chapter. Finally, impacts of climate and land-use changes on flowpath structure and transport are considered. An example of artificial tracer application in the unconfined, highly heterogeneous alluvial Zagreb aquifer performed in the GENESIS project is presented in an Annex.

List of GENESIS partners

Norwegian Institute for Agricultural and Environmental Research (CO)	Bioforsk	Norway
University of Oulu	UOULU	Finland
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Swiss Federal Institute of Technology Zurich	ETH	Switzerland
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1 Introduction

Groundwater is an essential water resource which, due to its nature, cannot be observed and quantified in a direct way. Quantitative assessments of groundwater resources and their vulnerability to adverse natural and anthropogenic impacts require conceptualization, quantification and modelling of often vast, complex and heterogeneous groundwater systems with inclusion of various physical, geochemical and biological processes. Therefore, there is a growing need for practical, cost-effective methods of groundwater systems characterisation that could be applied in the real-world management of groundwater resources. Environmental and artificial tracer techniques supplemented with mathematical modelling appear here as a particularly attractive approach that provides synthetic insights into functioning of groundwater systems. Information obtained by means of environmental tracers is integrative over a wide range of spatial and temporal scales and surpasses in this regard the conventional methods. In spite of this, tracer-based methodologies are not yet routinely employed as a tool in decision making process by groundwater managers and policy makers. Understanding and quantitative characterisation of groundwater systems has the following essential components related to groundwater flow, all of which can be significantly variable under anthropogenic forcings:

- three-dimensional structure of groundwater flow paths,
- timescales of water flow and solute transport,
- water fluxes across interfaces between system components.

Knowledge of groundwater flow paths through the system is necessary to locate and link recharge and discharge areas. Specific attention in this regard is paid to interactions between groundwater and surface water bodies, typical examples of which are indirect recharge from rivers and lakes and discharge of groundwater to them. Another area of growing scientific and practical interest is the role of groundwater as an essential supporting element for various types of groundwater dependent ecosystems. It has to be emphasized that reliable monitoring and predictions of contaminant movement requires comprehension of the three-dimensional structure of water flow paths even in unconfined, relatively homogeneous aquifers.

An essential characteristic of groundwater systems are time scales of the inherently coupled processes of water flow and solute transport. Knowledge of travel times between groundwater recharge and discharge sites is crucial for consideration of how such disturbances as contamination and effects of land-use and climate changes propagate through the groundwater system. Travel time distributions of water and solutes, obtainable through application of tracers and mathematical modelling, carry important information used to quantify time lags associated with responses of the system to both commencement and cessation of these disturbances, as well as to quantify mixing properties of the geological medium that influence dispersion and removal of contaminants.

Finally, quantitative assessments of groundwater resources and of contaminant transport typically derived through numerical modelling of groundwater systems require a thorough knowledge of water fluxes across the essential interfaces: surface-subsurface, unsaturated-saturated zones, between aquifers and aquitards. Particularly important are estimates of recharge rates because recharge processes control two interrelated characteristics of groundwater resources: their renewability and vulnerability to contamination. An inherent but often overlooked property of recharge is its spatial and temporal variability which can significantly affect reliability of the assessments of groundwater quantity and quality. A specific example of spatial recharge inhomogeneity is the phenomenon of preferential flow through the unsaturated zone which may considerably influence transport of contaminants by reducing their effective travel times to water table.

The central aim of this work is to present conceptual framework and operational tools for characterisation of flow in groundwater systems as related to surface waters and dependent ecosystems within the context of assessing and preventing threats to groundwater quantity and quality. Elaboration of adequate groundwater characterisation tools has a particular significance in the context of the Water Framework Directive (WFD) and the Groundwater Directive (GWD) – European Union legislation aimed at protection of groundwater resources from deterioration. Both directives explicitly recognize that knowledge of flow patterns in groundwater bodies is an inherent element of risk assessment and management schemes. Conceptual models describe functioning of the groundwater systems for different purposes – from communication with non-experts to development of detailed numerical models. Accordingly, complexity of conceptual models, their spatial coverage and temporal resolution may vary widely depending on the context of their use. Refinement of conceptual models is an iterative process in which observations and modelling performed to test the model provide new knowledge of the system that in turn is incorporated in the improved version of the conceptual model. This iterative nature of conceptual models development concords with the practice of environmental tracers where excessive sampling is avoided and previous results are used to plan additional sampling.

Annex II of the WFD identifies basic characteristics that should be determined for groundwater bodies at risk. The characteristics related directly to conditions of groundwater flow include: (i) hydrogeological properties, such as hydraulic conductivity, porosity and confinement, (ii) relevant physical characteristic of the superficial deposits and soils, (iii) stratification characteristics of groundwater, (iv) directions and rates of exchange with associated surface systems, (v) long-term annual mean rate of recharge. The GWD complements the WFD with respect to the issues of groundwater quality standards and of measures to prevent or limit inputs of pollutants to groundwater bodies. It is worth to mention here that GWD explicitly indicates groundwater-dependent ecosystems and water supply for human consumption as two equally important groundwater receptors with respect to which groundwater should be protected from deterioration and chemical pollution. Clearly, this indicates the need for explicit incorporation of the GDEs in the conceptual and numerical models of groundwater systems. The GWD establishes criteria for “the assessment of good groundwater chemical status” and for “the identification and reversal of significant and sustained upward trends” in groundwater pollution. The criteria for the assessment of good groundwater chemical status include threshold values that are to be established in accordance with Annex II of the GWD. The guidelines presented in Annex II clearly indicate that establishment of those threshold values should be based on the thorough characterisation of the given groundwater body, of the associated aquatic and dependent terrestrial ecosystems and of their interactions. Physical and chemical characterisation of the body of groundwater is also one of the bases of the procedure for identification of significant and sustained upward trends in pollution presented in Annex IV of the GWD. Part A, point 2 of this Annex explicitly states that the required temporal characterisation of the body of groundwater should include groundwater flow conditions, recharge rates and percolation times. Spatial delineation of recharge and discharge areas, identification of flow paths and interactions with surface water and quantification of fluxes and time scales of flow and transport become thus an indispensable part of the measures to protect groundwater resources against pollution and deterioration.

These Guidelines are meant to be an aid to groundwater managers, researchers and educators but also to policy makers and stakeholders concerned with understanding and quantitative characterisation of groundwater systems. Methods presented in these Guidelines provide information and data essential for building of conceptual, and further of mathematical models of groundwater systems relevant for the whole range of spatial and temporal scales. The Guidelines provide neither a comprehensive presentation of topics related to groundwater flow and transport nor a complete description of methods used to characterise groundwater systems. Instead, the guidelines aim at reviewing the interrelated processes that govern groundwater dynamics and present methods based on use of tracers and mathematical modelling. The coherence of this integrative, multidisciplinary effort is achieved by placing different processes and parts of groundwater systems in the framework of conceptual models development and putting emphasis on the tracer-based techniques whose application is to a very limited extent incorporated in groundwater management schemes.

The Guidelines combine expertise and experience of participants of the GENESIS project of the Seventh Framework Programme of the European Community. The project aimed at review and development of new scientific knowledge on groundwater systems and its incorporation into new tools for better integrated groundwater management. Integration of multidisciplinary efforts undertaken by project partners in test sites representing various geological, geographical and socioeconomic settings has become a staple of the whole project and also of the presented Guidelines.

2 Integrated characterization of groundwater systems

2.1 Conceptual models of groundwater systems

The Groundwater Directive and several Common Implementation Strategy Guidance Documents recognize conceptual models as an essential tool in groundwater management. However, these documents, do not present a comprehensive definition of a conceptual model. The CIS Guidance Document No. 26 “Guidance on risk assessment and the use of conceptual models for groundwater” reviews previous understanding and use of this concept and explains conceptual models as non-numerical, but optionally quantitative descriptions of groundwater systems, processes and their interactions. Conceptual models describe functioning of the groundwater systems for different purposes – from communication with non-experts to development of detailed numerical models. Conceptual models convey, in a synthetic way, understanding of how groundwater flow paths are organized within an aquifer system, at what rate groundwater and associated substances move through the system and how these processes vary over time. Such information may be required at the scale of the whole aquifer or for a subsection of an aquifer, for example in proximity to a pumping well or at groundwater discharge zone linked to an ecosystem. Accordingly, complexity of conceptual models, their spatial coverage and temporal resolution may vary widely depending on the context of their use. Environmental tracers integrate information on groundwater flow over wide range of spatial and temporal scales and as such are well suited to contribute to the development of conceptual models. Furthermore, refinement of conceptual models is an iterative process in which observations and modelling performed to test the model provide new knowledge of the system that in turn is incorporated in the improved version of the conceptual model. This iterative nature of conceptual models development concords with the practice of environmental tracers where excessive sampling is avoided and previous results are used to plan additional sampling.

Compared to surface hydrology hydrogeologists face a fundamental problem, i. e. they have only very limited access to the subsurface domain where groundwater flow and transport processes take place. Thus, they have to come up with a consistent interpretation of point data and/or data that integrate information over a certain area and period of time. To accomplish this task hydrogeologists make use of various methods from neighbouring disciplines like geophysics, geochemistry, geography, soil physics, (groundwater) hydrology or river hydraulics in addition to their own field of expertise. Corresponding data that are being evaluated may consist of e.g. well cores, seismic or georadar images, time series of several groundwater components including temperature as an example of an environmental tracer, remote sensing series that provide land and in particular water use information, lab analyses revealing grain size distributions, calculations of evapotranspiration to infer groundwater recharge, pump test data and surface water level among many others. Some of the mentioned methods yield only indirect or soft data that first need to be translated into hydrogeologic characteristics (typically true for geophysical or remote sensing data by using separate models for interpretation). From this example list it becomes clear that there is no single or unique procedure to explore and characterize a subsurface system. It depends on a lot of different conditions like extent of the area, problem to be solved, already existing information and last but not least time and financial resources which all individually influence the level of detail of the associated investigations. All the knowledge about the subsurface system gained from data interpretation is being coherently synthesized into a perception about how the real system works that is generally being referred to as a conceptual model. Conceptual models address both the quantitative and qualitative (chemical) status of groundwater. Due to the in every case limited access to information about the subsurface this perception inherently includes simplifications. It must be underlined that tracer techniques, promoted here as an appropriate and indispensable tool in groundwater management, work best when they supplement other methods and that the comprehensive conceptual models require integration of information related to different aspects of groundwater system functioning.

The intrinsic goals of developing a conceptual model can be divided into four main categories. The first purpose consists of being a tool for consistent data integration. Data are being interpreted as they are collected and may identify knowledge gaps where additional information is needed to complete the conceptual understanding. When new data become available in this procedure the assumptions made setting up the current conceptual model have to be tested. When there is significant divergence, this has to be explained. This could require the collection of more data (e.g. extension of monitoring network, increased monitoring frequency) or additional data (e.g. conditions of input of substances, degradation/retention capacities, flow/spreading velocities in groundwater/leachate) that explore previously unobserved processes. This process may need to be continued until the improved conceptual model can describe the measured data in a consistent way, with sufficient certainty and appropriate scales and complexity. Thus, refinement of conceptual models is an iterative process in which observations performed to test the model provide new knowledge on the system that in turn is incorporated in the improved version of the conceptual model. This improvement of the conceptual model is an important element in the groundwater management process in order to increase system understanding and to develop effective planning and control measures.

Although a conceptual model usually does not aim at a full quantification of processes, the availability of some quantitative information can help to strengthen conceptual models. The development of conceptual models requires a good understanding of the aquifer geometry, the location of groundwater recharge and discharge zones, and the organization of groundwater flow paths between them. Geological information and groundwater level data are key elements to develop first version of a conceptual model. However for complex aquifer systems, this information might not be sufficient as the organization of groundwater flow paths and connectivities between different parts of the system might remain unknown or are uncertain. Tracer data can provide key insight to develop and confirm conceptual models of aquifer functioning. For example for karst aquifers, tracer tests are an indispensable tool to demonstrate how different parts of the aquifer are connected to springs and to evaluate how different springs are related to each other. Tracer data are also extremely important for the calibration and validation of numerical models (see fourth category below).

Second, a conceptual model can be regarded as an instrument for communication with other hydrogeologists as well as with regulators, politicians or the general public. Through discussions the experts can complement their views and reach a common understanding of the groundwater system and will in particular be able to differentiate between geogenic and anthropogenic impacts. In this respect, visualization of the most significant relationships and processes is an important way to communicate conditions in even complex groundwater bodies in an understandable way. Thus, also non-experts will be able to comprehend how an aquifer system is working and how, where and when risks may impact groundwater.

Third, a conceptual model represents a (quantitative) basis where the understanding of the system allows to delineate first measures for groundwater protection without the application of further (e.g. numerical) models to a satisfactory level of accuracy. This also includes predictions of the effects of any measures, assessing risks related to groundwater and planning of monitoring systems. With relation to the WFD a conceptual model can be used to identify the reasons why a groundwater body fails to achieve any status objectives.

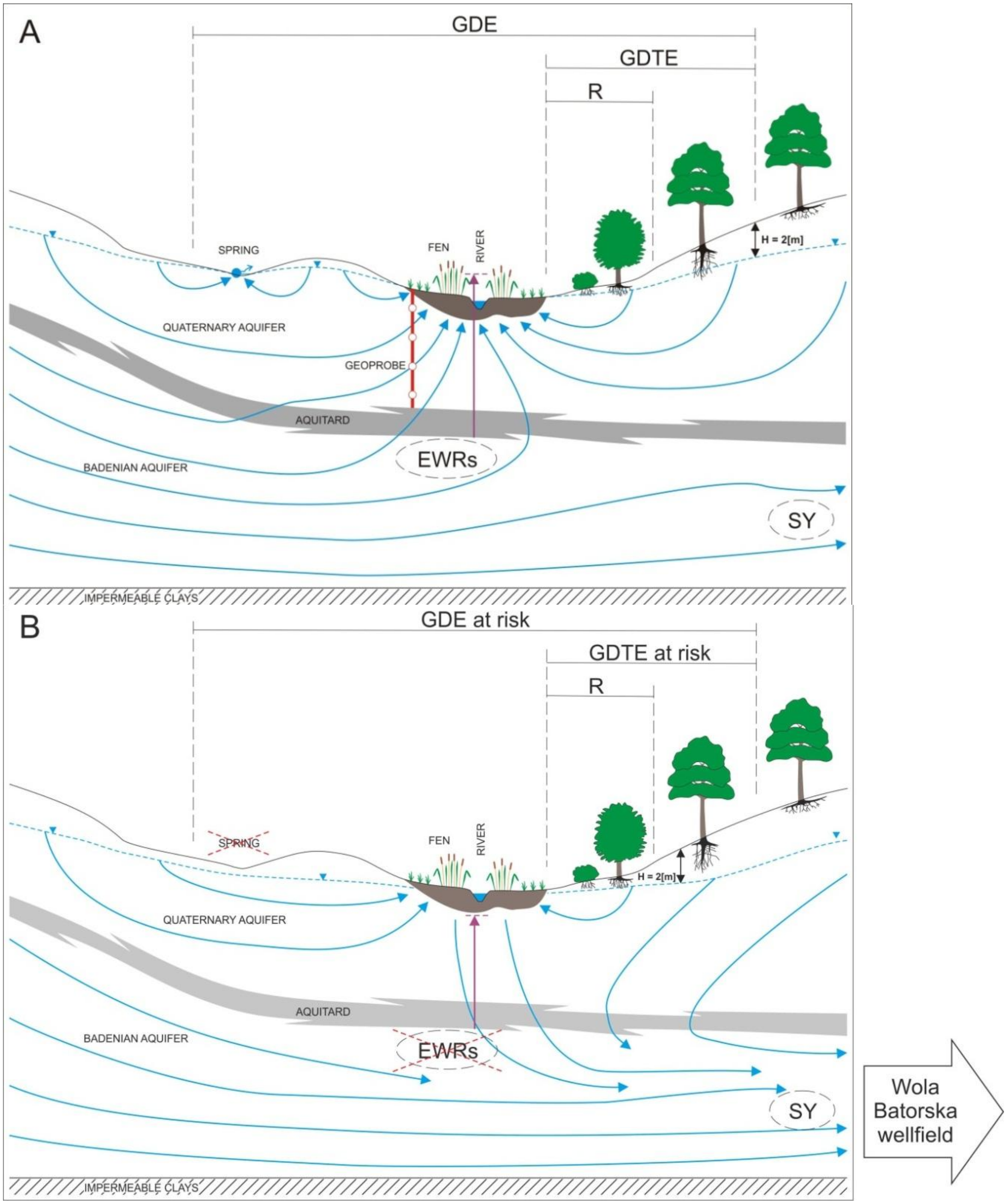


Fig. 2.1 Conceptual model of surface water/groundwater interaction in the area of Niepolomice Forest under natural conditions (A) and envisaged under new steady-state imposed by heavy pumping by Wola Batorska wellfield (B). GDE – Groundwater Dependent Ecosystems; GDTE – Groundwater Dependent Terrestrial Ecosystem; R – riparian and alluvial forest; EWRs –

Environmental Water Requirements; SY – Save Yield of aquifer.

Moreover, it allows for evaluation of potential measures that are most likely to remedy the situation in an effective and sustainable manner. Where there is a risk of failing to achieve good groundwater status the conceptual can justify exemptions or provide alternative objectives.

Finally, a conceptual model may serve as a preparatory work for setting up a numerical model. That is, it offers a sufficient understanding of the relationships between the principal characteristics of a system so that mathematical methods can be used to predict processes in groundwater and to evaluate possible outcomes of changes within the system for a range of feasible situations. In essence, what (e.g. processes, structures, pressures) is not properly considered in the conceptual model will most likely also not be revealed in the numerical model. This will rather lead to misguiding distribution of (fitted) parameters which are of particular harm in computing predictions (i.e. scenarios applying different boundary conditions).

Example graphical representation of a conceptual model is presented in Fig. 2.1. Problems related to this case are discussed in chapter 4.

2.2 Key issues in groundwater system characterization

The major obstacle in characterizing groundwater flow and transport are spatial and temporal variability of hydrogeological conditions and of water and solute inputs. Therefore, in order for the conceptual model of groundwater system to be relevant for the assessments of groundwater chemical status and its trends it has to comprehend spatially complex and transient patterns of water flow and contaminant transport. One of the key challenges in this regard is that processes occurring in the wide spectrum of spatial and temporal scales have to be considered. The level of detail required at different scales when characterizing groundwater flow systems strongly depends on the question to be addressed. When considering questions of groundwater quantity it might be sufficient to know average hydraulic conductivities or storativities for different units, derived from pumping tests. However, for contaminant transport a more detailed understanding of the geological structures within each unit is often necessary. While numerous methods are available to characterize aquifer properties at small spatial and temporal scales (e.g. drilling methods, lysimeters, hydrological testing methods or tracer tests), it is particularly challenging to investigate processes at larger spatial and temporal scales. For sustainable water management, it is important to understand the functioning of a system as a whole, and in the context of climate change or anthropogenic pressures on groundwater system, long term trends are of particular importance to react in time to increasing pressures. A common way to explore the functioning of large systems at long temporal scales is the use of numerical models. However, as the data density for large scale models is usually scarce and cannot represent local heterogeneity of hydraulic parameters, such models are highly uncertain (Refsgaard et al., 2012) and there is a need for their experimental verification. Environmental tracers are a unique means to investigate the functioning of large groundwater flow systems over time scales that reach beyond the period of observation of the system (Kazemi et al., 2006). In contrast to artificial tracers that are injected at a specific location, environmental tracers enter groundwater water flow systems over the entire recharge zone and hence reflect the global behaviour of the system. Environmental tracers are an important tool in the development and verification of the conceptual and numerical models of groundwater systems and presentation of their application in different aspects is a recurring theme of this work.

Spatial variability at different scales

Spatial patterns of groundwater flow have a hierarchical structure (Toth, 1963) and are controlled by the topography, the geological structure of the subsurface, climatic conditions and land uses (Bertrand et al., 2012; cf. Fig. 2.2).

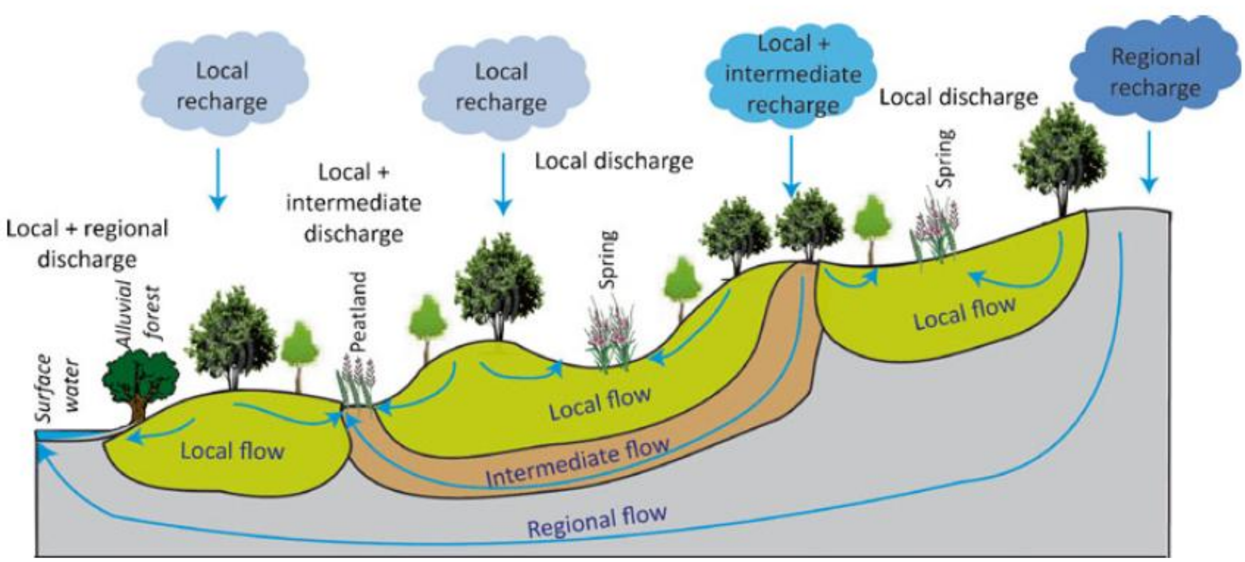


Fig. 2.2 General description of groundwater flow system (Bertrand et al., 2011, adapted from Toth 1963). Not to scale.

For many applications, an understanding of the functioning of the entire groundwater flow system and its interaction with related hydrological systems is required that integrates processes at different spatial and temporal scales (Alley et al., 2002). Such an integrated view is particularly important when addressing questions related to the sustainable management of an aquifer (Zhou, 2009) but also to put local phenomena into a large context. Particular aspects of groundwater system functioning have to be considered taking into account flow systems at relevant spatial scales, from the local to intermediate to regional with the corresponding time scales ranging from days to thousands of years. For example, the delivery of water into a GDE might depend on the detailed configuration of the aquifer-GDE interface but at the same time also on large scale groundwater circulation towards the GDE.

At aquifer scale rates and directions of groundwater flow are controlled by spatial distribution of hydraulic conductivity and, to a lesser extent, of porosity. Stratified deposits, fractures, discontinuities and other distinct heterogeneities of geological medium are obvious controls on groundwater flowpaths but irregular flow patterns may develop even in the apparently homogeneous aquifers (Sudicky and Illman, 2011). Hydraulic conductivity may range over 3 orders of magnitude within one geological formation what influences predictability of flow and transport patterns even in the absence of the directional dependency of hydraulic conductivity because dispersion of contaminants is primarily governed by spatial variations of groundwater velocity. Statistical and stochastic approaches are used to describe heterogeneity and predict contaminant transport in heterogeneous aquifers (e. g. Elfeki et al., 1997) but they are still evolving and their application is not widespread in hydrogeological practice. More commonly standard numerical models of flow and transport are used. Derivation of flow structure and fluxes in heterogeneous media from the knowledge of hydraulic heads only is usually difficult because of insufficient knowledge of hydraulic conductivity distribution. Values of hydraulic conductivities are derived from results of pumping tests, which, at regional scale, might require unrealistically long pumping times. Effectiveness of this approach may be enhanced by application of environmental tracers. Basically, they might provide information integrated over distances and times long enough to provide values of effective hydraulic conductivities in regional scales. In the context of conceptual model development environmental tracers provide not only such quantitative characterization of hydraulic parameters but also their presence or absence in groundwater verifies assumptions on flowpath structure. Environmental tracers should be seen as a method supplementing methods based on Darcy’s law because both methods have their limitations in highly heterogeneous aquifers (Larocque et al., 2009). Combination of different approaches, including numerical modelling and hydrochemistry, helps constrain biases and uncertainties associated with particular methods. Chapters 2.3, 3.1 and 3.2 address some specific questions related to use of tracers in heterogeneous systems.

Steady vs transient flow

In developing a hydraulic system's conceptual model, one must approximately define the study volume's boundaries. Once established, the next question may be: what are the fluxes across and between those boundaries and are they constant (steady state) or variable (transient) with time? For many studies, it is important to know if a groundwater flow system can be assumed to be at steady state or if transient conditions need to be considered. A groundwater flow system is at a hydrodynamic steady state when hydraulic heads (and thus groundwater flow velocities and directions) do not vary as a function of time anywhere in the system. Furthermore, a system is at steady state with respect to transport if concentrations do not vary in time (Incropera and De Witt, 1985). While groundwater flow systems are rarely at complete steady state, systems can often be assumed at hydrodynamic steady state in good approximation, which greatly simplifies the interpretation of tracer data and the numerical simulation of flow and transport processes.

In determining whether an aquifer system maintains steady state or transient flow, one must think of the spatial and temporal scales in question. For example, steady-state groundwater flow may be reasonably assumed when decadal flow averages or great distances are considered. However, this same system may be thought of as transient when considering the long-term environmental changes associated with climate change. Such was the consideration when Scibek and Allen (2006) developed a methodology linking climate and groundwater models to investigate future climate change impacts to groundwater resources. Using groundwater head for comparison within a MODFLOW three-dimensional transient flow model, the effects of spatial and temporal recharge distribution, associated respectively with four climate scenarios, on groundwater levels were compared.

In a more refined temporal review, the steady state of an aquifer's low-flow conditions, observed between individual precipitation events, may be terminated by a storm-event, inducing transient flow. In a study on the topic, Novakowski and Gillham (1988) applied simulated rainfall to a study site near Chalk River, Ontario to study the transition from steady state to transient flow. Using tensiometers and pressure transducers, transient changes in hydraulic head and tension were measured to investigate shallow water-table response to precipitation. Similarly, Kayane and Kaihotsu (1988) reviewed transient flow in the vadose zone, focusing particularly on rapid water table response to rainfall and pulsating flow due to vadose zone pressure perturbations.

Furthermore, an aquifer's geologic configuration is paramount when determining whether steady state or transient flow prevails. For example, the highly responsive nature of karst systems to precipitation events, where the shift from steady state to transient flow can be very rapid, necessitates the evaluation of individual precipitation events to understand the system (Herman et al., 2009; Yang et al., 2010). In contrast, the less responsive nature of deeper and geologically homogenous systems may assume steady state. This was the case when Chen (2009) reasonably assumed steady state flow existed within a homogeneous isotropic porous aquifer while assessing migration of a non-reactive solute within the context of Monte Carlo simulations.

Changes from steady state to transient flow not only result from natural events, but from anthropogenic impacts as well. Anthropogenic effects on flow regimes can be very diverse ranging from the minor effects of turning on and off a singular domestic pumping well to the compounding effect of engaging multiple municipal pumping wells (Budhu and Adiyaman, 2010; Calderhead et al., 2012; Hayashi et al., 2009) which can even induce fissure genesis in geologic parent material (Hernandez-Marin and Burbey, 2012).

Steady state flow may be further anthropogenically interrupted with the construction of tunnels, modifications of river streambeds, and mining of surface ores. Shin et al. (2011) addresses how altered hydraulic boundaries resulting from tunnel installation beneath the water table can shift hydraulic gradients, inducing seepage into the tunnel. Hapuarachchi et al. (2008) discusses the effects of streambed modification on hydraulic conductivity of riparian and riverbed reaches of the Mekong River and their resulting impact on basin hydrology. The anthropogenic impacts of surface mining to groundwater quality and flow regimes have become so prolific and vast that both the United Kingdom and the USA have developed task forces specifically to address mitigation of these effects.

Transient transport

Transport of contaminants in groundwater is by its nature a dynamic and transient process. Unsteady contaminant transport in anthropogenically influenced groundwater systems stems from the transient nature of contaminant inputs and their subsurface transport. Loads of contaminants, whether from point or diffuse sources, vary in time and their input to groundwater with infiltrating and percolating water is affected by a number of processes operating at land surface and in the unsaturated zone. The need for temporal characterization of groundwater bodies in the context of contaminant spreading is recognized in the Groundwater Directive where it is presented as a basis for design of monitoring schemes.

A basic feature of solute transport in groundwater is that its time scales are different than for propagation of hydraulic heads. According to the general groundwater flow equation rate at which hydraulic disturbances propagate through the aquifer are directly determined by its properties, namely by the ratio of hydraulic conductivity (transmissivity) to specific storage (storativity). Rates of pressure propagation are much faster than rates of solute transport because the latter is controlled by advection and dispersion of solute particles, which, in turn, depend on the velocity field and on the presence of immobile water. Spatial distributions of hydraulic heads and of concentrations of solutes transported with groundwater flow are created by different processes and cannot be used to define parameters of the same model (Voss, 2011a,b; Konikow, 2011). Fig. 2.3 demonstrates different time scales at which the hydrodynamic field and solute (represented here by a tracer) distribution reach steady state. Temporal aspects of solute transport in groundwater and the duality of the flow and transport models are further discussed in chapter 2.4.

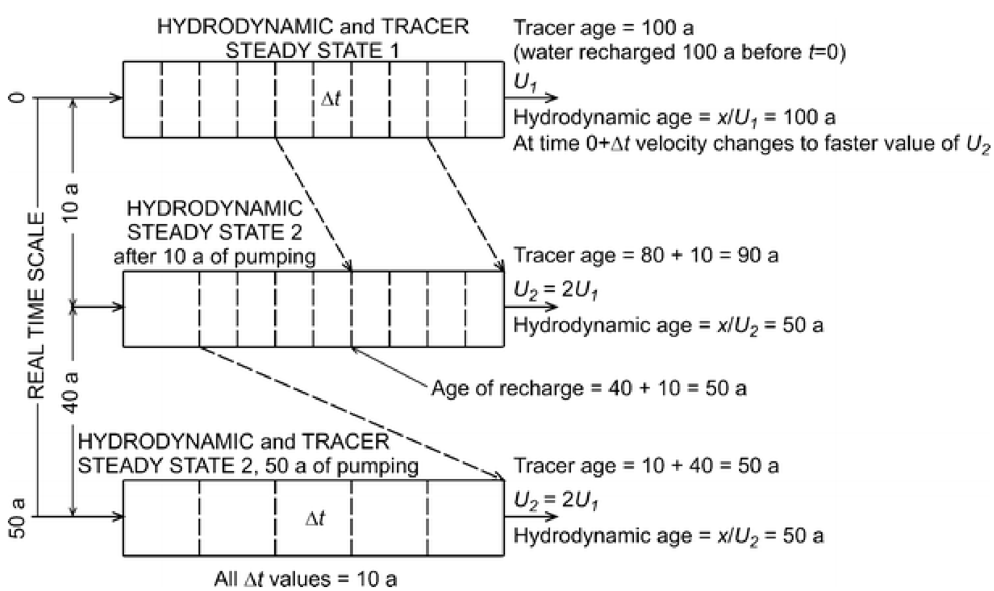


Fig. 2.3 A schematic model of piston flow showing that a fast change of hydrodynamic conditions from one hydrodynamic steady state (first column) to another steady state (second column) is not immediately followed by an adequately fast change in the tracer state. In such a case, the new tracer steady state (third column) is reached after the time period, which is equal to the new hydrodynamic (advective) age (Zuber et al., 2011). Symbols explained in chapter 2.4.

2.3 Tracers as tools in integrated characterization of groundwater systems

Tracer-based approaches have a special role in characterization of the temporal and spatial inhomogeneities in groundwater systems. Information derived from environmental tracers observations integrates system properties over a wide range of spatial and temporal scales. As such, tracers supplement the conventional approaches based on hydrodynamic observations and numerical modelling of flow and transport providing a new dimension of information.

Enviromental tracers used for calibration of the numerical models help constrain aquifer-scale estimates of hydraulic conductivity and storativity that are rarely available with sufficient precission from direct measurements. Interpretation of environmental tracer results, especially for the highly heterogeneous aquifers, is not always straightforward and free from ambiguities and might often provide only qualitative information. Nevertheless, use of tracers in the integrated management of groundwater resources is highly recommended because even a very limited application might provide important insights into the functioning of groundwater systems and considerably improve their conceptual models. Environmental tracers have proven an effective tool in conceptualization of groundwater systems, yet their application in hydrogeology and in groundwater resources management is still limited and insufficient.

2.3.1 Principles of environmental tracers application

Environmental tracers are understood here as naturally occurring and man-made substances that pervade environment and can be traced throughout different environmental compartments and processes. There are, however, different understandings of this term and some authors restrict its use to the naturally occurring substances. Nevertheless, many anthropogenically released substances, like for example radioactive products of atmospheric nuclear explosions or freons, are so ubiquitous in the hydrosphere and the atmosphere that they have already become inherent components of the global environment.

Application of tracers in the field of groundwater resources is not restricted to tracing of water flow and of solute transport through geological media but can be extended to cover hydrological and biogeochemical interactions between groundwater bodies and related environmental compartments like soil, surface water bodies and ecosystems. Information provided by tracers contributes to both qualitative and quantitative characterization of groundwater systems and can be used at all stages of conceptual models development, from delineation of system boundaries, to calibration and validation of numerical models, to monitoring effects of impacts and measures on the system. Environmental tracers applications are described in detail in several monographs (Clark and Fritz, 1997; Kendall and McDonnell, 1998; Cook and Herczeg, 2000; Mook, 2001; Kazemi et al., 2006; Leibundgut et al., 2009; Gat, 2010) and journal papers (see articles in the special issue of Hydrogeology Journal, 2011, vol. 19) provide numerous examples of such applications. This chapter presents basic concepts behind use of environmental tracer techniques and discusses actual and potential applications of tracers as tools for developing conceptual models with attention paid to peculiarities, advantages and limitations of this approach.

The above-mentioned definition of the environmental tracers is wide and encompasses a whole variety of substances and isotopic species with a wide spectrum of physicochemical properties. Potential applications of most tracers are diverse and related to various aspects of groundwater systems characterization. Clear and distinct categorization of environmental tracers with respect to their applications is therefore difficult. A basic division can be made between tracers used to infer properties of groundwater systems that are related to:

- origin, movement and mixing of water;
- origin, transport and transformations of solutes.

The latter will not be treated here in detail but within the context of conceptual modelling two common approaches have to be mentioned. Stable isotope systematics of carbon, nitrogen and sulphur provide information on sources and transformations of these biogenic elements in the subsurface and surface environments. Such information may be of value for understanding of behaviour and transfers of nutrients and contaminants in and between groundwater and related ecosystems. For example, stable isotopes are commonly used to identify natural and anthropogenic sources of nitrates or sulphates, to provide evidence for denitrification and in studies on biodegradation of organic pollutants. Use of stable isotopes in ecology in relation to hydrological and biogeochemical cycles is presented by Fry (2006) and Michener and Lajtha (2007) while application of compound specific stable isotopic analysis in studies of pollutant degradation is described by Hunkeler et al. (2008) and Aelion et al. (2009). Another common usage of reactive solutes as tracers relies on deconvolution of geochemical signals in groundwater, which is commonly supported by geochemical modelling with popular models like NETPATH and PHREEQC. Hydrochemical patterns in wells and springs reflect origin of dissolved substances and thus indirectly provide information on subsurface lithology, geochemical conditions, weathering processes, sources of contamination and even on groundwater flow structure (Herczeg and Edmunds, 2000).

The environmental tracers of groundwater movement and mixing might be, in essence, any physicochemical properties of water that prove suitable in the following applications:

- determination of groundwater flow pathways and mixing ratios (through end-member analysis),
- quantification of groundwater flow timescales (*groundwater dating*) and of groundwater matrix properties.

Tracers most appropriate for tracing water movement are those which possess conservative properties, i. e. their concentrations are not altered by any physicochemical or biological processes that operate along groundwater pathways. All tracers can be, in specific conditions, subject to such alterations but abundances of the isotopic species of hydrogen (^{1}H, ^{2}H, ^{3}H) and oxygen (^{16}O, ^{18}O) contained in water molecules are closest to being the conservative tracers unless groundwater comes into contact with atmospheric air when isotopic modification of water becomes possible due to isotopic fractionation processes. Hydrogen and oxygen atoms of the water molecules can also undergo isotopic exchange with minerals of rock matrix but this process is usually extremely slow and negligible except exchange of oxygen between water and carbonate minerals in hydrothermal conditions. Other non-reactive tracers considered commonly as conservative are halogen ions (e. g. Cl^- and Br^-) or dissolved gases (e. g. SF_6 and freons). However, in near-surface environments plants can take up ionic substances and exchange with the atmosphere or ebullition can affect dissolved gases. The isotopic species of water and the non-reactive dissolved substances are good tracers of the advective water flow but molecular diffusion influences their behaviour in fractured or karst systems with significant matrix porosity, which is of great significance in groundwater dating applications (Zuber et al., 2011).

Some tracer applications can be, in principle, based on a single measurement of tracer content (e. g. radiocarbon dating or lack of tritium as indicator of “old” groundwater) but information provided by tracers is usually contextual and case-specific. Understanding of the extent and internal structure of groundwater systems, of pathways, directions and timescales of groundwater flow is inferred from observed patterns of tracer concentrations (abundances in case of the stable isotopic tracers) in precipitation, infiltration and groundwater. Spatial or temporal differentiation of tracer signatures that exceeds the sampling and analytical precisions is a prerequisite for such applications and can arise from a number of factors which are specific for different categories of tracers and are discussed below. This short review presents also typical applications.

2.3.2 Review of environmental tracers

Stable isotope composition of water

Stable isotopic signatures of water (expressed as $\delta^{18}O$ and δD or the deuterium excess; see the above cited monographs for definitions) are the most commonly used environmental tracers not only due to their wide applicability but also because sample collection is easy and costs of analyses are moderate. Moreover, further dissemination of recently developed laser spectroscopy will increase accessibility of stable isotope techniques in hydrogeology. Stable isotopes of water have diverse applications as tracers related to many aspects of their natural variations in the hydrological cycle. This variability arises in two stages:

1. Spatial and temporal differentiation of the isotopic composition of atmospheric precipitation driven by rain-out processes. Isotopic composition of precipitation depends generally on air temperature (through the so called seasonal, altitude, latitude and continental effects) but may as well vary considerably between rain events and even in the course of a single rain event (amount effect).
2. Evaporation from interception, surface water occurrences and soil as well as sublimation from snow cover affect fluxes and isotopic signatures of infiltrating water. The degree of this alteration is controlled by meteorological conditions, vegetation and soil properties (cf. *Isotope Transfer Function* concept of Gat (2010)).

The resulting spatial and temporal (mainly seasonal) differentiation in isotopic composition of infiltrating water provides a basis to infer pathways and timescales of groundwater flow. The spatial differentiation of infiltration is significant only across the largest or mountainous drainage areas. Isotopic contrasts in the system can be, however, enhanced when indirect recharge occurs. Isotopic composition of surface water bodies may differ significantly from that of local precipitation or direct recharge because lakes and ponds are enriched in heavier isotopes by evaporation. Rivers may convey precipitation from areas of isotopically distinct precipitation (e.g mountains) and isotopic composition of small rivers can be also influenced by evaporation from surfaces of flow-through lakes and reservoirs. Typical applications of the spatial isotopic differentiation are related to identification and delineation of recharge zones and to identification and quantification of mixing between isotopically different parts of groundwater systems, including surface water bodies.

Temporal differentiation of stable isotopic composition in infiltrating or recharging water is used to derive timescales of flow and the values of transport parameters (i.e. dispersivities). In the unsaturated zone, seasonal fluctuations of the infiltrating water or unusual isotopic signatures of single infiltration events can be traced downwards in the soil and vadose zone giving information about water flow velocities. These isotopic variations are attenuated in soil but in some cases may propagate even through the saturated zone to discharge points what allows estimation of water travel times past the system. Depending on transport parameters and scale of seasonal differences, transit times of up to four or five years can be determined. An indirect application of stable isotopes of water for dating uses distinct signatures of waters recharged in different climates, particularly during glacial and interglacial periods. Groundwaters recharged at the end of the last glacial period are common in Europe and are easily distinguishable from the Holocene recharge by the significantly lower $\delta^{18}O$ and δD values. Overall, natural (climatic) or anthropogenic (e.g. river damming and irrigation) shifts in isotopic composition of direct or indirect recharge can be used to locate the moving border between groundwaters with different signatures and thus to infer groundwater ages. Differences between the isotopic composition of precipitation and recharging water may also provide information on the mechanisms and timing of recharge. Evaporative losses of water reduce summer recharge enriched in the heavier isotopes in favour of winter recharge enriched in lighter isotopes while in cold climate areas, particularly on slopes, infiltration of snowmelt may be hindered by snowpack and frozen ground.

Tritium

Tritium is a radioactive isotope of hydrogen (half-life of 12.43 years) naturally produced in the atmosphere through interactions of cosmic radiation with nitrogen and deuterium atoms. Airborne tritium is incorporated in water molecules and in that way it enters the hydrological cycle. The occurrence of natural tritium in precipitation might be potentially used to date young (up to several decades) groundwater basing on decrease of tritium activities due to radioactive decay. Such an obvious dating application is for the time being practically obstructed by presence of anthropogenic tritium released by nuclear weapons testing in the atmosphere that began in 1952 and reached its peak in 1963. There are also other minor artificial (nuclear reactors, luminescent paints) and natural (granitic rocks) tritium sources that additionally interfere with the natural levels of tritium in precipitation at local or regional scales.

Present-day applications of tritium in characterization of groundwater systems are related to the direct and indirect estimation of groundwater ages. First of all, lack of detectable tritium in groundwater shows that it does not contain “modern” components, i.e. it is derived exclusively from infiltration that occurred before commencement of nuclear weapons testing in 1952. On the other hand, the detectable occurrence of tritium does not exclude contribution of older infiltration as mixing between tritium-free pre-bomb and recently recharged tritium-containing groundwaters might produce arbitrary low tritium concentrations. This straightforward application of tritium is useful in assessments of vulnerability to anthropogenic pollution. A single measurement showing lack of tritium in points of discharge indicates that groundwater is not vulnerable to recent pollution. In springs and other groundwater dependent ecosystems proportions between the old and recent components may differ at wet and dry seasons and tritium concentrations should be checked at different times accordingly.

Time series of measurable tritium concentrations spanning at least several years are used for groundwater dating. In this approach the distinct peak of bomb tritium in precipitation that occurred in the 1950-60’s is traced through the groundwater system and its delay, dispersion and mixing with tritium-free water is mathematically modelled by use of lumped parameter (box) models (Zuber and Małoszewski, 2001) that provide synthetic characterization of the flow system through residence time distribution. Application of these dating methods requires knowledge of time series of tritium in infiltration (tritium input function) which can be constructed (Zuber and Małoszewski, 2001) on the basis of GNIP records of tritium activity in precipitation (http://iaea.org). This version of tritium dating method is, due to the radioactive decay of bomb tritium, approaching its expiration date and nowadays cannot be already applied to the youngest (ages up to around one tritium half-life) waters.

The tritium method can be in some cases replaced by the tritium-helium method that bases on simultaneous observations of tritium and its non-radioactive decay product ^{3}He. Because the $^{3}H/^{3}He$ ratio is insensitive to the initial content of tritium in groundwater this method overcomes many limitations of the tritium method and can be applied for the youngest waters. On the other hand this method has its own limitations and its application is expensive. It is practically inapplicable to waters older than 40 years and in shallow groundwater where helium diffuses to the atmosphere. Due to the high diffusivity of helium the tritium-helium method does not include period of percolation through the unsaturated zone and thus the transit times in this zone (Kazemi et al. 2006).

Anthropogenic gases

Similarly to tritium, atmospheric concentrations of gaseous substances of anthropogenic origin like freons, SF_6 and ^{85}Kr have revealed strong and abrupt changes in the XXth century but in contrary to tritium they have none or only minor natural sources. Time-series of the atmospheric concentrations of these tracers are well-known. Applications, like for tritium, are twofold: (i) differentiation of waters recharged before and after introduction of these gases into the atmosphere, (ii) groundwater dating based on the known input functions of tracers. Unlike tritium, these tracers equilibrate with groundwater at its table, therefore they do not represent percolation through the unsaturated zone.

Other tracers used for groundwater dating

Other environmental tracers used for dating cover wide range of water travel times (from tens to millions of years). Tracers filling the gap between young and old groundwaters (50 to 1000 years) ^{32}Si and ^{39}Ar are not widely used, mainly because of analytical difficulties and complex geochemistry of ^{32}Si. Dating of very old waters (Kazemi et al., 2006) is less important from the perspective of risk assessment and vulnerability of groundwater resources though, in principle, it contributes to the overall understanding of regional flow systems.

Radiocarbon (^{14}C, halflife of 5730 years), one of the most popular environmental tracers in hydrogeology is a radioactive isotope of carbon produced in the atmosphere by cosmic radiation. Some amounts of ^{14}C were also introduced into the atmosphere by nuclear weapons testing. It is suited for dating of groundwaters in the range a thousand to tens of thousands of years. Atmospheric ^{14}C enters the global carbon cycle and is transferred to groundwaters as dissolved inorganic carbon mostly via soil respiration of CO_2. Radioactive decay of groundwater ^{14}C is basis for its dating application which however usually gives uncertain results. The ^{14}C content in infiltration is difficult to determine and in groundwater it is subject to modifications by various biogeochemical and geological processes. Even if ^{14}C does not provide absolute ages it is a useful and commonly applied qualitative tracer used to identify age inhomogeneities in aquifers and to identify admixture of modern recharge (Kalin, 2000).

^{36}Cl (halflife of 301,000 years) is a product of nuclear transformation in the atmosphere, soils and rocks and this fraction of the radionuclide is used for dating of very old groundwaters. Anthropogenic ^{36}Cl released to the atmosphere by nuclear weapons testing at maritime locations in the years 1952 – 1958 can be used in a manner similar to tritium (Phillips, 2000). Being chemically conservative and non-volatile ^{36}Cl is a good tracer of water movement through the unsaturated and saturated zones and is used to estimate recharge rates and to quantify mixing and dispersion.

Atmospheric helium (^{4}He), like other gaseous tracers, attains equilibrium concentrations at groundwater table but groundwater becomes enriched in ^{4}He from alpha decay of uranium and thorium series radionuclides. Concentration of this excess ^{4}He increases with time which is a basis of the ^{4}He dating method applicable in a wide range of ages but underground production of ^{4}He is difficult to estimate making this method highly uncertain.

2.3.3 Role of environmental tracers in conceptual models development

Applicability of particular environmental tracers depends on the nature of problems to be solved and on peculiarities of studied systems. Generic rules for tracer application are therefore difficult to formulate and tracers are not a ready-to-use tool. Proper use of tracers relies on thorough understanding of their sources, pathways and behavior in groundwater systems and, primarily, on understanding of principles of these techniques. Environmental tracers can provide critical improvements in conceptual models but on the other hand selection of the appropriate tracers and their correct application require some degree of knowledge of the inquired system. Tracer tools are from this perspective an inherent part of building and testing of conceptual models, which is an iterative process relying on qualitative and quantitative information provided by various methods, including tracers. The advantage of tracer techniques lies in their ability to provide information integrated over different scales from the mesocosm to regional flow system scale and over the corresponding temporal scales. Even a limited number of tracer analyses can provide crucial information on groundwater flow rates equivalent to results of long-term hydraulic observations. Environmental tracers are particularly important in highly heterogeneous systems where hydraulic approaches give very uncertain results due to large spatial variability of hydraulic conductivity. Tracers can provide unique information about the functioning of groundwater flow systems that are not accessible by other means.

For sustainable aquifer management, information about the rate of groundwater recharge and flux of water through an aquifer system are extremely important but are very difficult to quantify reliably. Numerical models are a standard tool to derive quantitative information about water fluxes by integrating a wide range of different data. However, even a groundwater flow model that perfectly reproduces hydraulic heads does not necessarily represent the water fluxes into and across the aquifer correctly as they also depend on the hydraulic conductivity which is often not known accurately throughout an aquifer. A relatively small uncertainly in the hydraulic conductivity (e.g. a factor of 2) might influence strongly the conclusions drawn from models for example regarding the sustainable yield of aquifer or the time required to reverse groundwater quality trends. Tracer data provide invaluable information to constrain numerical models by providing direct information about rates of water movement through aquifer systems, while data on transmissivity and hydraulic head only provide indirect information on groundwater flow rates. When dealing with questions of groundwater quantity it is usually sufficient to know the average rate of groundwater movement through a representative volume of the aquifer. When using such artificial tracers, this information can be obtained by evaluating the first moment of the tracer breakthrough curve. When using environmental tracers, flux data are implicitly taken into account by calibrating models to tracer data. It must be however underlined that tracer techniques have their limitations and sources of uncertainties which are specific for each category of tracers. Simultaneous application of several tracers supplemented by the conventional methods, like hydraulic head and chemical observations, is commonly advised as a way to overcome those difficulties.

Common in hydrogeological practice are experiments with tracers artificially introduced in groundwater systems (Leibundgut et al., 2009). Artificial tracer experiments are mostly applied to verify specific flow processes gained from general investigations of environmental tracers or hydraulic parameters. This includes for example the quantification of preferential flow, recharge under specific intitial or boundary conditions as well as mixing ratios. Tracers used in such experiments are most commonly fluorescent dyes, inorganic anions, drift particles, isotopically labelled water (with tritium or stable isotopes) and artificially produced radionuclides. Typical applications are related to estimation of water velocities and of hydraulic parameters of geological medium. In most aquifers, flow velocities will strongly deviate from the average velocity at different scales for example due to the presence of layers with a strongly varying hydraulic conductivity in alluvial systems. When considering the transport of contaminants across short distances (e.g. in the vicinity of wells), a good understanding of preferential flow paths becomes very important. Travel times estimated from the average movement of groundwater will fail to adequately characterize the risk of rapid transfer of contaminants to wells or springs. Here again, tracer tests can provide very valuable information on the presence of preferential flow paths. Important advantage of the tracer experiments is that the input of tracer to the system is controlled by the experimenter what limits uncertainty related to knowledge of the tracer input function. On the other hand the spatial and temporal scales covered by artificial tracer experiments are obviously limited. Moreover, performing tracer experiments encounters many practical problems and interpretation of their results is often difficult and limited to the boundary conditions during the time of experiment. An example of artificial tracer application in the unconfined, highly heterogeneous alluvial Zagreb aquifer performed in the GENESIS project is presented in the Annex to the Guidelines. The experiment was undertaken in order to to determine transport parameters of the aquifer, namely longitudinal and transversal dispersivities as well as effective (seepage) velocity.

To sum up, environmental tracers applied in the process of conceptual model development provide:

- understanding of how the groundwater system functions (sources and pathways of water, interactions between aquifers and with surface waters and with dependent ecosystems),
- temporal characteristics of groundwater flow and solute transport (flow and transport velocities, recharge and flow rates, renewability of resources, detection and monitoring of trends in pollution, vulnerability mapping, prediction of contaminant spreading),
- hydraulic properties of groundwater flow media (hydraulic conductivity, porosity, mixing characteristics).

Estimation of the temporal characteristics of solute transport is a particular contribution of environmental tracer techniques to the development of conceptual models. Knowledge of contaminant travel times is an indispensable element of risk assessment schemes which depend on determination of trends and prediction of future pollutant behaviour. According to the Groundwater Directive assessment of trends in pollution is a crucial element of groundwater management. Detection of trends is aided by dating of the contaminant-bearing samples of groundwater what allows to relate pollution levels with times of recharge and thus to reconstruct time-series of contamination and assess extent of non-conservative pollutant removal. Prediction of future trends in pollution also depends on groundwater dating because knowledge of time lags associated with response of groundwater systems to commencement or cessation of pollution is essential for such projections.

Finally, environmental tracers can be followed through groundwater dependent ecosystems and used to evaluate degree of their dependency and vulnerability to deterioration of groundwater quantity and quality. Application of tracers assists integration of groundwater dependent ecosystems into conceptual models of groundwater systems.

2.4 Timescales of transport: methods and applications

Timescales of solute transport are quantified on the basis of groundwater ages or residence time distributions. Transport depends on flow but characterization of flow does not suffice to describe all transport phenomena (Konikow, 2011; cf. chapter 2.2), therefore different approaches to groundwater age evaluation based on hydraulical and tracer observations might give inconsistent results. In this context, one has to be aware of fundamental differences between formulations of groundwater age (water age, advective age and tracer age). Generally, groundwater age is defined as the time span since the last contact of water with the atmosphere (Zuber et al., 2011). The mean water travel time (t_w) is defined for the whole system as the turnover time of water, i.e., the volume of mobile (advective) water in the system divided by the volumetric flow rate through the system. The advective (hydrodynamic) age t_{ad} is defined by pore water velocity (advective velocity) U which results from the Darcy velocity q divided by effective porosity n_e (cf. equation 3.8). The advective age of individual flow lines t_{ad} at any point along this line is given by following equation (e.g. Varni and Carrera 1998; Castro and Goblet 2005):

$$t_{ad} = \int_{x_0}^{x_1} \frac{dx}{U(x)} = \int_{x_0}^{x_1} n_e(x) \frac{dx}{q(x)} \tag{2.1}$$

where x_0 is the beginning of the flow line in the recharge area and x_1 is the observation point on that line. This definition also applies to entire flow systems when they can be approximated by the piston flow model.

The exit age distribution function *E(t)* represents the exit distribution of ages of water flowing through the investigated system. It can be described as the exit distribution of the normalized concentration of a conservative tracer C_I instantaneously injected at the entrance to the system:

$$E(t) = \frac{C_I(t)}{\int_0^\infty C_I(t)dt} \tag{2.2}$$

Equation (2.2) represents the exit distribution of flow lines, i.e., the distribution of advective ages when tracer is not exchanged between flow lines. For systems in the hydrodynamic steady-state, the mean value of water age (transit time) can be derived from the *E(t)* function as:

$$t_t = \int_0^\infty tE(t)dt = \frac{\int_0^\infty tC_I(t)dt}{\int_0^\infty C_I(t)dt}, \tag{2.3}$$

where the mean tracer age t_t is by definition equal to the mean water age t_w. Both mean ages are equal to the mean advective age t_{ad} regardless of the exchange between the flow lines. In the presence of stagnant water zones tracer exchange by diffusion between the advective and stagnant zones results in delay of tracer with respect to the advective flow of water. Mean tracer age t_t and mean water age t_w are in such case larger than the mean advective age t_{ad}. Mean ages t_t and t_w may differ when water molecules exchange with stagnant water differently than tracer molecules due to differences in coefficients of molecular diffusion or in case when significant fraction of micropores is not accessible for large tracer molecules.

Tracer concentrations or isotope ratios observed in groundwater discharge points or within aquifers need to be translated into mean groundwater ages or groundwater age distributions. There are two different strategies to evaluate tracer data (Kazemi et al., 2006; Zuber et al., 2011). In the first approach groundwater ages are calculated by simple mathematical equations (lumped parameter or box models) with only a few parameters (Maloszewski and Zuber, 1982). The second approach involves calibration of a numerical model so that the tracer data are reproduced. The numerical model can then be used with a higher confidence to quantify travel times through the system. The lumped parameter models used in the first approach rely on simplified conceptual models of the aquifer functioning and assume that the system is at a hydrodynamic steady state. Numerical models can be applied to transient conditions as the movement of the tracer through the subsurface is explicitly simulated.

2.4.1 Operational approaches for timescale estimation

Development of sophisticated numerical models requires extensive data sets and is time-consuming, yet their ability to reliably predict solute transport is not always granted (Konikow, 2011). Instead, valuable insights into timescales of contaminant spreading might be provided by simple operational approaches: (i) derivation of transport timescales for simple flow systems, (ii) use of timescales approach in vulnerability mapping of shallow aquifers, (iii) timescales of transport through the saturated zone.

For simple flow systems theoretical relationships between depth in the aquifer and the groundwater age can be developed. This allows predictions on conservative contaminant migration to specific points of interest in the flow system. Environmental tracers help to constrain such estimates (Cook et al., 1995; Staufer et al., 2011). An example of such approach for the unconfined, homogeneous aquifer in the low relief topography is provided by Broers and Van der Grift (2004, see Fig 2.3). This approach provides also estimates of time lags between changes in contaminant loads to the system and changes in their concentrations in particular monitoring points. Consideration of these time lags should become a routine element of measures implementing the EU directives on the protection of water resources. Stockmarr (2001) compares nitrogen fertilizer loads in Denmark with age-corrected concentrations of nitrates in groundwaters. Age dating with the CFCs allowed to adjust timescale of nitrate data to fertilization record.

Incorporation of timescales in groundwater vulnerability mapping facilitates transfer of knowledge and information to decision makers. Yet, there are only few examples of such vulnerability assessment applications, all of them developed for shallow aquifers (Duda et al., 2007, 2011; Himmelsbach et al., 2005 etc.). According to Duda et al. (2007) time lag for vertical transport of conservative contaminants from the surface to shallow aquifer can be a basis for vulnerability classification (Fig. 2.4). These time lags can be calculated either as the ratios of exchangeable water content in the unsaturated zone to recharge flux (typically natural infiltration) or from conductivity and active porosity of soil layers above saturated zone of aquifer. In the first case the time lag is practically equal to Mean Residence Time (MRT) for piston flow. The second method requires more detailed knowledge of hydraulic parameters and application of the nonlinear equations governing flow and transport in unsaturated media. Both methods rely on proper representation of the boundary conditions.

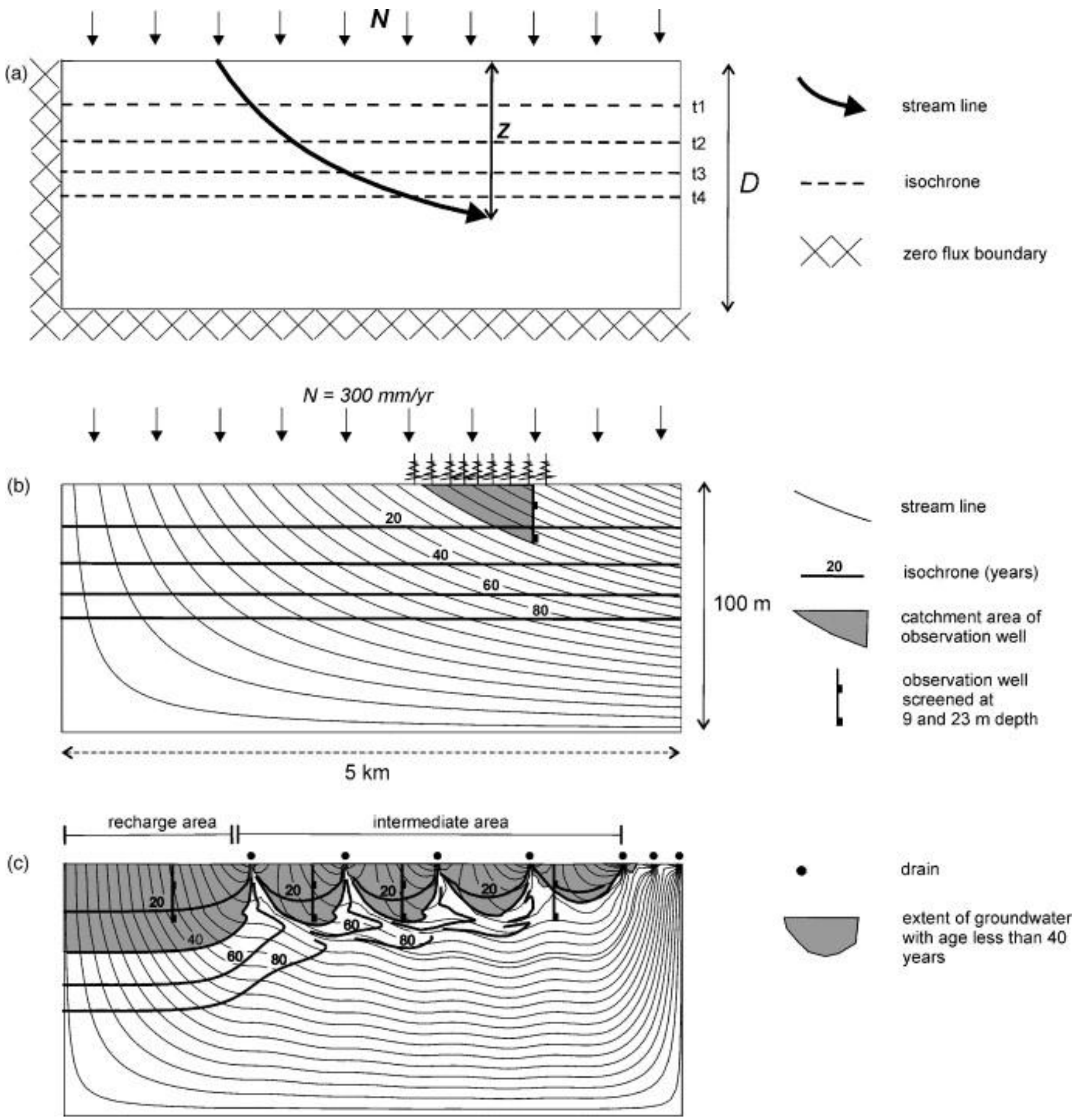


Fig. 2.3 Groundwater flow and isochrones patterns in a homogeneous unconfined aquifer with constant groundwater recharge, N. (a) elementary concept (b) concept used for the set-up of the monitoring networks, (c) hypothetical case with drainage system. Local flow systems in (c) result in distortion of the vertical pattern of isochrones and larger variations in groundwater age in the drained areas (after Broers and Van der Grift, 2004).

Class code	Color on the map	MRT estimated Mean Residence Time of water in vadose zone[b)] [years]	Groundwater vulnerability to pollution	Vulnerability characteristics [c)]
1		<5	very vulnerable	aquifer vulnerable to most water pollutants with rapid impact in many pollution scenarios
2		5 – 25	vulnerable	aquifer vulnerable to many pollutants, except those strongly absorbed or readily transformed
3		25 – 50	moderately vulnerable[d)]	aquifer vulnerable to some pollutants, but only when continuously discharged or leached
4		>50	low and very low vulnerable[d)]	aquifer only vulnerable to conservative pollutants in the long term when continuously and widely discharged or leached. Aquifer confining beds present with no significant vertical groundwater leakage

Fig. 2.4 Example of vulnerability classification for shallow aquifers based on Mean Residence Time quantification (Duda et al., 2011).

Timescales of transport through the saturated zone are an important component the above mentioned simple conceptual models. A convenient way of presenting timescales on maps and cross-sections are scaled arrows (cf. Fig. 2.5). Figures associated with the arrows reflect travel time of water over the distance corresponding to the length of the arrow. Fragment of the vulnerability map reproduced in Fig. 2.5 presents an operational method of coupling of vertical travel times through the unsaturated zone (colours) and laterally through saturated zones (arrows). The map provides estimates of time lags between introduction of contaminant and its appearance in surface water of a given catchment More accurate picture can be obtained by using numerical models (e.g. FLOWPATH) but simple operational methods like the presented above prove to be useful in water resources management practice.

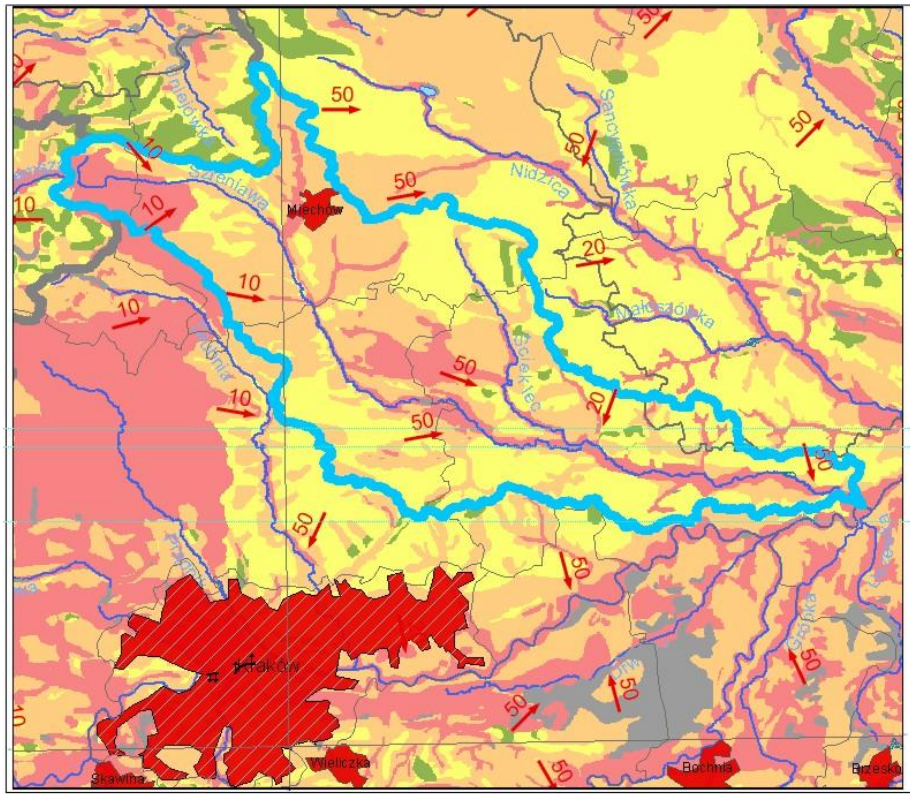


Fig. 2.5 Vulnerability map of Poland – fragment with Szreniawa river watershed marked with heavy blue line. (Witczak et al., 2011).

Half-time of contaminant attenuation

A separate issue is a dynamic response of the river system to changes in contaminant loads to catchment area. Reaction of groundwater systems to anthropogenic pressures is slow and response of the related surface waters to commencement and cessation of contaminant loads is delayed. It is particularly important for shallow, unconfined groundwater systems that are tightly linked to surface waters. In typical river catchments, the response of phreatic groundwater flow system to changes in contaminant loads has an exponential character with characteristic times of response typically measured in tens of years. Response of the Trześniówka River catchment in Poland was quantified by numerical modeling (Kania and Witczak, 2007). Half-time of contaminant removal characterizes timescale of system response (Fig. 2.6).

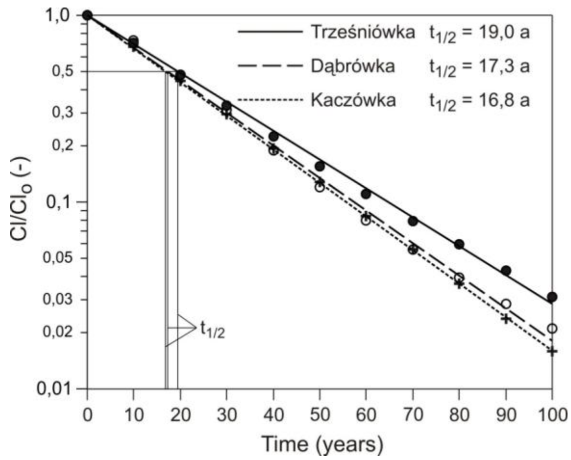


Fig. 2.6 Change of the modeled conservative contaminant concentration in three rivers after cessation of the contaminant load (Kania et al., 2006; Kania and Witczak, 2007).

Retardation factor R and attenuation factor AF for characterization of reactive solutes transport

All operational methods presented above consider that dissolved solutes (including contaminants) are transported with average velocity of groundwater. This approach applies to conservative substances but many solutes are to a different extent reactive. Sophisticated numerical models can deal with transport of reactive substances but, again simplified operational approaches can be proposed. Basic parameters for characterization of natural attenuation (NA) are: (i) retardation factor *R* and (ii) attenuation factor *AF*. The attenuation factor is a composite index taking into account processes of contaminant degradation and so-called dilution factor DF (Fig. 2.7).

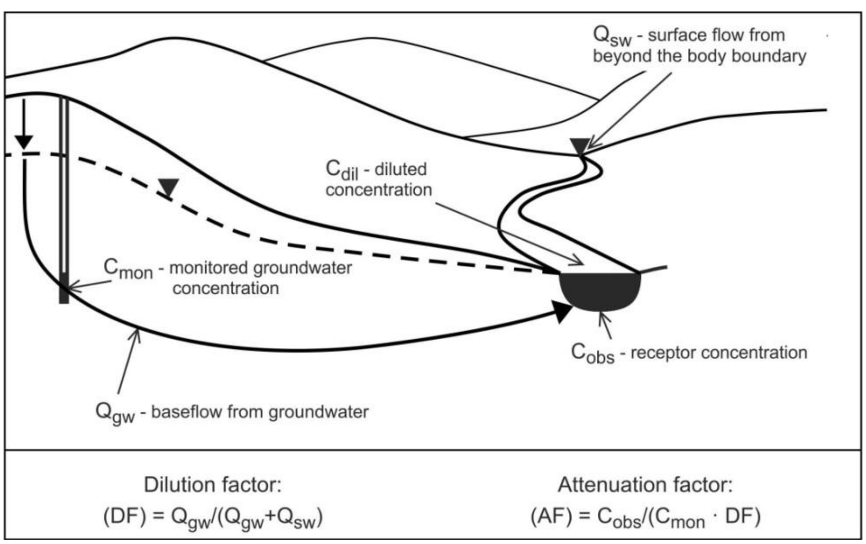


Fig. 2.7 Simplified scheme of processes occurring in the river catchment with respect to contaminant transport (Müller et al., 2006, modified).

The retardation factor *R*, multiplies travel time of water to reflect retardation of solute due to sorption and or diffusion to rock matrix. As a rule, the simplest linear sorption isotherm is used. The same concept may be applied in the case of matrix diffusion (Fig. 2.8d). In many cases of regional groundwater flow in rocks with matrix porosity solutes contained in fractures and in the porous matrix equilibrate (Zuber and Motyka, 1994, Zuber et al., 2001) and the simple linear retardation factor *R* may be applied:

$$R = \frac{n_p + n_f}{n_f}, \qquad (2.4)$$

where n_p is matrix porosity and n_f is fissure porosity.

Attenuation Factor *AF* (Fig. 2.7) reflects time necessary for naturally occurring physical, chemical and biological processes to reduce the concentrations of pollutants on their journey to the receptors. e.g. surface water ecosystems or generally GDE (Müller et al., 2006). Kinetics of typical natural attenuation processes like biodegradation can be described analogously to radioactive decay with half time ($T_{1/2}$) of decay, biodegradation or elimination of pathogenes serving as a useful parameter in simplified operational calculations.

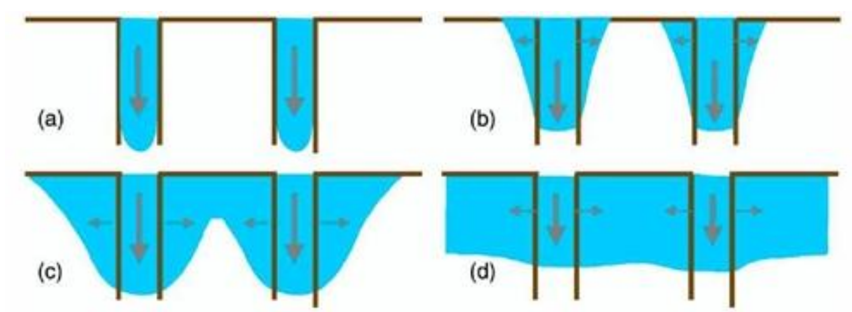


Fig. 2.8. Schematic representation of tracer movement through an infinite set of parallel, evenly spaced fractures. (a) No diffusion into the rock matrix. (b) Partial exchange between fracture and matrix concentrations, but with diffusion penetrating less than half-way between adjacent fractures. (c) Partial exchange between fracture and matrix concentrations, with diffusion penetrating more than half-way between adjacent fractures. (d) Complete equilibration of fracture and matrix concentrations (Newman et al., 2010).

2.4.2 Environmental tracers in numerical modelling

Hydrogeological numerical models have become a standard tool in management of groundwater resources and in predicting future trends in their quality and quantity. Most commonly calibration and validation (Refsgaard and Henriksen, 2004) of these models is performed only against hydraulic heads and flow rates. Pumping tests and sampling of geological media provides permeability data but their density for large scale models is usually scarce and cannot represent local heterogeneities what results in large uncertainties of model predicitions (Refsgaard et al., 2012). Performance of the numerical models can be improved by applications of environmental tracers, which provide a completely independent data set for calibration and validation (Newman et al., 2010). One has to be, however, aware of some inherent duality of the models of flow and transport (Konikow, 2011; Voss, 2011). Parameters of flow model cannot be defined on the basis of tracer data because of different physical nature of processes that control diffusion of hydraulic heads and transport of solutes. Tracer data are indispensable for calibration of transport models and, indirectly, for confirmation of the plausible conceptual models of the geological systems (Refsgaard et al., 2012) on which the numerical models were built. Another fundamental difference between the practice of flow and transport modeling is that the parameter calibrated in flow models is transmissivity while in transport models it is the ratio of hydraulic conductivity to effective porosity. Flow models can succesfuly reproduce the observed heads without paying attention to the vertical structure of hydraulic conductivity in the aquifer unless transmissivity is kept at a proper value. Flow models cannot provide velocities of water whose spatial distribution governs transport of solutes. Figure 2.9 shows that for known transmissivity and volumetric flow rate unambigous determination of flow velocity is impossible because it depends on hydraulic conductivity, aquifer thickness and on effective porosity. Under favorable conditions environmental tracers provide information on water ages, hence on the flow velocities. The knowledge of that parameter often leads to the recalibration of the flow model and/or to corrections of the conceptual model of the geological system, for example by recognition of the layered structure of the aquifer (Zuber et al., 2011; Refsgaard, 2012).

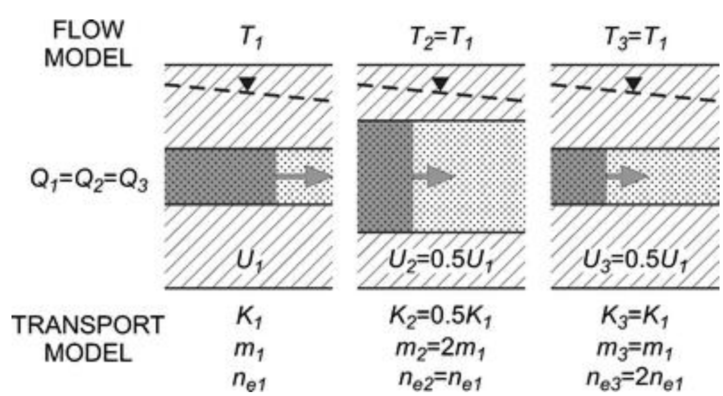


Fig. 2.9 Differences between governing parameters of flow and transport models, *T is* transmissivity and *m* is aquifer thickness.

Calibration of transport models with the aid of environmental tracers is by no means a straightforward process. Usually, several steps of such calibration are required in order to get reasonable agreement between modelled and measured concentrations of particular tracers in different parts of the studied system. Calibration and validation of transport models requires information on the migration of substances over wide range of times. Because historical data on contamination are very limited in time and space the environmental tracers that are ubiquitous components of the hydrological cycle provide the necessary information on pathways and timescales of solute transport. Transient tracers (tritium, freons, SF_6, ^{85}Kr) are well suited for calibration in time range of few tens of years. Calibration of models for older groundwaters requires application of steady-input tracers like radiocarbon, ^{39}Ar, heavy noble gases and stable isotopes of water. Calibration of numerical models with tracer data is performed by comparison of the simulated tracer concentrations with the measured values (Fig. 2.10).

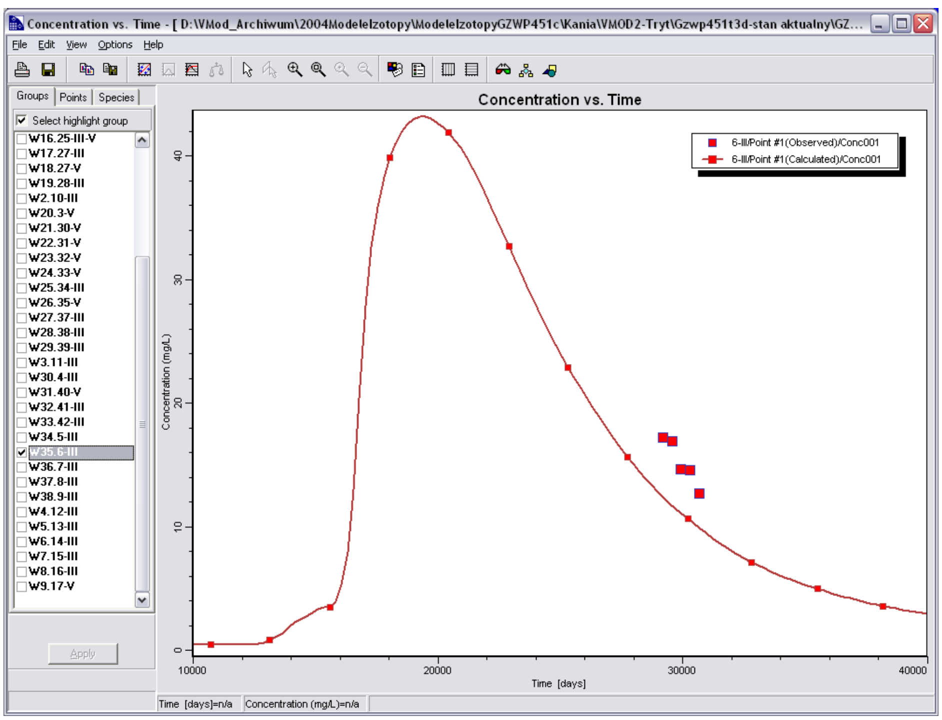


Fig. 2.10 Simulated tritium concentrations and measured values in well 6 of the Bogucice well field studied in the BRIDGE project (Kania, Witczak, 2011).

Once calibrated against tracer concentrations, the transport model can be used to generate the residence time distributions as the response of the system to the instantaneous injection of tracer.

Transit time distribution functions and their applications

A properly calibrated and validated numerical model can provide residence time distribution function (RTD) of a solute for any point of the modeled groundwater flow system (see Fig. 2.11 for an example) while the lumped parameter (box) models give RTDs only for points at which time series of environmental tracer concentrations are available. Knowledge of groundwater age distributions is a crucial factor in vulnerability assessments (Eberts et al, 2012). As shown in Fig. 2.11 the RTD functions may have complex shape due to multiple flowpaths of contaminant movement. In such cases RTD functions provide information crucial for understanding patterns of flow and transport in the system in the context of vulnerability assessments. In the case of well 7 the mean residence time is about five larger than the arrival time of the first peak of the RTD and this early peak determines risks to groundwater receptors.

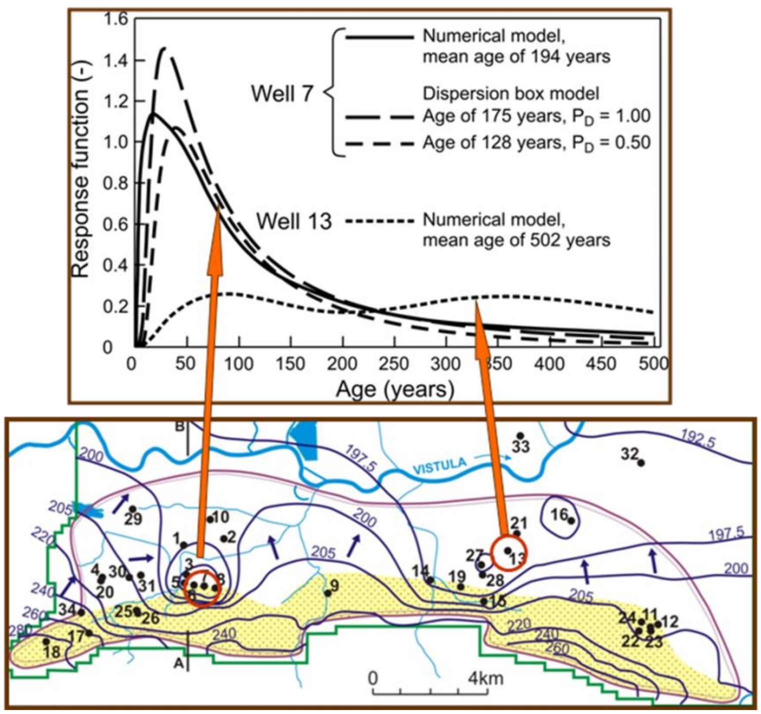


Fig. 2.11 RTD functions generated for two wells of the Bogucice aquifer (Zuber et al., 2005).

Asymmetrical and multimodal RTDs are typical for karst-fissured flow systems where time lags associated with fast channel drainage are important for assessing risks due to bacterial contamination but the mean residence time characterizes water quality changes during baseflow conditions. Asymmetrical RTDs are also characteristic for flow through the unsaturated zone (cf. chapter 3.2.1) where preferential flow phenomena are common.

Because flow and transport in the unsaturated zone depend in a non-linear manner on moisture content, intensive rainfall events may result in the RTDs resembling those influenced by preferential flow.

3 Groundwater flow-path characterisation

3.1 Infiltration - influence by land use, measurement techniques and knowledge gaps

Infiltration, the process when rain or meltwater enters into the soil, is essential for characterization of groundwater systems and flow paths; infiltration acts as a dynamic interface between the climatic forces and land-use, and the groundwater flow systems. Infiltration fluxes and their spatial and temporal variations thus set the upper boundary conditions for unsaturated zone processes, possible preferential fluxes and therefore also for the fate of pollutants - central inherent elements of risk assessment and management schemes.

Infiltration capacity (IC) or potential infiltration rate is a function of soil texture, structure, moisture, frost etc. and only when the water supply at the soil surface reaches or exceeds the IC is the infiltration rate equal to the IC (Lei et al., 2006). For most natural soil surfaces the IC is larger than the maximum precipitation intensity (including possible snow melt). In such cases the infiltration rate can simply be estimated as the precipitation intensity minus a temporary surface storage which usually evaporates directly from the soil surface (about 2 mm per event). In the simplest cases the remaining water is assumed to infiltrate fairly evenly through the soil surface. For many soils, however, preferential flow (also called macro pore flux; fingering and column flow in the field) and spatial variation in infiltration will be the rule, rather than the exception (e.g. Morales et al., 2010). The simplified approach does not work for soil surfaces with low IC such as outflow areas, solid rocks and intentionally or unintentionally sealed or compacted soils, such as housing areas and agricultural soil affected by heavy machinery. Neither does it work for areas where winter precipitation is stored as snow and released on frozen ground during spring snowmelt. It also neglects the fraction of precipitation that evaporates/sublimates directly from vegetation surfaces and never reaches the ground, and the spatial redistribution of precipitation by forest canopies, by terrain topography and wind (especially important for snow). Such processes are particularly important in steep mountain areas where climate, vegetation, soil and terrain parameters can vary greatly over short distances.

Whereas hydrological processes above the surface, evaporation, sublimation, transport and precipitation, determine the temporal and spatial distribution of precipitation available for infiltration at the ground surface, infiltration properties and topology of the ground surface are crucial for the relationship between infiltration, surface storage and runoff of water.

Influence of land use and snow and ground frost on infiltration

In the following influence of land use and terrain types infiltration are discussed. Particular attention is given to spatial distribution (SD) and areas covered by snow, seasonal frost and forests or agricultural land in rough terrain. Commerce, services, and residential areas with large fraction of sealed surfaces cover about 10% of the EU land area (Eurostat, 2009) and Fig. 3.1 illustrates how large fractions of a city that can be sealed to different degrees.

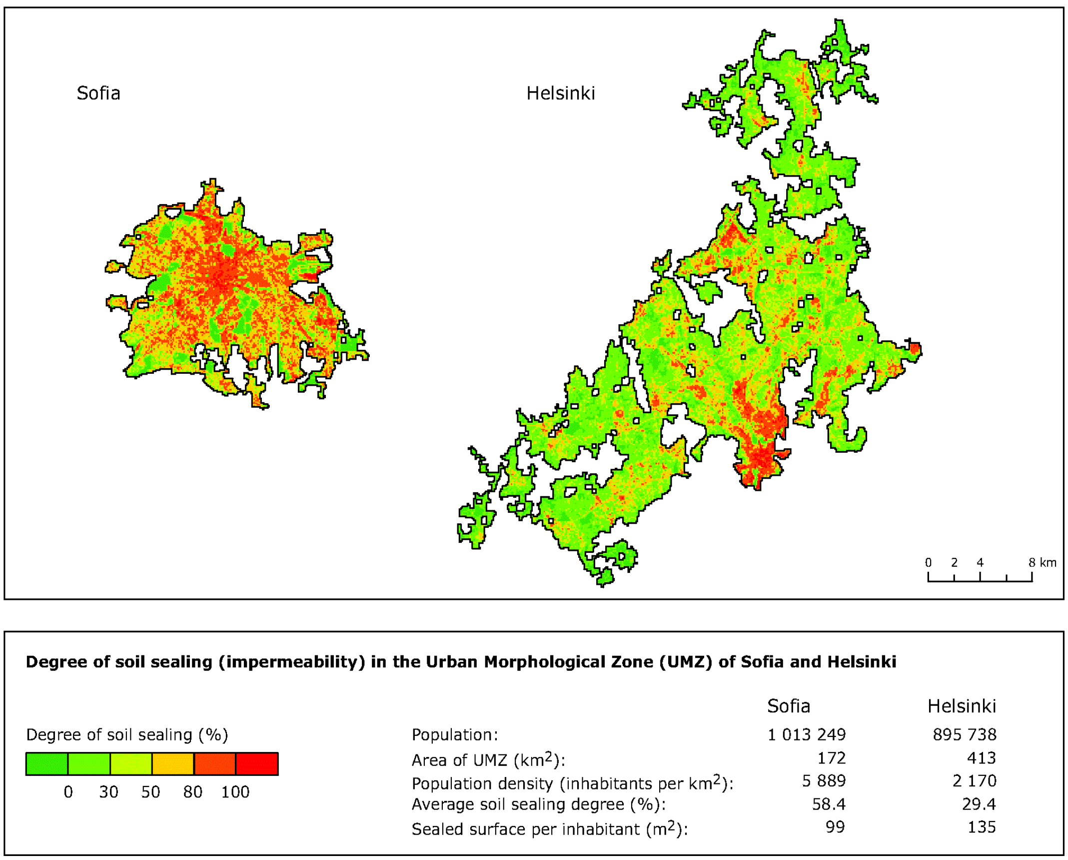


Fig. 3.1 Degree of soil sealing for the two cities Sofia and Helsinki. [From European Environmental Agency, web: www.eea.europa.eu].

Several studies have confirmed that forestry (see Fig. 3.2) and agriculture, due to soil compaction and the large areas they cover (around 40% each of the EU land area; Eurostat, 2009) are responsible for most of the human reduction of natural soil infiltrability (Van den Akker and Canarache, 2001).

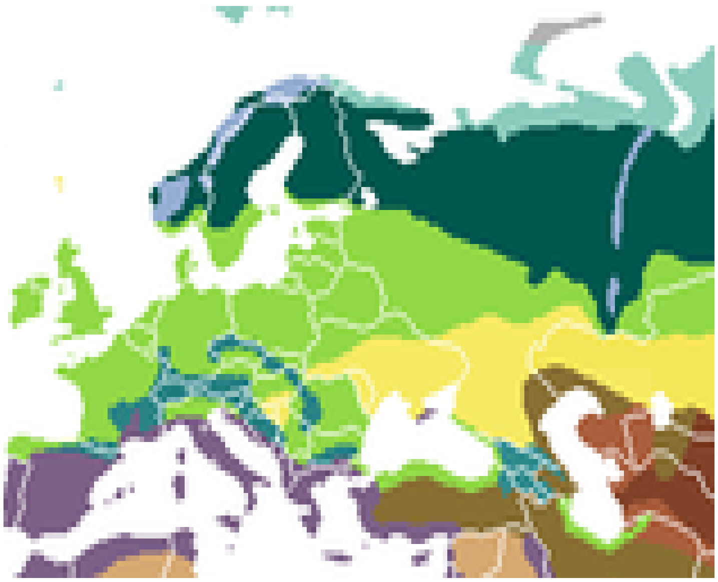


Fig. 3.2 Extent of forests in Europe. Modified from http://commons.wikimedia.org/wiki/Commons:GNU_Free_Documentation_License_81.2 GNU Free Documentation License,

- Taiga
- Temperate broadleaf forest
- Subtropical rainforest
- Mediterranean vegetation
- Tree savanna
- Subtropcial dry forest
- Mountain forest

Snow and seasonal ground frost greatly affects the hydrology in Northern Europe (Fig. 3.3) and meltwater from snowmelt in spring can dominate annual infiltration and recharge of groundwater.

In forests part of the precipitation is intercepted by the canopy and evaporates directly from stems and branches. The remaining fraction is partitioned into throughfall and stemflow that reach the ground concentrated around tree trunks and tree crown perimeters (Lundberg, 1996).

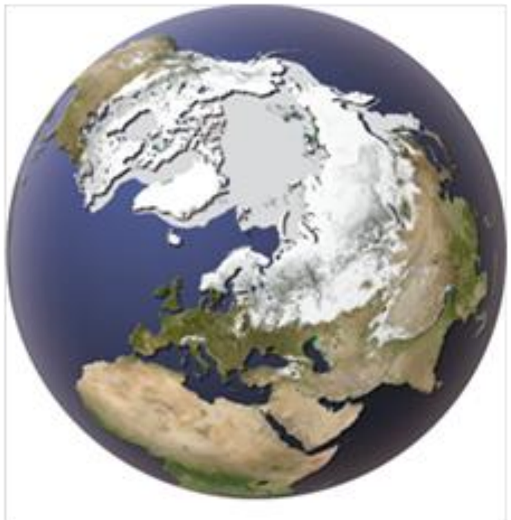


Fig. 3.3 Extent of snow and ice covers in March for the northern hemisphere. http://maps.grida.no/go/graphic/cryosphere-winter-seasons-northern-and-southern-hemispheres.

Snow deposition and redistribution is heavily influenced by wind. Terrain parameters interact with wind patterns and create areas with enhanced and reduced snow accumulation, especially pronounced in mountain regions (Fig. 3.4 a and b) (e.g. Dadic *et al.*, 2010).

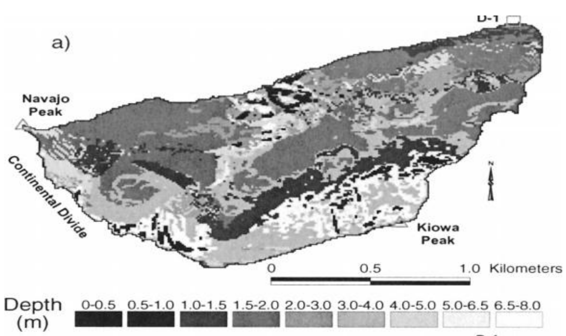


Fig. 3.4a) Modeled mountain snow depths (from Winstral et al., 2002).

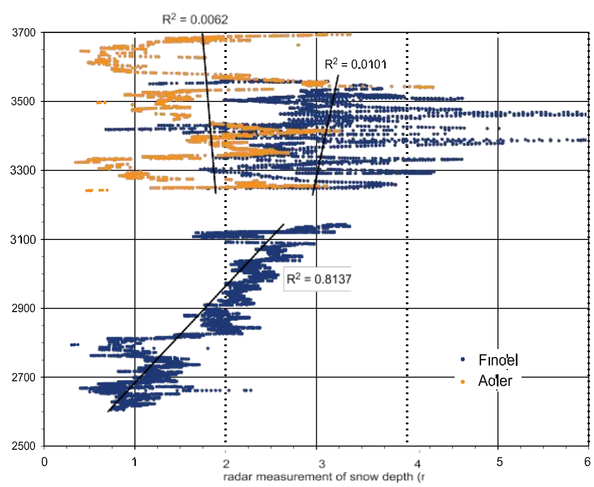


Fig 3.4b) Measured snow depth versus altitude for two Glaciers. (From Macguth et al. 2006)

Effects of wind on snow accumulation can also be observed on much smaller scales such as at wind and lee sides of forest edges (See Fig. 3.5) and forest clearings (Pomeroy and Gray, 1995).

Prevailing wind direction

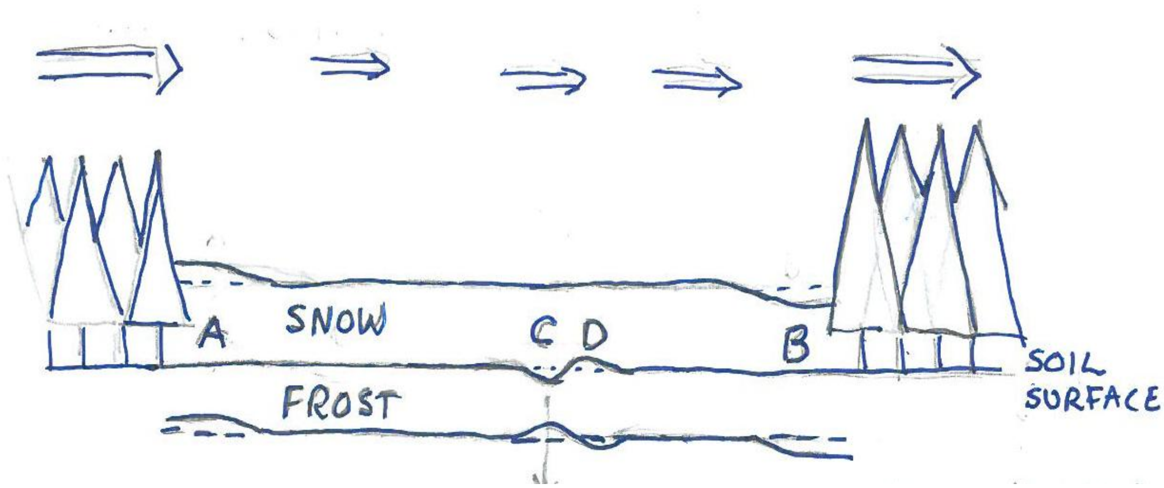
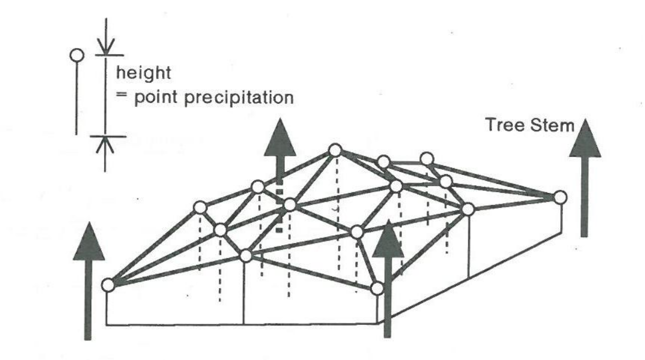


Fig. 3.5 Expected snow and frost depth patterns for a field surrounded by forests.

Forest canopy also redistributes precipitation; e.g. can snow water equivalent (SWE, equivalent water height the snowpack will correspond to when melted) be more than twice as large in the gap between coniferous trees compared to under the tree crowns (Nakai, 1996). Depending on canopy structure the precipitation might be concentrated as stemflow or to the outskirts of the tree crowns (See Fig 3.6).



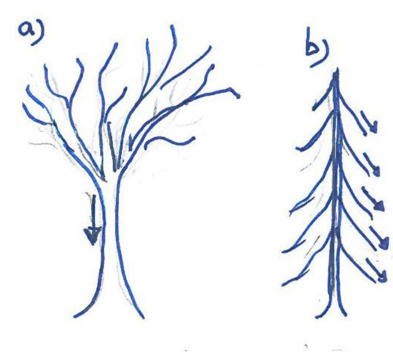


Fig 3.6a) Illustration of SWE concentration to center of gap between tree stems in a coniferous forest plantation (From Nakai 1996).

Fig 3.6b) Tree canopy structures favoring a) stem flow and b) redistribution of snow towards outskirts of branches.

A snow surface is typically more even than a soil surface; therefore snow depth will be larger and frost depth shallower over soil depressions (frost depth is inversely correlated to snow depth if other parameters are constant) (See Fig 3.5).

In tundra type climates snow will be lost during snow drift and for arctic environments 10 to 50 % of seasonal snowfall is lost by sublimation of blowing snow, but this loss can be reduced by leaving fallow or stubble on agricultural land, reducing snow drift and sublimation (Pomeroy and Gray, 1995).

The IC of frozen soil depends on the type of frost (Table 3.1) and decreases dramatically with the ice content of the soil. Soil water freezes first in the largest pores and once these are blocked the flow paths tortuosity increases radically causing severe reduction of the IC, but unless the soil is extremely wet when it freezes, macropores remain open for infiltration also after freezing (Flercinger *et al.*, 2005). Repeated freeze – thaw cycles usually can reduce soil hydraulic conductivity and infiltrability even more.

Table 3.1 Frost types with IC (Summary based on Flercinger *et al.*, 2005).

Frost type	**Typical occurrence in…**	**IC**
Granular	woodland soils containing organic matter	High
Honeycomb	highly aggregated organic soils with loose porous structure	High
Stalactite	bare soil, saturated at the surface	Low
Concrete	bare, fine-textured, agricultural soils with significant upward water migration	Low*

*Depend on water content but may be almost impermeable

In natural forests IC is high and this in combination with redistribution of the precipitation favors preferential flow around swelling and shrinking roots, with the potential of rapid bypass of nutrients and pollutants. Observations of soil water dynamics after rainfall on a forested hillslope confirmed that concentrated stemflow quickly reached deeper soil layers *(*Liang *et al., 2009)*. However forest IC might be reduced by compaction from heavy forest machinery (Schüler, 2006).

Agricultural practices employed in most of Europe depend heavily on wheeled tractors exerting repeated mechanical stress on the soils resulting in reduced IC and so does also stock trampling (Alaoui *et al.,* 2011). SD of agricultural soil IC is quite well researched, while temporal changes are not (Hu *et al.,* 2009). Due to the low IC, frozen soils retain snowmelt water and allow it to infiltrate after thawing. Several studies show the importance of depression focused infiltration in areas with seasonally soil frost (see Fig. 3.7), which in some areas are believed to be a major source of groundwater (Hayashi *et al.*, 2003; Berthold *et al.*, 2004). Focused infiltration may cause preferential flow processes, and rapid bypass of water and potential contaminants through unsaturated layers.

Fig 3.7 Depression with meltwater on seasonally frozen ground that result in focused recharge in spring. Grue, southeastern Norway. Photo: Geir Tveiti, Bioforsk.

For urban areas sealing of roofs, streets, pavement etc. and unintended reduction of IC during construction work favors stormwater formation diverted to sewage treatment plants and/or directly to recipients. There are several studies on how to reduce urban flooding (and mitigate pollution) and thus indirectly increasing infiltration using e.g. semipermeable pavements, grassed swales and retention ponds (Damodaram *et al.*, 2010; Yang and Li, 2010).

However the IC of such surfaces tends to decrease with age due to accumulations of dust, foliage, oil, etc. Gregory et al. (2006) report reduction in IC rates with between 70 and 99% due to inadvertent soil compaction during urban lot construction work.

In areas with snow, polluted snow is typically transported from city centers to snow deposits or to recipient while less polluted snow is deposited in parks etc. within the cities. During snowmelt large runoff volumes often coincide with frozen ground and frozen water pipes (Oberts, 2003) but Diertz (2007) claims that pervious pavements remain permeable also with frost in the ground. Infra-structure also contributes to soil sealing primarily with asphalt and concrete (Van den Akker and Canarache, 2001).

In humid areas aquifers normally exfiltrate into water bodies while in arid regions water bodies (fed from e.g. cooler and wetter highlands) might lose water to aquifers. Regulated water bodies might due to regulation change from gaining to loosing water and *vice versa* within hours causing complicated pattern of in- and exfiltration (Kløve *et al.,* 2011). Quick alterations in air pressure, tides and wind directions along sea coasts might cause similar swift changes in sea level with alternating patterns of aquifer infiltration and exfiltration in coastal areas (Ekdal *et al.,* 2011; Schulz and Ruppel, 2002).

Measurement techniques

Most of the hydrometric infiltration measurement methods deal with determining IC (tension disks and pressure ring infiltrometers) while techniques to measure actual infiltration rates seems more rare. Infiltration rates can be computed as the difference between rainfall and surface runoff from well-defined plots when constant artificial rainfall is applied at a rate high enough to produce saturation from above (Dingman, 2002). Rain simulators/sprinklers have been used for such measurements, and portable devices have also been developed for field use Yuan et al. (1999). Infiltration rates may also be estimated from measurements of increase in water content at various soil depths during a natural or artificial water input event. Infiltration processes and measurements of infiltration under unfrozen conditions are described in detail in several textbooks, e. g. Dingman (2002) and papers e. g. Angulo-Jaramillo et al. (2000).

Measurement techniques for land surface/atmosphere exchange processes in high-latitudes landscapes are reviewed by Lundberg and Halldin (2001) and they conclude that ssnowfall measurements are very complicated in windy and cold environments since snow then blow past the gauges. Different types of wind shields and correction coefficients (functions of wind speed and air temperatures) have been developed to compensate for this (Yang et al., 1998; 2001) but it is still impossible to truly measure snow precipitation at very wind exposed sites (Liston and Sturm, 2002).

Ground penetration radar (also known as georadar) has been used for a variety of applications in snow and soil research and they come in many different designs (e.g. systems with different antenna frequencies). They can be operated from vehicles, such as, helicopters, airplanes or snow mobiles and can thereby cover large lateral distances in short times, or they can be mounted stationary and then monitor temporal changes (Lundberg et al., 2010). Spatial distribution in snow depths are recorded by Machguth *et al.* (2006), in SWE by Gustafsson (2006), in depths to thawing front by Wollschläger et al. (2010) and in depths to the water table by Arcone (1998). Temporal variations in snow-pack layering are reported by Heilig et al. (2009) and in shallow soil moisture content by Minet et al. (2011). Analysis of radar measurements can however be complicated and require a skilled operator. Terrestrial laser scanning also known as LIDAR techniques can give spatially detailed altitude information and have been used to identify depressions with focused infiltration in areas with seasonal frost as exemplified at the Grue research site (www.thegenesisproject.eu). Snow depth SD can be retrieved if the technique is applied on both bare and snow covered soil (Prokop et al., 2008).

Environmental as well as artificial tracers have been used to estimate flow pathways in snow packs and soil infiltration. Bründl et al. (1999) used dye to show that meltwater drip from trees seep more or less vertically through the snowpack to the soil but that water from different melt events follow different preferential flow channel. Conservative tracers (bromide) have often used to track infiltration path ways (French et al., 2002; Berthold et al., 2004; French and Binley, 2004).

The stable environmental isotopes ^{18}O and D are particularly suited for providing information about meltwater infiltration in areas with frost and seasonal snow cover due to the normally low δ-values in snowfall and meltwater compared to groundwater and annual mean of precipitation (Rodhe, 1998), and these isotopes have been used in several studies of snowmelt infiltration processes and assessments of degree of preferential flow processes in soils in spring (Buttle and Sami, 1990; Bengtsson et al., 1991; Murray and Buttle, 2005). When snow reaches tree branches or the ground, the initial isotope signal will be modified by rain, condensation, sublimation, partial melting and percolation of meltwater. Meltwater isotopic signatures are therefore influenced by the presence of forests and Koeniniger *et al.* (2008) showed that heavy isotopes in the snow pack were progressively enriched as canopy stand density increased. An enrichment in ^{18}O of meltwater can arise during percolation through the snow cover (Gibson et al., 2005). To obtain useful δ-values in studies of snowmelt infiltration and recharge, melt water should therefore be collected and analysed for water isotopic composition (Cooper, 1998; Rodhe, 1998).

Electrical resistivity measurements can complement tracer experiments with SD data regarding the infiltration (Berthold et al., 2004; French and Binley, 2004; French et al., 2002) and time domain reflectometry (TDR) measurements with in situ information regarding the temporal changes (Stähli et al. 1996; Oberdörster et al., 2010) and impedance tomography for a 3D picture of the infiltration process (Gutiérrez Gnecchi et al., 2010).

Several numerical models that include forest, snow and soil frost processes such as e.g. the 1-D model COUP exists (Jansson and Karlberg, 2012). Two more recent 3D snow models are presented by Essery and Pomeroy (2004) and Lehning et al. (2006) where the first model is designed for gently sloping terrain while the latter works also for steep terrain. When over 30 snowpack models, including forest processes were assessed it was found hard to model SWE and snow depths in forests and no universal ''best'' model could be appointed (Essery et al., 2009). One of largest differences between models was linked to how precipitation phase was determined and a recent study indicates possible ways to tackle this (Feiccabrino et al., 2011). Even if there are numerical models that simulate precipitation redistribution, stemflow concentration is usually disregarded (Liang et al., 2009).

Conclusions

Precipitation gauge measured snow has to be corrected for measurement errors, redistribution and sublimation before used as input for groundwater models. Redistribution causes spatially distributed infiltration; snow accumulation in steep and windy terrain is extremely uneven, net precipitation in forests is concentrated to tree trunks and crown perimeters and on agricultural frozen ground to depressions; all processes favoring preferential flow. Forestry and agriculture practice tend to compact soils reducing the infiltration capacity (IC). Conservative and natural tracers (^{18}O and D) are suitable for flow path characterization in areas with frost provided that melt water isotopic signatures are determined for the natural tracers. Ground penetration radar, electrical conductivity, and terrestrial laser techniques can provide spatial distributed data relevant for flow path characterization (terrain topography, snow depth, depth to thawing front and to groundwater table, soil water content and actual flow paths). Knowledge regarding temporal changes in IC and reductions in IC during construction works seems limited as well as knowledge regarding the actual fraction of preferential flux for different types of surfaces. Infiltration and flow through the unsaturated zone are closely connected parts of one flow continuum. Therefore, concepts and methods presented in this and the next chapter are supplementary.

3.2 Subsurface flow characterisation

Groundwater flow is an essential component of the complex freshwater hydrological cycle. Soils and geological formations act as media for the transmission and storage of water in the subsurface where water constantly moves in the interconnected spaces of the porous media from regions of higher hydraulic heads to regions of lower hydraulic heads. Flow velocities of the water in the underground depend on hydrogeological properties (permeability) of the subsurface material, amount and distribution of water in the system (moisture content, hydraulic gradient). However, compared to surface water systems, groundwater flow is usually slow. Spatial distributions of permeability are commonly heterogeneous and anisotropic what causes complex and difficult to describe flow path networks. Within the hydraulic cycle groundwater flow occurs across a wide range of distances and time scales until it returns to the surface by action of natural flow, vegetation, or human intervention.

In the subsurface water flow occurs in two zones: the unsaturated and saturated zone. Generally, the unsaturated zone evolves below the land surface and above the groundwater table where voids contain both water and air (water content is less than saturated). The unsaturated zone serves as a transitional reservoir which discharges water in excess to the saturated zone. Below the water table, in the saturated zone, all interconnected spaces are filled with water under hydrostatic pressure.

Natural groundwater recharge and discharge processes are related to climate, landform, geology, and biotic factors (hydrogeological environment). In humid temperate regions groundwater recharge is predominated by direct infiltration of precipitation; whereas, focused groundwater recharge (surface-groundwater interactions) is more prominent in arid regions (De Vries and Simmers, 2002). Groundwater discharge occurs when water seeps from the saturated zone into surface water ocurrences like springs, streams, rivers, lakes, and wetlands. In areas with a shallow water table, groundwater may be transferred to the atmosphere due to evaporation or uptake and transpiration by plants. Therefore, the amount of water in the unsaturated zone (moisture content) is highly sensitive to climatic and biotic factors. In particular, in the last decades the attenuation of groundwater resources due to evapotranspiration by crops has continued to reach alarming levels in arid and semi-arid regions (Rengasamy 2006). This process causes not only a reduction of available groundwater resources but also the accumulation of salt and a degradation of the soil.

Groundwater can cover long distances and often remain in the underground for a long time; thus, groundwater systems act as a buffer, ensuring a continuous base flow into surface systems and therefore, delivering water for groundwater-dependent limnic and terrestrial ecosystems. Consequentially, a decrease in groundwater availability or the deterioration of groundwater quality has direct implication on these ecosystems (Kampa and Hansen 2004). [An introduction to groundwater-dependent ecosystems is given in chapter 3.3 of these Guidelines and is to be found in literature: Newbold and Mountford, 1997; Hatton and Evans, 1998; Murray et al., 2003; Baba et al., 2006; Smith et al., 2006; Eamus et al., 2006; Colvin et al., 2007; Younger, 2007; Kløve et al., 2011]. In this context, the comprehensive understanding of flow and transport processes through the unsaturated and saturated zone is vital to evaluate impacts and threats such as climate change, over-exploitation (intensive groundwater use), and pollution to groundwater and groundwater-dependent ecosystems. This chapter presents the basic concepts of water flow and solute transport in the subsurface. It provides governing equations and relevant parameters, gives a brief overview of measurement and observation methods, and introduces numerical solutions and interpretations for real world situations.

3.2.1 Unsaturated zone

The unsaturated zone encompasses a broad (including soil and rock) zone between the surface and the groundwater table that is variable saturated over time and space. Water infiltrates into the subsurface and percolates through the unsaturated zone. Water in excess to the soil-water deficit (i.e. the storage capacity) and evapotranspiration reaches the groundwater table and contributes to diffuse groundwater recharge, which is also called direct groundwater recharge. Information about flow patterns in the unsaturated zone and the quantity of groundwater recharge is indispensable for efficient and sustainable use of groundwater resources (e.g., drinking water, irrigation) and critical for the assessment of contaminant transport and health of groundwater dependent ecosystems. Details of conceptual models and techniques to estimate groundwater recharge (e.g., water balance methods, direct measurements, tracer techniques, numerical modelling, flux methods, groundwater table fluctuation method) are given in Scanlon et al. (2002) and Healy and Scanlon (2010). Basic concepts and methods used to characterize pathways and timescales of flow and transport through the unsaturated zone are presented below.

Flow and transport processes in the unsaturated zone

Water flow through the unsaturated zone is governed by gravity and matrix forces of porous media (Hillel, 1998; Jury et al., 1991) and is mainly in vertical directions; lateral flow components get important in strongly layered systems with anisotropic hydraulic properties or in fractured systems according to the fracture orientation. Still, even vertical flow and transport is characterised by strongly variable, non-equilibrium conditions. The transient nature of flow in the unsaturated zone as well as the spatial heterogeneity of physical and geochemical properties makes it difficult to characterise water flow and transport in the unsaturated zone. Common methods to determine water flow gradients in the unsaturated zone rely on point measurements (like TDR-probes for water content and suction cups for soil potential measurements) only giving point information. High resolution measurements are required to cover spatial and temporal heterogeneities (Stumpp and Hendry, 2012) which is often not feasible. This in turn emphasizes the need of appropriate artificial or environmental tracers gaining integrative information about flow and transport processes at the scale of interest. Combined with other experimental techniques as well as modelling, tracers are a perfect tool to investigate qualitatively (flow paths, heterogeneity) and quantitatively (transit time distributions, dispersivities, recharge rates) flow and transport in the subsurface.

For homogeneous flow conditions in the unsaturated zone, variably-saturated water flow is described by the Richards equation:

$$\frac{\partial \theta}{\partial t} = -\frac{\partial q}{\partial z} = \frac{\partial}{\partial z}\left[K(h)\frac{\partial h}{\partial z} + K(h)\right] - S \tag{3.1}$$

where z is the depth below the soil surface (positive upward) [L], q is the water flux [L T^{-1}], t is time [T], *S* is a sink term representing root water uptake [T^{-1}], and K(h) is the soil hydraulic conductivity [L T^{-1}], which is a function of the pressure head h [L] and the volumetric water content θ [-]. The water retention characteristic $\theta(h)$ and the hydraulic conductivity function K(h) can be described by several empirical relationships (Brooks and Corey, 1964; Durner, 1994; Konsugi, 1996; Priesack and Durner, 2006) as e.g. suggested by van Genuchten (1980) and Mualem (1976):

$$\theta(h) = \begin{cases} \theta_r + \dfrac{\theta_s - \theta_r}{\left[1 + |\alpha \cdot h|^n\right]^m} & h < 0 \\ \theta_s & h \geq 0 \end{cases} \tag{3.2}$$

$$K(h) = K_s \frac{[1-(\alpha \cdot h)^{n-1} \cdot [1+(\alpha \cdot h)^n]^{-m}]^2}{[1+(\alpha \cdot h)^n]^{\frac{m}{2}}} \tag{3.3}$$

where θ_s [-] and θ_r [-] are the saturated and residual water contents, respectively, α [L^{-1}], n [-], and m (=1-1/n) [-] are empirical parameters defining the shape of the retention curves, and K_s is the saturated hydraulic conductivity [L T^{-1}]. Water retention characteristics and saturated hydraulic conductivities are specific for different sediment and vary according to the pore/grain size distribution of the sediments. These functions can be determined in laboratory experiments, from in-situ measurements of water contents and suctions or are estimated from pedotransfer functions (e.g. Vereecken et al., 2010; Wösten et al., 2001; Shein and Arkhangel'skaya 2006, Pachepsky and Rawls 2004).

Provided transient water fluxes are known from the Richards equation, solute (conservative tracer) transport is described using the advection-dispersion equation assuming a single porous medium (all water considered to be mobile):

$$\frac{\partial(\theta C)}{\partial t} = \frac{\partial}{\partial z}\left(\theta D \frac{\partial C}{\partial z}\right) - \frac{\partial(qC)}{\partial z} - SC \tag{3.4}$$

where C [M L^{-3}] is the tracer concentration, D is the dispersion coefficient [L^2 T^{-1}], and *S* is a root water uptake [T^{-1}]. Note that the last term accounts for the passive root solute uptake. For one-dimensional transport, D is defined according to Bear (1972):

$$D = \frac{\lambda_L q}{\theta} + D_w \tau_w \tag{3.5}$$

where λ_L is the longitudinal dispersivity [L], D_w is the molecular diffusion coefficient in free water [L^2 T^{-1}], and τ_w is the tortuosity factor [-]. Applicability of this Fickian model of solute transport, especially for highly heterogeneous media, is disputed (Konikow, 2011). However, the alternative approaches have not yet been implemented in routine applications and these new methods imply additional data requirements (Konikow, 2011).

Solutes and contaminants are transported with the water flow through the sediment matrix. In the unsaturated zone, biodegradation takes place as mean transit times are often great (weeks to months). Therefore, the unsaturated zone is an important filter and buffer protecting groundwater resources from contamination. However, these functions can be impaired by preferential flow and contaminates can leach extremely fast (<days) through fractures or preferential flow paths. Knowledge about pathways, heterogeneities, fluxes, transit times and other parameters describing transport and mixing of contaminants as well as their dynamic is required to sustainably protect and manage groundwater resources.

Scales of investigations and sampling methods

The right choice of tracer, its application, as well as the experimental setup and sampling methods strongly depend on the objectives and scale of interest. In the unsaturated zone, most powerful are applications on the plot scale (decimetres to meters) covering spatial and temporal heterogeneities. At this scale appropriate non-destructive and destructive methods are available for sampling soil water with tracers including in-situ measurements like suction cups, suction plates or lysimeters. Despite high costs, the advantages of lysimeters are the controlled and measurable boundary conditions enabling mass balance calculations for both, water and solutes (e.g. tracers). Stable isotopes of water or/and artificially applied salt were used in lysimeter experiments to determine flow heterogeneities and improve model approaches to recharge estimation (Maciejewski et al., 2006; Maloszewski et al., 2006; Schoen et al., 1999; Stumpp et al., 2007; Stumpp et al., 2009b). A wide range of possible techniques for soil water extraction is provided. Advantages and disadvantages of these methods are given by Weihermueller et al. (2007) which need to be considered for both, choosing a method and data interpretation.

Smaller (< decimetres) scales are most unlikely including the representative elementary volume. However, when studying flow and transport in relatively homogeneous media or looking at specific transport processes, many tracer experiments have been successfully performed in column experiments containing disturbed or undisturbed material in the laboratory (e.g., Ghodrati et al., 1999; Joergensen et al., 1998; Köhne et al., 2006). This experimental setup enables to study flow and transport processes such as sorption and microbial interaction under controlled and known initial and boundary conditions (Stumpp et al., 2011). Still, results from soil cores and soil columns should be taken with care and are only transferable to field conditions to some extent as for example dispersivities also depend on the investigated scale of interest (Vanderborght and Vereecken, 2007).

Larger scales (meter to kilometre) are either difficult to assess at all (deep vadose zone) or to assess in the required spatial resolution. Environmental tracer applications at larger scales, like catchment areas, give integrative signals for the entire investigation area (from infiltration to runoff) not specifically aiming in estimating unsaturated zone processes (Kendall and McDonnell, 1998; McGuire and McDonnell, 2006). Nevertheless, results from the plot scale can be upscaled to the catchment scale considering differences in soil/sediment structures and land use as well as thickness of the unsaturated zone. A summary about general upscaling methods for water flow processes and hydraulic parameters is provided by Vereecken et al. (2007).

Tracer methods in the unsaturated zone

Tracers are an important tool in recharge estimations adding information about recharge rates, velocities, transit times and transport processes in the unsaturated zone. Generally, the application of several tracers is often required to get unique information about transport processes and flow paths. Combining environmental and artificial tracers adds in understanding the system integratively and under specific initial and boundary conditions. Tracers are ideal tools to calibrate flow and transport models. However, costs and the limited access to analytical facilities, particularly for measurements of various isotopes or noble gases often restrict the use of environmental tracers.

Environmental tracers

The most common applied environmental tracers are stable isotopes of water which can be used at various scales for local and regional applications in the unsaturated zone (Abbott et al., 2000; Barnes, 1988; Robertson and Gazis, 2006; Stumpp et al., 2009a). As being part of the water molecule, stable isotopes of oxygen and hydrogen provide a tracer signal with every precipitation event over a certain space. Due to fractionation effects, stable isotopes of water have a seasonal distribution in precipitation with heavier isotopes depleted in winter and enriched in summer. Following this distribution in the soil water can give integrative information about flow and transport processes over time and with depths below ground. The seasonal distribution is attenuated due do dispersion and thus enables to study flow in systems with transit times about ≤ 5 years depending on the dispersivity of the system. In humid regions, water isotopes were used to determine transit time distribution functions in different soils according to the land use (Stumpp and Maloszewski, 2010; Stumpp et al., 2007). In arid regions, water isotopes give information about evaporation rates due to fractionation processes close to the surface. Thus, from vertical depths profiles of stable isotopes and water content measurements recharge rates can be estimated (Allison, 1982; Allison, 1983). Chloride ions are an environmental tracer used to estimate direct recharge rates in the unsaturated zone of arid or semi-arid regions (Allison and Hughes, 1978; Edmunds and Herczeg, 2000). From the chloride mass balance of the input and vadose zone, the amount of evaporation is estimated from the increase in chloride concentrations which indirectly gives information about recharge rates.

Particularly new methods for the analysis of stable isotopes in the vapour phase like Cavity Ring Down Spectroscopy will enable a broader application in the unsaturated zone avoiding in-situ and laboratory soil water extraction methods in future. Thus, water isotopes can be directly measured in soil cores (Hendry et al., 2011; Stumpp and Hendry, 2012; Wassenaar et al., 2008). However, a major challenge is the determination of the correct input function of stable isotopes which is different from time series of the stable isotope contents in precipitation. Thus, the actual infiltration signal contributing to the recharge can be different due to surface runon-runoff, fractionation processes or evapotranspiration. Adjustment of this input function and estimation of isotope ratios in the effective precipitation enable the application of water isotopes and lumped parameter modelling in the unsaturated zone to calculate transit time distribution functions (Stumpp et al., 2009c). The transit time distribution functions vary according to the land use and give information on water flow velocities and dispersivities (Stumpp et al., 2009c). Besides lumped parameter modelling also numerical modelling can be combined with water isotopes to determine water flow and solute transport parameters (Stumpp et al., 20092; Stumpp et al., 2012).

Another major challenge applying stable isotopes of water is the knowledge of isotope fractionation processes altering the isotope ratios for example in snow packs (Herrmann et al., 1981). Such knowledge would be important to take snow infiltration and surface runon-runoff processes caused by frozen soils into consideration (Stumpp et al., 2012) which is discussed in more detail in Chapter 3.1. The lack of well-defined input function applies also for other environmental tracers like tritium or gas tracers (e.g., CFC's, Helium, SF6) (Leibundgut et al., 2009).

Artificial tracers

The mass input function is known when artificial tracers are applied. Artificial tracers used in the unsaturated zone are salts, radioactive tracers, dyes (with and w/o fluorescence) and particulate tracers (e.g. colloids, bacteria, phages). In soil columns and lysimeters or having permission, also contaminants can be directly applied and used as reactive tracers; however, always in combination with conservative tracers to distinguish between solute and reactive transport.

Artificial tracers are applied over a certain time and space; however, the space is mostly restricted to punctual injections up to the plot scale due to feasibility of this application method. Further, care needs to be taken when injecting the tracer at the surface. Water needs to be spilled after injection in order to minimize tracer loss due to wind drift or interception. Artificial tracers are applied for systems with expected mean transit times ≤ 1 year. The gained information strongly depends on the initial (water content) and boundary conditions (infiltration, precipitation, evapotranspiration). Thus, results are only valid for these specific conditions and might not be representative for the system at all times (Leibundgut et al., 2009). However, it can give information about specific processes under specific initial and boundary conditions. For example, it can be studied under which boundary conditions (infiltration rates) and initial conditions (water contents) preferential flow takes place (Allaire et al., 2009). An example of a lysimeter experiment, with bromide and deuterated water used as artificial tracers to identify flow and transport processes is presented by Stumpp et al. (2009b). From the tracer breakthrough curves, the flow and transport were quantified by comparing different modelling approaches. Thus, different flow components were identified.

Most commonly used artificial tracers are salts and dyes (Flury and Wai, 2003). Only a small amount of mass is required for the application of fluorescent dyes (e.g., Uranine, Eosine) due to low detection limits and high sensitivity of simple analysis. However, it needs to be considered, that fluorescent dyes lose their fluorescence due to photolytic decay. Thus, enough water needs to be spilled after injection assuring complete infiltration, and extracted water samples have to be analysed quickly or/and stored in darkness and cold. Furthermore, use of fluorescent dyes is restricted to stable chemical conditions because both, sorption and fluorescence (spectrum and intensity) are affected by the pH value and temperature (Leibundgut et al., 2009). Further, high organic content (Kasnavia et al., 1999) or salt concentrations (Magal et al., 2008) were identified to enhance sorption of fluorescent dyes, which needs to be considered as well as the background fluorescence of the soil water.

Non-fluorescent dyes (e.g., Brilliant Blue) are a good tool to visualize flow and transport; in particularly three dimensional infiltration processes (Javaux et al., 2006; Öhrstrom et al., 2004; Sander and Gerke, 2007; Weiler and Fluhler, 2004). However, it has to be emphasized that most dye tracers undergo sorption processes and therefore transport is retarded. Using dye tracers alone only gives qualitative insight into flow and transport processes. To gain quantitative information, dye tracers have to be combined with conservative tracers not being retarded.

Heterogeneities

Tracers are of particular interest when investigating heterogeneities like structural differences in space, patchy infiltration patterns or water content distributions, preferential flow paths or immobile water as well as variable flow velocity distributions. Generally, the application of several tracers at the same time is beneficial when investigating heterogeneities; provided that tracers with different properties are chosen. For example, tracers whose particles are of different size are chosen (e.g. drift particles and solutes) to determine fractions of preferential and matrix flow (Benischke 1992; Benischke and Harum, 1992; Göbel and Goldscheider; Zviklesky and Weisbrod 2006).

Preferential flow, which is a very fast flow component bypassing the matrix, can be caused by fractures, earth worm activities, root channels or structural heterogeneities (Gerke, 2006). For visualization dye tracers are applied to the surface and soil profiles are excavated. Such investigations actually proofed and identified flow processes like fingering, preferential flow and heterogeneous flow patterns at all (e.g., Javaux et al., 2006; Öhrstrom et al., 2004).

Stable water isotopes were also used to identify and actually quantify the amount of preferential flow depending on land use (Stumpp and Maloszewski, 2010; Stumpp et al., 2007). Based on a two component flow approach considering parallel flow, water flow through preferential flow paths ($\leq$ 1 week mean transit time) and the matrix was estimated from known stable water isotope contents in precipitation and lysimeters' discharge (Stumpp and Maloszewski, 2010; Stumpp et al., 2007).

Besides preferential flow, also immobile water regions might influence water flow and solute transport (Zuber and Motyka, 1999). These zones do not actively contribute to water flow and thus, the effective mean water content is smaller than the total mean water content. Such information is gained from tracer experiments by comparing the measured mean water volume with the calculated mean volume. Further, solutes (like contaminants) can be transported into and out of immobile water regions by diffusion which increases residence times of contaminants in the unsaturated zone compared to water residence times. The amount of immobile water and its transient storage behaviour can be identified by performing tracer experiments (Brouyere, 2006; Köhne et al., 2004; Maraqa et al., 1997); however, for an explicit proof and quantification of immobile porosity multi tracer experiments need to be performed provided that tracers with different diffusion coefficients are used. Then, under steady state flow conditions breakthrough curves of a Dirac's impulse tracer injection show differences in breakthrough peaks being higher and having more pronounced tailing of the breakthrough curve for higher diffusion coefficient.

Mathematical Modelling

From temporal distribution of tracer breakthrough curves or of environmental tracer contents in sampled soil water, information about flow and transport parameters can be quantified choosing the appropriate mathematical modelling approach. Particular in the unsaturated zone due to its transient and heterogeneous nature, the choice of the model approach is often difficult and its application complex. Generally, simple lumped parameter approaches can only be applied to investigate flow and transport in the unsaturated zone under quasi steady state conditions like it was shown for bare, coarse sandy sediments (Maloszewski et al., 2006) and -in the case of environmental isotopes- requiring some modification of the input function and model application like it was shown in sandy soils with different land use (Stumpp et al., 2009a; Stumpp et al., 2009c).

Under transient or even non-equilibrium conditions numerical modelling is essential. A variety of models exist which range from models assuming homogeneous conditions to dual-porosity, dual-permeability, and multi-region type models concerning water flow (De Smedt and Wierenga, 1979; Gerke and van Genuchten, 1993; Haws et al., 2004; Jarvis et al., 1991; Zurmühl and Durner, 1996) or solute transport (Flury et al., 1999; Maciejewski et al., 1992; Nützmann et al., 2002; Šimůnek and van Genuchten, 2008). An overview about these an other approaches is given in Feyen et al. (1998) and Simunek et al. (2003). However, non-equilibrium flow and heterogeneities like preferential flow can be strongly dynamic and their mathematical description is generally difficult to determine (Jarvis et al., 2007). The most prominent programs and state of the art software are the HYDRUS-codes including a variety of these different model approaches for 1 to 3 dimensions (Simunek et al., 2008; Radcliff and Simunek, 2010). HYDRUS has been applied for modelling several applications of environmental and artificial tracer experiments to estimate flow and transport processes and parameters (Stumpp et al., 2009; Zhang et al., 2002; Vanderborgth et al., 2002; Persson et al., 2005).

3.2.2 Flow and transport through saturated zone

Groundwater percolates passageways between the interconnected spaces in the saturated zone and in this way links zones of recharge with zones of groundwater discharge. In unconfined aquifers groundwater is directly recharged at the water table which forms the upper boundary to the unsaturated zone, equal to the hydraulic head. Confined aquifers, on the other hand, evolve as the result of a sealing to the land surface or overlaying groundwater bodies where the water table is below the hydraulic head. These aquifers need to be connected to an unconfined area through which groundwater is recharged (Fetter, 2001).

Along the flow path through the saturated zone the groundwater interacts with the rock matrix influencing the movement of dissolved substances, particularly pollutants, owing to physical, chemical and biological processes. Besides hydraulic and geochemical properties of the aquifer the occurrence of these processes is strongly affected by characteristics of the substance and its influx into the system. Numerous studies of groundwater resources indicate exposure not only to local contamination sources, but also mainly to regional sources, such as the long-term application of agricultural additives. For example, near-surface groundwater in agricultural areas often shows high concentrations of substances like nitrate, sulfate or chloride (Gehrels, 2001).

Investigation methods

A sustainable management and protection of groundwater systems requires the qualitative and quantitative characterization of flow and transport parameters. Depending on the nature of the problem to be solved and aquifer properties different investigation methods and approaches are available. For example, methods such as exploratory drilling are used to determine geological and hydraulic properties of the porous media (drill core analyses, geophysical borehole logging, etc.; see Dawson and Istok, 1991; Brassington, 2007). Core drillings enable to extract samples of the sediment or rock for geochemical-mineralogical analyses or flow cell experiments. However, the limitations of these methods are mainly related to their representativity since the provided information is spatially discrete. Investigation methods such as geophysical measurements (geoelectric and seismic; see Kelly and Mares, 1993) are applied to survey the structure of geological formation and water filled porosity (water abundance) on a large-scale (meter to kilometre). The applicability of these methods is, however, limited at complex geological conditions and due to the ambiguity of geophysical interpretation.

Methods based on naturally occurring or intentionally introduced traces have found a large spectrum of application investigating spatial and temporal aspects of the saturated zone. Tracer techniques enable to quantify hydraulic properties of the porous media (**permeability** and **porosity**), determine flow and transport pattern like mean **transit time**, **dispersion** and **diffusion**, and study **physico-chemical processes** in the saturated zones. Furthermore, spatial issues such as preferential flow paths, physical parameter of the porous media or the **heterogeneous distribution of hydraulic properties** may be characterized. A large variety of tracer techniques is available as numerous tracer types, injection (artificial tracer) and sampling methods may be combined according to local conditions and investigated issues (see Chapter 2.3). [For more information, see Pearson, 1991; Clark and Fritz, 1997; Kaess, 1998; Kendall and McDonnell, 1998; Mazor, 1998; Cook and Herczeg, 2000; Geyh, 2000; and Leibundgut et al., 2009.]

In order to properly plan tracer experiments and minimize inconsistencies, the basic principle of flow and transport processes in the saturated zone must be understood clearly. The following section gives an overview about important processes, governing parameters and factors influencing groundwater flow and transport processes.

Groundwater flow in the saturated zone

Although water flow in the unsaturated and saturated zone are both governed by gravity and resulting pressure forces, groundwater flow has a three dimensional orientation where the horizontal flow component is predominant. In the saturated aquifer, groundwater moves from areas of a high hydraulic head to areas of a low hydraulic head (water pressure above geodetic datum). The properties of laminar groundwater flow can be approximated by the empirical relationship expressed in Darcy’s law:

$$Q = -kA\nabla h\,, \tag{3.6}$$

where the volumetric flow rate Q [m^3/s] of the percolating groundwater is proportional to the hydraulic conductivity k [m/s] of the porous media, the percolated area A [m^2] and the specific hydraulic gradient ∇h. The hydraulic gradient is a vector (gradient) which is defined by the decrease of the hydraulic head between two or more points over the length of the flow path:

$$\nabla h = \left(\frac{\partial h}{\partial x}, \frac{\partial h}{\partial y}, \frac{\partial h}{\partial z}\right) \tag{3.7}$$

By rearranging the Darcy equation the net flux q [m/s] may be calculated which characterizes the apparent flow velocity through the medium. In order to estimate actual groundwater velocity U [m/s] in the pores the flux is divided by the porosity n [-]:

$$q = \frac{Q}{A} = -k\nabla h\,,\ U = \frac{q}{n_{eff}} \tag{3.8}$$

Flow characteristics in a porous media are controlled by the concept of permeability which describes the ease with which the pores permit water. Thus, the spatial distribution of permeability is an important property when determining the availability of groundwater (flow rates, flow velocity) and the potential for groundwater contamination including the understanding of processes such as pollutant transport, remediation and (bio-) degradation in the saturated zone.

The hydraulic conductivity is defined by the volume of water [m^3/s] passing through a cross section of the medium under the action of a specific pressure gradient (Darcy). In this context, saturated conductivity is affected by both, properties of the porous matrix (size of pore spaces, interconnection of pores) and the percolating fluid (density, viscosity). In a homogeneous medium where the hydraulic conductivity is equal in all directions (isotropic), water flow is in the direction of the steepest hydraulic gradient. In contrast, the heterogeneous distribution of effective porosity in (unconsolidated) layered sediments may cause anisotropic (rock) permeability. Flow and transport pattern in these systems are controlled by the thickness and structure of layers. In fissured bedrocks the spatial distribution of hydraulic conductivity is determined by the orientation, aperture and spacing of fissures. Similarly, heterogeneous groundwater flow in karst systems evolves along conduits which are characterised by the orientation, volume and diameter. In order to characterize groundwater flow in heterogeneous porous media, the Darcy equation has to be solved for the 3-D space:

$$q = -\begin{bmatrix} k_{xx} & k_{xy} & k_{xz} \\ k_{yx} & k_{yy} & k_{yz} \\ k_{zx} & k_{zy} & k_{zz} \end{bmatrix} \nabla h \qquad (3.9)$$

In this context, tracer experiments have proven to be an important tool to a) examine regional flow direction of groundwater (Maloszewski et al., 2002); b) investigate hydraulic connections between important areas of recharge and discharge (e.g. in karst: swallow holes and karst outlets); c) determine borders of the catchment and capture zones (Kendal and McDonnell 1998). Fully quantitative tracer experiments result in concentration time series (breakthrough curves) and concomitant discharge data which enable to obtain detailed information about the spatial distribution of hydraulic properties of the porous media (permeability and effective porosity) and groundwater flow (e.g. flow rate and flow velocity). For example, experiments using artificial tracers help to a) investigate inaccessible parts of cave and conduit networks, and to provide information about the geometry and volume of the conduits in karst systems, (Leibundgut et al, 1997); b) to determine hydraulic properties of fissures in fault structures (Maloszewski et al., 1999); and c) to identify and characterize different flow components through layered sediments (Maloszewski et al., 2006).

More complex flow conditions develop in groundwater systems which combine two or more “porous media” with varying permeability (double or triple-porous media). Thus, in a fissured rock, groundwater slowly percolates the porous matrix (primary porosity) which is surrounded by a network of fractures (secondary porosity) of a high permeability. In karst aquifers secondary porosity is modified by dissolution. These systems show a highly heterogeneous and often turbulent groundwater flow where Darcy’s law is not applicable. [For detailed information about hydrogeological processes, see Davis and DeWiest, 1966; Freeze and Cherry, 1979; Stumm, 1992; Stumm and Morgan, 1996; Fetter, 2001; and Fitts, 2002; Bear 2007.]

Transport processes in the saturated zone

Groundwater vulnerability to contamination is best understood in relation to mean transit time (residence time) t_0 [a] which defines the amount of time a particle needs to reach the discharge source or monitoring location by percolating the subsurface. In general, a short transit time (weeks to months) indicates a high sensitivity to contamination as the natural degradation and retention potential of pollutants is low. In this context, the transit time distribution is a fundamental hydraulic characteristic describing the variability of time in which a specific fraction of pollutants may be "removed" from the system. Methods used to measure transit time distributions are generally based on qualitative tracer experiments determining the transport of solutes/suspended particles, and colloids in the saturated zone.

Conservative (non-reactive) transport of substances in the saturated zone is controlled by advection, diffusion and dispersion. Advective flow is described by the net flux of water in which the substance is dissolved:

$$j_{adv} = q \cdot c = U \cdot n_{eff} \cdot c \qquad (3.10)$$

where j_{adv} is the 3-D advective flux [kg/m²s], c the concentration and n_{eff} the effective porosity. Mass transport caused by molecular diffusion (j_{diff} [kg/m² s]) along concentration gradients is mathematically expressed by Fick's law:

$$j_{diff} = -n_{eff} \cdot D_m \cdot \nabla c \qquad (3.11)$$

In the porous media the molecular diffusion coefficient D_m [m²/s] is influenced by the tortuosity τ [m] of the media which determines the elongation of flow paths in pores compared to the transport in free water ($D=D_0/\tau$, D_0 – molecular diffusion coefficient in open water). Diffusive mass transport, however, in groundwater systems is a very slow process which predominates at low flow velocities. In strongly heterogeneous systems such as fissured or karstified rocks, flow and transport processes are often affected by a diffusive exchange of solutes between the mobile water in the fractures or conduits and (quasi-)stagnant water of the porous matrix.

Unlike molecular diffusion hydrodynamic dispersion only evolves in direction of the groundwater flow. The phenomenon of hydrodynamic dispersion strongly depends on the scale under consideration. Thus, substances spread owing to variations in the flow velocity within a given pore, and between pores (micro-scale effect). More important are large-scale effects of dispersive mass transport (m to kilometre) caused by the inhomogeneous distribution of rock permeability. Substances gradually spread in all direction around the mean flow path as groundwater flow may occur through or around regions of lower permeability or preferential flow may occur in regions of higher permeability while flow velocity in the surrounding media is low. Hydrodynamic dispersion is mathematically described by Fick's law (cf. 3.2.1 for discussion on its applicability):

$$j_{diff} = -n_{eff} \cdot D \cdot \nabla c \tag{3.12}$$

The dispersion coefficient D [m^2/s] is determined by the dispersivity α [m] and flow velocity ($D=\alpha \cdot U$). In general, hydrodynamic dispersion accounts in the direction of the main flow component which is characterized by the longitudinal dispersivity (α_L), and orthogonal to the main flow direction defined by the transversal dispersivity (α_T). Usually, the longitudinal dispersivity is 10 to 20 times higher than the transversal. At a very low flow velocity ($U \ll 0.1$ m/d) diffusive mass transport outweighs dispersion.

In some situations, dispersive and diffusive mass transport reduces pollutant concentration which may be a positive effect when the concentration fall below the value considered to be harmful. However, it also causes larger volumes of contaminated water spread over a greater area. Thus, dispersion and diffusion are important factors for determining groundwater contamination.

In the saturated zone dissolved substances may interact with the rock matrix owing to processes such as (ad-/ab-/de-)sorption, decay, and (biotic/abiotic) degradation. There are numerous factors which control the interaction of a solute with the aquifer matrix. These include physical and chemical characteristics of the substance, the interface, and the pysico-chemical composition of the fluid media encompassing both. By understanding these processes and controlling factors conclusions can be drawn about the impact on the migration of contaminants in the subsurface. Failure to take account of these processes can result in a significant under- or overestimation of the contaminant concentration at a site as well as the time required for it to migrate between two points (transit time). [For more information about transport processes in the saturated zone see Matthess et al., 1992; Stumm and Morgan, 1996; Fetter, 2001; Appelo and Postma, 2006].

Tracer experiments provide insights into transport processes that may not be gained by conventional methods (see Annex). This information generally complements data obtained from other methods. In particular, tracer techniques are well suited to investigate issues related to water quality, pollutant migration and remediation methods when contamination already exists. However, it is to some extent difficult to distinguish between diffusive mass transport in double porous media (mobile-stagnant water interaction) and dispersive transport as both processes cause a more or less pronounced tailing of tracer breakthrough which may lead to incorrect system interpretation. In particular, diffusive mass transfer between mobile and (quasi-)stagnant water in a double-porous system slows the migration of pollutants, and complicates the removal or remediation of pollutants. Thus, it is important to distinguish between diffusive and dispersive processes by applying two or more non-reactive tracers that have different diffusion coefficients (Witthüser et al., 2000).

Hydrogeologic environment

Groundwater flow pattern in the (unconfined) saturated zone are controlled by the configuration of the water table. Groundwater moves from areas of a higher hydraulic head where the water table is recharged to areas of a relative lower head where groundwater discharges by seeping through the water table. The water table represents the upper boundary between the saturated zone and adjacent compartments of the water cycle. This hydrogeologic environment significantly influences the groundwater system in many aspects. Physical and chemical conditions typically mentioned in this context result from a combination of climate, landform, and geology. For example, in areas with a steep topographic relief, groundwater recharge may be low owing to surface runoff. These groundwater systems are characterized by a less accentuated water table in the underground which leads, in turn, to flow rates and flow velocities which are less than the potential maximum. In areas with a less pronounced topography, however, groundwater recharge depends on soil properties such as infiltration capacity, permeability and soil moisture. In addition, climate and vegetation has an impact on groundwater recharge by determining precipitation and actual evapotranspiration (for more information see Chapter 3.1).

Many aspects of the recent hydrogeological environment are primarily the result of human activities including changes e.g. in landscape, vegetation/ecosystems, climate and infiltration capacity into the soil (surface sealing). Furthermore, groundwater flow pattern has been modified by direct human intervention due to irrigation, abstraction, drainage and mining (see Chapter 5; Gehrels et al., 2001; Marsalek et al., 2008).

Groundwater modelling

Groundwater flow and transport processes in the saturated zone are very complex and difficult to observe. Investigation methods provide spatially and/or temporally discrete information about the system. However, information between and beyond monitoring locations and investigation campaigns are needed to evaluate impacts and threats to groundwater systems, and therewith support informed decisions related to the protection of groundwater and groundwater-dependent ecosystems.

In this context, models of the groundwater system are a versatile tool e.g. a) to interpret observed signals such as tracer data determining properties of groundwater flow and transport, particularly to provide travel time distributions for solutes; b) to interpolate observations between monitoring locations/campaigns and to assess future system conditions by reproducing flow and transport processes; and c) to study interactions between the saturated zone and adjacent compartment such as the unsaturated zone and surface water systems including groundwater-dependent ecosystems.

Conceptual models are used to develop an understanding of the complex groundwater system by defining a working description of the prevailing processes active in the groundwater body. In order to quantify relationships between system characteristics, the conceptual model has to be transferred into a mathematic description (analytical, numerical, etc.). A large number of groundwater models, based on a variety of conceptual models and a huge number of analytical and numerical methods are available, each with their own capabilities, operational characteristics and limitations. Each groundwater project and problem under investigation has specific requirements regarding to modelling and field data available; thus, the choice of an appropriate model approach is most important. Many articles and books have been published providing various guidelines and examples, how to develop a conceptual model of the groundwater system, e.g. Spitz and Moreno, 1996; Rushton, 2003; Merkel and Planer-Friedrich, 2008; Bear and Cheng, 2010 and Haimes, 2011.

For example, mathematic models applied for the evaluation of tracer data in hydrological systems are commonly classified into three categories of different model complexity (Yurstever 1995):

1. **Lumped-parameter models** determine the mean transit time of groundwater and its distribution in the system based on a linear system analysis. Here, concentrations of tracer input and output are related by (steady state flow):

$$C_0(t) = \int_0^\infty C_i(t - t_0)h(t_0)dt_0 \tag{3.13}$$

where C_i and C_0 are input and output tracer concentration, t is the time, and t_0 the transit time. So, the observed tracer breakthrough depends on the distribution of transit time in the system. Specific transit time distribution functions in models such as piston-flow model, exponential model or dispersive model are applied to describe the system response to the time-variable input of tracers.

2. Complex natural processes are often described by **discrete state compartmental models**. Interconnected compartments (mixing cells) are used to analyse tracer data with regard to mixing and dispersion processes.

$$C_{Q_n} = C_{V_n} = \left[\frac{V_{n-1} C_{V_{n-1}} I_n C_{I_n}}{V_n + Q_n} \right]^{-\lambda \Delta t} \qquad (3.14)$$

where C is the concentration of the tracer, V is the volume of the cell, I and Q are the inflow and outflow volumes into and out of the cell during the time increment. The term $-\lambda\Delta t$ is a radioactive decay correction factor.

3. **Mass-transport models** based on advective-dispersion formulations provide a more accurate and complex description of tracer transport processes; however, data requirements for model calibration and validation increase substantially. The deterministic model approach uses a conservation of mass, momentum, and energy, and describes cause and effect relations. The conceptual approach of the prevailing processes determines the number and type of applied partial differential equations. The underlying equations are solved either by analytical or numerical algorithms.

Groundwater models are a simplification of real groundwater systems which cannot replicate the natural behaviour in all aspects. Consequentially, the understanding of flow and transport processes in the saturated zone and interactions with the hydrogeological environment is never complete which may cause some level of error and model uncertainties. In this context, a thorough description of model uncertainties is needed to weight the significance of model results used to support the decision making process in groundwater management and protection.

3.3 Surface-Groundwater interactions

3.3.1 Role of groundwater storage in surface water flow

Groundwater moves along flow paths from recharge areas to discharge areas within GDEs. Infiltration occurs when meteroric water (including retarded fractions such as snow and glaciers) enters the ground. Water then usually moves through the unsaturated zone and reaches the saturated part of the aquifer contributing to groundwater recharge. Some surface waters both receive and recharge groundwater. Groundwater recharge may include contribution from adjacent aquifers. Discharge from the aquifer occurs at springs, streams, lakes and wetlands, as transpiration by plants with roots that extend to near the water table, and by direct soil evaporation. Groundwater can also discharge to adjacent aquifers (e.g. downward leakage from an aquifer to a deeper one).

Groundwater often forms the largest freshwater storage in catchments with porous soil cover or porous rock (e.g. sandstone). Other important water storages include surface water in lakes, rivers, wetland water storage (peatlands), snow and ice. The role of storage is seen as even flow in rivers as precipitation is released slowly through the soil layers, lakes or glaciers. Even flow of water can also be caused by an even annual distribution of rainfall such as in the tropical region where the largest rivers are found. Larger catchments respond slower to rainfall than smaller catchments. Highest variation in flow is typically found in headwater systems where also difference in storages wary considerably in space depending on positions of soil layers, aquifers, wetlands, slope and time depending on distribution of rainfall.

3.3.2 Groundwater in ecosystems

The flow in ecosystems depends on how the hydrogeological system responds to rain, snow and ice melt. Sometimes also surface water storage influences the groundwater dependent ecosystem, either permanently, seasonally or only in some occasions. Bertrand et al. (2011) present a classification of ecosystem depending on the amount of groundwater they receive. The variation of flow influences also the variation of temperature, pH, nutrients that are important for ecosystems. The source of water is important too and GDEs can be completely dependent on groundwater and only partly dependent on groundwater. In river classification, extreme end-points are emerphal rivers where flow occur only occasionally and rivers with a constant flow throughout the year either due to storage-release characteristics, regulation or no seasonality in climate (Torabi Haghighi and Kløve 2012). It is likely that this classification is also useful for GDEs in general as flow regimes are important controls of ecosystem habitat and biodiversity.

In surface water systems receiving groundwater, such as streams, the contribution of groundwater can vary from large contribution in the headwater, to single point input in large surface water systems (springs in rivers and seas). The contribution of groundwater amount compared to surface water can also decrease as the river flows from headwater towards the sea and surface water mix with upstream groundwater. Groundwater interaction can be seen and conceptually understood at small and local scales (e.g. hyporheic interaction) or larger scales (loosing and gaining streams). From aquifers, groundwater can seep out on large seepage fronts (porous aquifers) or concentrated in small regions (fractured aquifers). Also the groundwater-surface water interaction can change due to anthropogenic influences related to irrigation, drainage, river regulation, artificial recharge, climate change, and sea and surface water elevation changes.

The first step to understand the groundwater flow system and its interaction with surrounding water systems and terrestrial systems is to make a conceptual model of the hydrogeological layer with the assumed flow system. The actual conceptual model for a given aquifer will vary locally depending on water use, slope, topography, climate and geology. This should also include the unsaturated zone which plays a very important role both for groundwater quantitative and qualitative aspects. Local groundwater flow is often near the surface and occurs over short distances, i.e. from a higher elevation recharge area to an adjacent discharge area such as small springs. Intermediate and regional flows usually occur at a greater depth and over greater distance. Steeper and undulating landscapes have the most local flow points (Fig. 3.8).

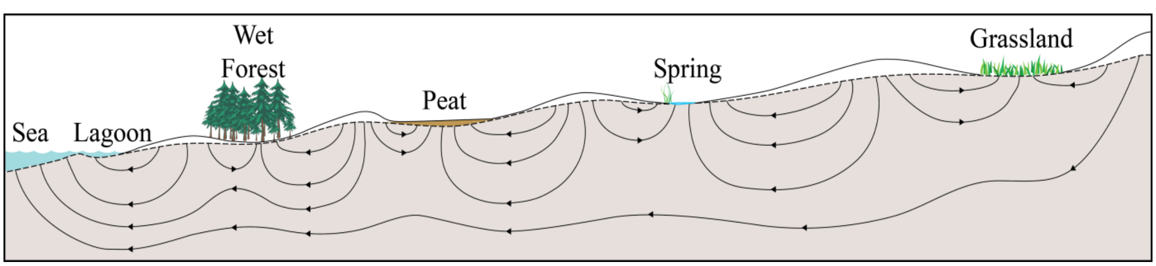


Fig 3.8 Flow lines and groundwater levels in a cross-section of soil/rock with homogeneous and isotropic hydraulic conductivity, with possible locations of GDEs (Klöve et al 2011a).

Groundwater flow is always three-dimensional, but can often be analyzed in two-dimensional sections. Analysis of these flow paths is important when studying GDEs because it can provide valuable information about potential threats to both the quantity and quality of groundwater.

3.3.3 Overview of tools addressing groundwater-surface water interactions

Before designing a measurement campaign to detect groundwater in ecosystems one must make a conceptual model of the ecosystem with all water fluxes, storages and aquifer interaction. This models must include potential points where groundwater is expected to flow into ecosystem. Groundwater typically discharges to surface water bodies where the slope of the water table changes suddenly (e.g. Winter et al., 1998). In many cases springs are found where geological layer and hydraulic conductivity change. Also, the spatial extent of groundwater outflow can range from punctual to regional. The iterative scheme of conceptual model development applies naturally to models of groundwater-surface interactions, measurements lead to a refined model of the system studied and this model needs to be updated continuously depending on the purpose of the investigation. The measurement that typically are necessary are: I) measurement of geology and geomorphology of the system including measurement of porosity, hydraulic conductivity and transmissivity, II) hydrological measurement of water fluxes and pressures, and III) use of environmental tracers for track groundwater inputs by observing composition of different water storages and fluxes, IV) add artificial tracers to detect groundwater residence time an flow lines. In many cases also the measurements must be linked to simple or complex mathematical modeling effort to interpret data in the most efficient way and also to make a good experimental plan. Finally the selection of method depends on experience, availability of measurement devices and capital and human resources.

Hydrogeological measurements

The soil layers can be measured directly using soil cores and drilling and indirectly with geophysical measurement equipment. Standard soil measurements include soil and rock type and sediment particle size distribution. Standard methods are also available to measure porosity, hydraulic conductivity and transmissivity. In many cases also geophysical measurements provide important information in GDE. Typically geophysical methods are complemented with soil cores as the interpretation of geophysical observations relies on calibration data. The figure (Fig. 3.9) below shows an example of lake sediment layer survey using ground penetrating radar driven on lake ice. In some cases mapping of recharge and flow patterns in space can be valuable. This can be done using maps e.g. to detect fracture zones that potentially carry groundwater.

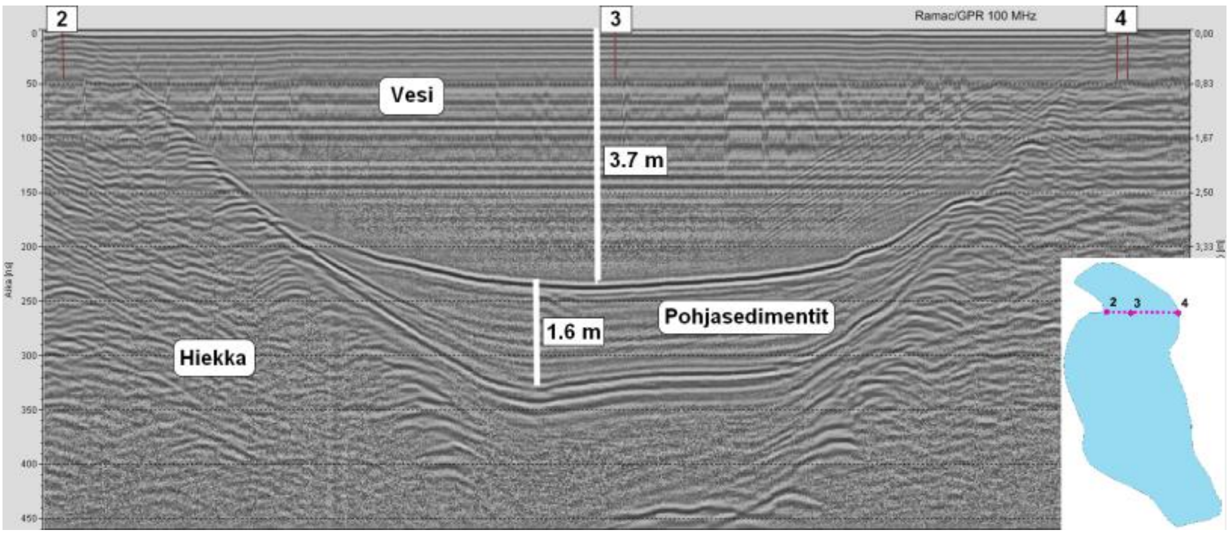


Fig. 3.9 Lake bed profile from ground penetrating radar measurement.

Hydrological measurement of water fluxes and pressures

Hydrological measurements form the first fundamental tool to water resources observation such as groundwater. These measurements give information on quantity of water at a given time and space. Sometimes this can directly indicate groundwater exfiltration. For example if base flow is high the input of groundwater to the ecosystem is usually high. Hydrological data on water quantity is also needed to establish water balances that are needed to understand many systems. Water levels and pressure head in groundwater and GDEs can directly indicate the direction of flow and show interactions. Other methods can be powerful to show flow pathways and flow lines.

Lake, groundwater or river water level measurements should be carried out with fixed points to ensure no movement of the base level and for later comparison of data. Lake stages can be monitored with a method often used in stream stage monitoring. Water level is recorded from a stilling well which is hydraulically connected to the stream. For lake or river level measurements in cold conditions, the monitoring should be done from shore undergrounds to ensure also monitoring during frost (Fig. 3.10).

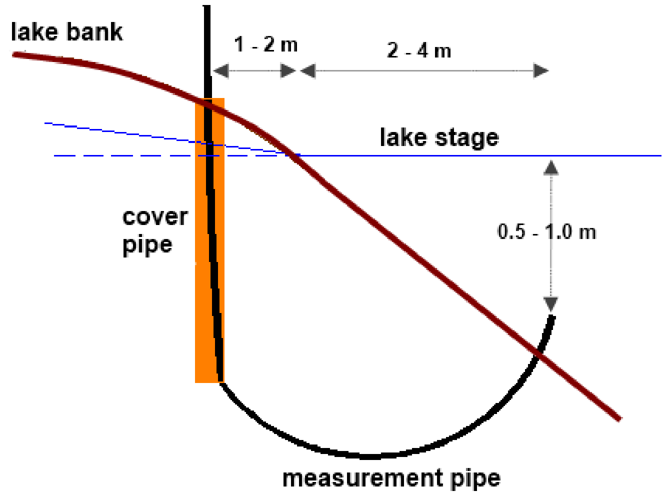


Fig. 3.10 Lake level monitoring.

Seepage meters are useful to measure the inflow of groundwater to and from lakes. A potentiomanometer can be used to determine the direction of hydraulic gradient between surface water and groundwater (Fig. 3.11). Method can be applied to small streams in the groundwater discharge area where seepage meter is not applicable.

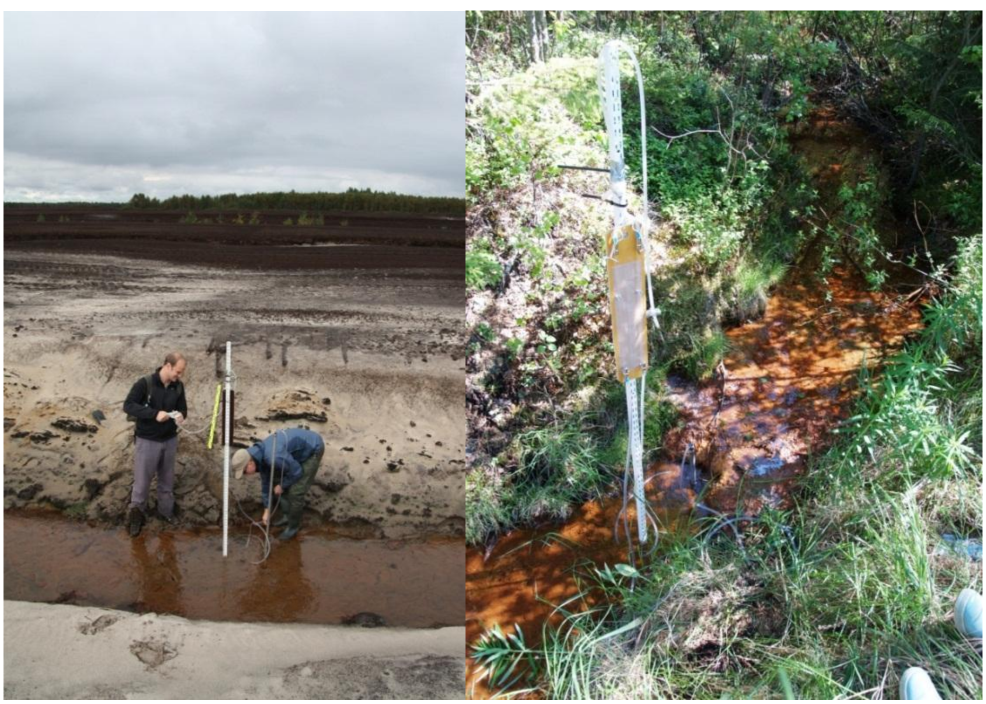


Fig. 3.11 Use of potentiomanometer in a small streams located at peat production area (left) and groundwater discharge area (right) to determine the direction of water seepage.

Tracing of surface and groundwater inputs

The flow of groundwater into GDEs or surface water can be estimated comparing water properties between GDEs and groundwater. As these are often different the amount of groundwater can be estimated from water samples using mas balance equations or just comparing water compositions. Several elements are used to trace groundwater including I) temperature, II) electrical conductivity, III) pH, IV) SiO_2 and other geochemical elements and IV) stable and radioactive isotopes.

Temperature measurements are an affordable and simple way to observe groundwater inflows. Groundwater temperature is relatively stable throughout the year whereas surface water temperature heavily depends on daily and seasonal air temperature variations. From a technical point of view, most of the temperature sensors are portative, simple to set up, robust, accurate (accuracy ±0,1°C) and inexpensive in comparison to other environmental measurements devices. An example of the interpretation of temperature observation is shown in the figure 3.12. If the piezometer shows a response to surface water it is likely that surface water flows into the groundwater system, whereas when the temperature in the piezometer is not related to surface water temperature the groundwater discharges to surface water.

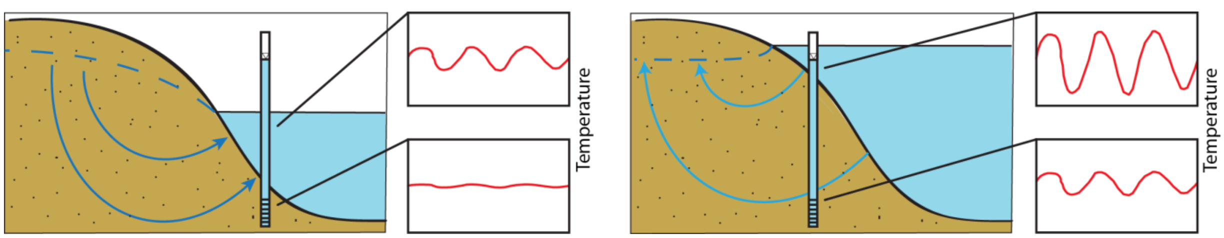


Fig. 3.12 Conceptual scheme of temperature use to assess SW-GW exchanges in a gaining (left) and losing (right) reach of a river.

Apart from direct measurements of temperature using deployed sensor techniques an airborne IR technology can be applied where large scale spatial distribution of recharge/discharge zones should be defined. An example of IR measurements from a stream is shown in Fig. 3.13. Due to retardant behavior of temperature (especially where conduction is important in comparison to advection), this tracer cannot be easily used to evaluate water transit times over long distances. Combination with another tracer technique is often necessary.

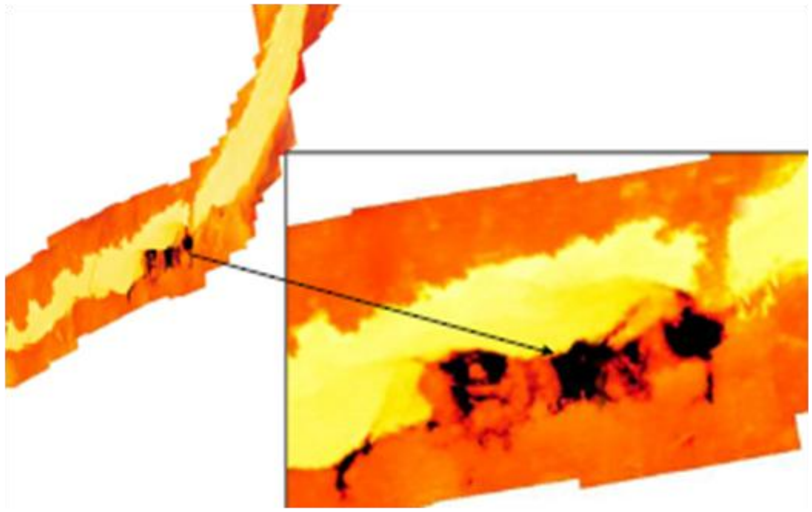


Fig. 3.13 Image of temperature photography from a stream with groundwater intrusion (black color, photo Pöyry Ltd).

Geochemistry of groundwater is usually characterized by the bedrock and porous media where it flows. This leaves a signal to the groundwater that can be distinctly different from surface water. Precipitation is usually free from or low in most weathering products. The potential use of geochemistry as indicator depends on i) the stability or conservative nature of the chemical compound, ii) differences in end-members (e.g groundwater and precipitation). In theory chemical composition of water can be used to determine age and perform hydrograph separation to estimate the portion of groundwater. Such age determination is qualitative (older vs newer water). In many cases groundwater chemical composition is stable whereas surface water responds more rapidly to precipitation events and biological in-stream retention and release of substances. Geochemical compounds that have been used in hydrological studies include SiO_2 and electrical conductivity (EC). SiO_2 is a weathering product and its content increases with groundwater age. Similarly EC increases with age and is higher in groundwater than in rainwater. As EC is easily measured automatically, it can give information on residence times in ecosystems such as fens with a raid variation of flow during peak flow (see e.g. Kværner and Kløve 2008).

Chloride (Cl^-) in precipitation is a useful tracer. Its mean concentration in rainwater depends on distance from the sea. It is a conservative compound with no or little reactivity and its content increases only due to evaporation. It is also commonly linked to pollution such as application of road salt, municipal waste and sewage. It can indicate sea water intrusion or relict sea water or marine and salt deposits in the ground. Following Cl^- as a tracer can be valuable with other tracer measurements as it is conservative and therefore indicates external input from contaminated sites or different waters. It is also useful for mass balance studies in case of evaporation being a major component. Cl^- normally correlates well with EC which is easily and affordably measured in the environment, at least when the Cl^- concentration is high.

There are some difficulties in using geochemistry however. The compounds can be influenced by pH-Eh environment. Also the concentration can be time dependent so different end members are difficult to define for hydrograph separation. Also, they are not as widely used as stable isotopes.

Stable isotopic composition of water reveals significant spatial and temporal variability in the hydrological cycle that can be used to differentiate waters of different origin and even to estimate time scales of water flow. These differences can be used to identify local and regional discharge to GDEs where the isotopic signatures can differ from those of local precipitation and infiltration due to evaporative effects. Areas of groundwater upwelling would be identified by isotopic signatures different than in areas that receive surface water only. Water isotopes can thus show areas where groundwater interacts with the GDEs. A classical example is the study of stream water influence on groundwater in a pumping well along the stream bank (Fig x, after Stichler et al., 1986). Applying mathematical flow models to environmental tracer data it is possible to obtain the following practical information in bank filtration research problems: (1) calculation of the portion of river water infiltrating to the groundwater; (2) determination of flow parameters: mean transit time of water, T, and dispersion parameter, D/vx; and (3) prediction of possible contamination of the groundwater by pollution of the river water.

Water isotope measurement within a GDE show areas where flow occur and this can be related to flow fields in GDE which is useful for calibration of models. In systems with small amount of inflow with constant properties, areas of elevated $\delta^{18}O$ would indicate stagnant zones with no flow if system is sampled after a dry period. Evaporation of surface water bodies (E) leads to enrichment of the liquid phase in heavy isotopes ^{2}H and ^{18}O. Consequently, stagnant zones within the wetlands will have a high evaporation/inflow (E/Q) ratio and should be characterized by elevated ^{2}H and ^{18}O content compared to the inflow of wetlands when E/Q is low. Therefore, properly designed survey of stable isotope composition of water within the given wetland system should yield important information concerning spatial heterogeneity of isotopic composition of water in this system. Isotopic composition can be linked to the water flow patterns, residence time and preferential flow. Stabile isotopes are useful also when the residence time in GDEs is very long and tracer additions cannot be used due to (i) unsteady flow caused by changing hydraulic load and weather, (ii) density currents (Schmid et al., 2004) and (iii) high costs or intensive time requirement. The principle of this method is highlighted in Fig. 3.14 (Ronkanen and Kløve, 2008) that shows measured ^{18}O and artificial tracer addition in a peatland wetland that received runoff water (treatment wetland).

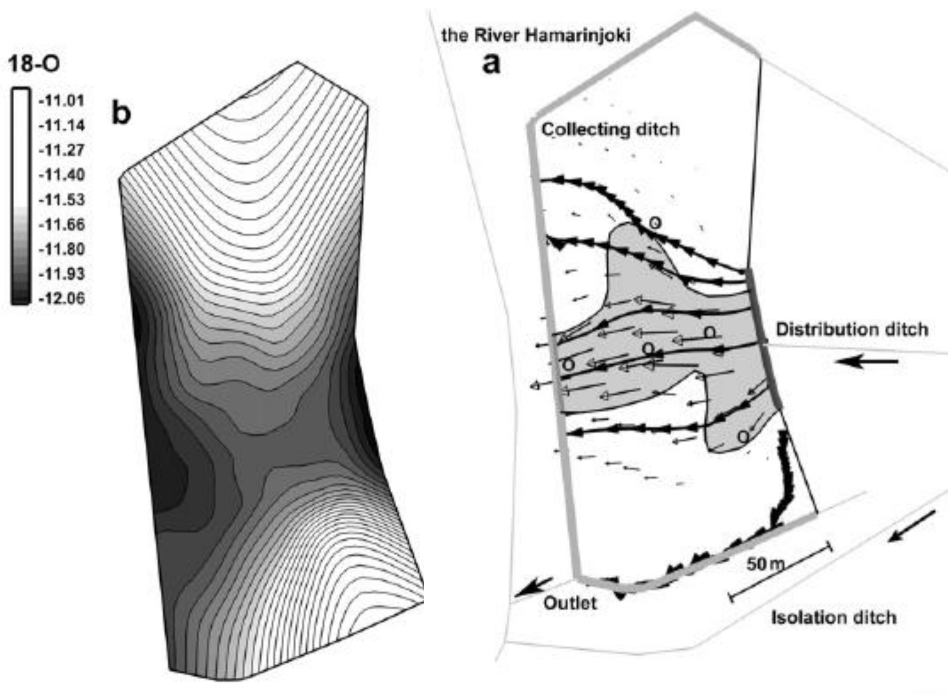


Fig. 3.14 Distribution of measured ^{18}O and delineation of surface water flow field in a peatland that received peat harvesting runoff water (treatment wetland). The main flow field is shown with a thick line. (Ronkanen and Kløve, 2008).

Present-day applications of tritium in characterization of groundwater systems are related to the direct and indirect estimation of groundwater ages. First of all, lack of detectable tritium in groundwater shows that it does not contain “modern” components, i.e. it is derived exclusively from infiltration that occurred before commencement of nuclear weapons testing in 1952. On the other hand, the detectable occurrence of tritium does not exclude contribution of older infiltration as mixing between tritium-free pre-bomb and recently recharged tritium-containing groundwaters might produce arbitrary low tritium concentrations. In springs and other groundwater dependent ecosystems proportions between the old and recent components may differ at wet and dry seasons and tritium concentrations should be checked at different times accordingly.

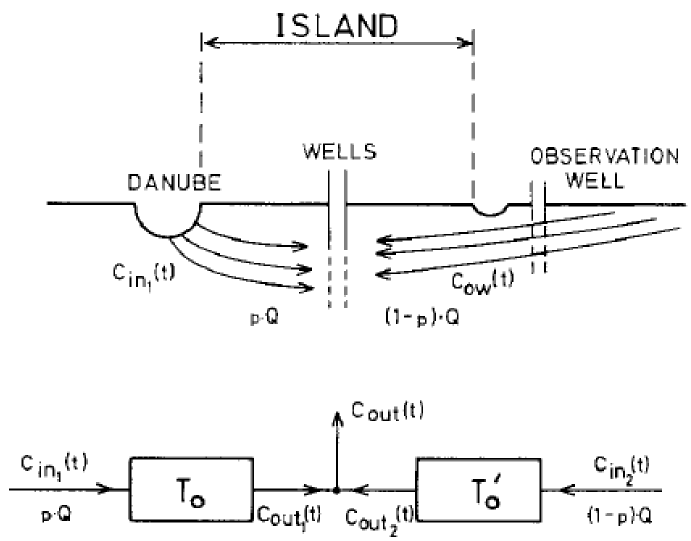


Fig. 3.15 Schematic model of streamwater mixing into a groundwater pumping well along a stream groundwater area of the Danube river (Stichler et al 1986).

Examples of use of the environmental tracers in studies of GDEs are unexpectedly rare and limited mostly to stable isotopes of water and tritium. Matheney and Gerla (1996) applied stable isotopes of water and tritium to evaluate ages and origin of water to the North Dakota wetland and particularly to find out that the deep groundwater has a small contribution to the wetland water budget. Hunt et al. (1996) compare four methods, including stable isotope mass balances, to estimate inflows of groundwater to wetlands in Wisconsin. Hunt et al. (1998) used stable isotopes of water and strontium to discriminate between sources of water, estimate evapotranspiration and trace solute provenance in wetlands. Chapman et al. (2003) used stable isotope composition of water to quantify spatially and temporally variable groundwater contributions to valuable high-altitude fens in Colorado. Clay et al. (2004) analysed stable isotopes of water in a limited number of samples to demonstrate large spatial and temporal (seasonal) variability of water sources to the headwater wetland in England. Harvey and McCormick (2009) compared stable isotope composition of oxygen and hydrogen in groundwaters, surface waters and precipitation to distinguish the relative importance of water sources to the Everglades in Florida. Pang et al. (2010) stable isotopes of water and tritium to study groundwater recharge and flow patterns in a degraded riparian vegetation. They found that high tritium levels indicate conditions favourable for the riparian vegetation as it depends on groundwater recharged from the river.

Tracer tests

Artificial tracers (isotopes, salts, fluorescent dyes and color) can be added to groundwater or surface water to study flow processes in aquifers and related ecosystems. Typical addition points are groundwater wells or stream points with good mixing conditions. The benefit of using salt such as NaCl is that it can be easily measured with electrical conductivity after calibration of conductivity probes. The use of salt pose a risk of density currents and the flow velocity (Reynolds number) of the system must be sufficient. If used in groundwater piezometers, these must be properly mixed after salt addition.

Tracers show flow pathways and give information about aquifer structure including hydraulic conductivity. Tracer tests in streams can give information on hyporheic exchange. Sometimes conservative tracers are used in combination with reactive tracers if retention of substances is studied. Typically also several tracers are used in parallel. Sometimes simple tracers can be used first before a more detailed analysis with e.g. radioactive ^{3}H. The use of radioactive tracers normally requires a permit from authorities where risk of use is estimated. Tracer test require detailed plans for monitoring design. Normally, they give important new information about the groundwater system.

4 Groundwater renewal

Groundwater renewal has direct implications for sustainability of groundwater resources. Low renewal often leads to groundwater mining. This concept is also important from the perspective of vulnerability of groundwater systems against pollution. Fast renewal means faster cleaning of groundwater system after cessation of the pollutant input.

4.1 Conceptual framework

In the framework of these Guidelines groundwater renewal has a broader meaning than groundwater recharge. Groundwater renewal is meant here as an exchange of water in the entire groundwater flow system (GroundWater Body – GWB), starting from recharge areas, through the saturated parts, down to the area(s) of discharge. From this perspective, it is important to consider three-dimensional character of groundwater flow as well as timescales of water exchange.

Three-dimensional character of groundwater flow is important even in simple, one-layer unconfined aquifer because the knowledge of flowpaths of water may serve as important source of information on pathways of contaminants transported by water recharging the system. This is illustrated in Fig. 4.1 (see also Fig. 2.3 in chapter 2.4.1

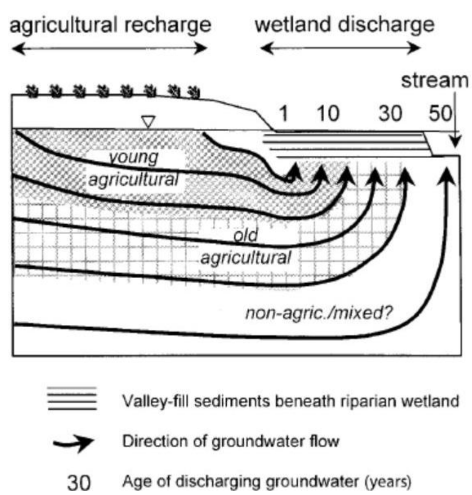


Fig. 4.1 Simplified representation of groundwater flow from an upland agricultural recharge area to a riparian wetland (Böhlke et al., 2002). Arrows indicate directions of flow as determined from gradients in hydraulic heads and groundwater ages (range: 0–50 years). Lateral variations in the concentrations of agricultural contaminants discharging upward beneath the riparian wetland correspond in part to vertical variations in the ages and concentrations of NO_3 in the recharge area, as indicated by representative groundwater ages in years: 1 - young groundwater with low-NO_3 non-agricultural recharge; 10 - moderately young water with high-NO_3 agricultural recharge; 30 - moderately old water with low-NO_3 agricultural recharge (result of denitrification and/or variations in historical input); 50 - old water with non-agricultural or

low-NO_3 agricultural recharge.

It shows that riparian wetland in a discharge area may receive groundwater of different ages and characterized by different chemical load, as a direct consequence of three-dimensional nature of groundwater flow.

Timescale of groundwater flow adds additional useful dimension to characterization of groundwater renewal. There is an approximate inverse proportionality between groundwater age and groundwater renewal. Mapping of groundwater age (flowtimes) helps to identify recharge and discharge areas and their relative importance for the studied system (De Smedt, Batelaan, 2001). Ages of water at discharge point(s), along with other information such as extension, thickness and porosity of water-bearing formation(s), provide the basis for quantification of time scales of groundwater renewal.

By nature renewal processes are variable in time and space. This variability leads to quantitative changes of groundwater resources (storage), and qualitative changes of groundwater chemical status. This natural variability of the renewal processes, linked to natural variability of the hydrologic cycle, can be seriously affected by men's activity of various nature.

The most important element of groundwater renewal is the process of groundwater recharge. According to Healy (2010) recharge is defined as gravitationally imposed downward flow of water reaching water table and adding to groundwater storage. This definition is similar to those given by Meinzer (1923), Freeze and Cherry (1979), and Lerner et al. (1990). Recharge can be classified according to type of water taking part in the process (precipitation, surface water, artificial recharge, etc) or according to the origin of water (natural, artificial).

Natural recharge

Natural recharge is usually variable in space and time and may have regional and local scale of variability (Healy, 2010). It is true for both focused and diffuse recharge. Regional scale of variability of recharge depends on geology, surface topography, climatic conditions and their variability, and land use. Local-scale variability of recharge may arise due to natural heterogeneity of soil cover, variability of vegetation cover, local morphology, preferential flow in unsaturated zone (e.g.; chapter 3 of these Guidelines), preferential flow in saturated zone, local hyporheic flows near surface water and wetlands (e.g. Alley et al., 2002; Maloszewski et al., 2002; Smith, 2005; Buss et al, 2009; Stumpp and Maloszewski, 2010; Nimmo, 2012; see also Chapter 3 of these Guidelines)). Figure 4.2 after Fetter (1999) illustrates specific cases of local scale of variability of recharge due to various mechanisms of preferential flow in the vadose zone.

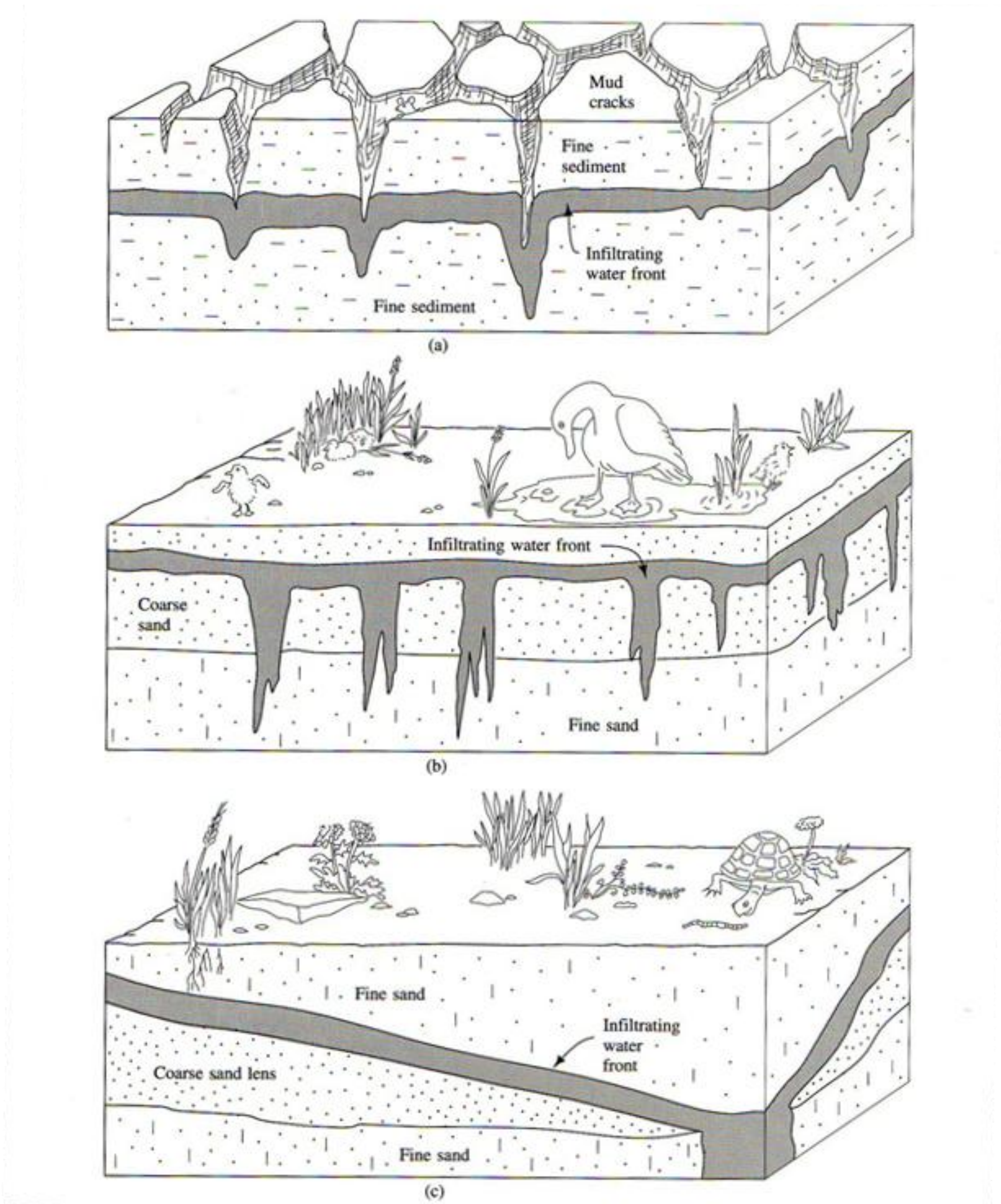


Fig. 4.2 Preferential flow of water in the vadose zone induced by short circuiting (a), fingering (b) and funneling (c). (Fetter , 1999).

Preferential flow may also occur in the saturated zone, in dual- or triple-porosity systems, the latter commonly associated with karstic systems. Fig. 4.3 shows conceptual model of groundwater flow through a karstic system of Schneealpe massif in Austria. In such systems the concept of groundwater renewal should be formulated separately for each of the dominating modes of groundwater flow.

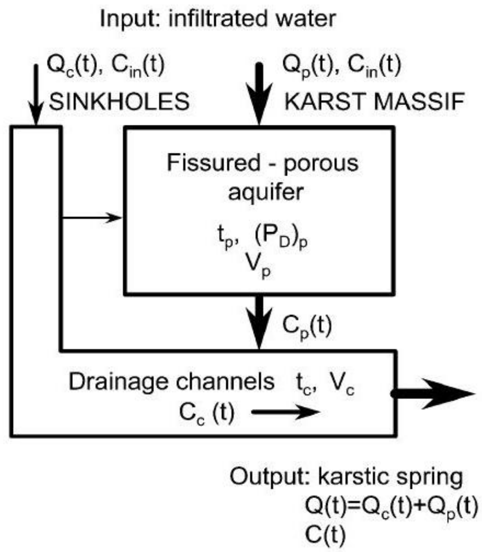


Fig. 4.3 Conceptual model of water and associated tracer flow through a karstic massif in Austria (Maloszewski et al., 2002). Portions of the system characterized by fast and low renewal of groundwater can be easily identified.

Hyporheic zones associated with river channels constitute characteristic examples of groundwater renewal on a local scale (Fig. 4.4). Depending on river stand and local hydraulic conditions water may flow from the stream into the riverbed sediments and then returning to the stream, within timescales of days to months (e.g. Buss et al., 2009).

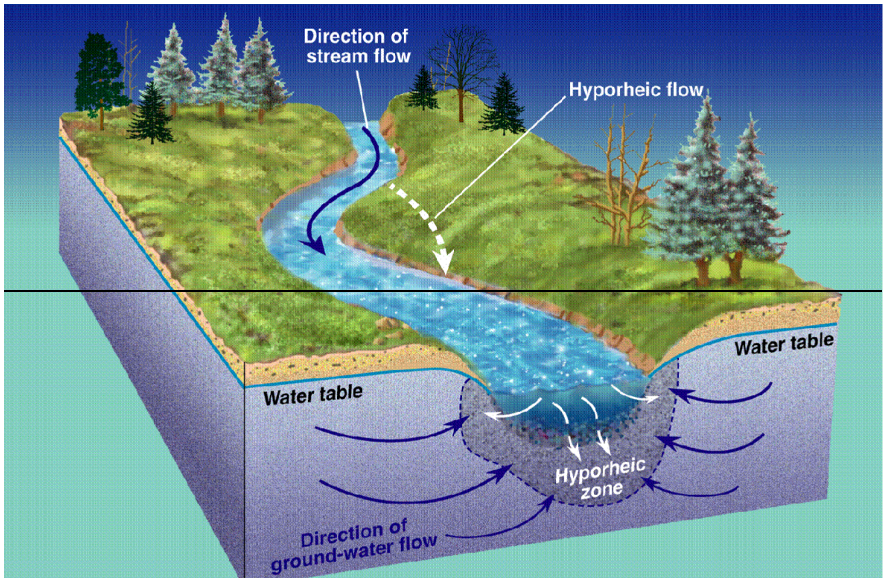


Fig. 4.4 Conceptual model of groundwater - river water interaction within hyporheic zone (Alley et al., 1999, 2002).

Recharge affected by anthropogenic activity

Impact of man on groundwater storage and renewal may occur in two fundamental ways: (i) pumping will affect groundwater storage and, if water table is lowered, it will induce new recharge (Zhou, 2009); (ii) changes of land use, either due to agriculture activities (converting natural land to crops or pastures) or in urban environment (surface sealing, leakages of drainage and sewing networks, etc.) will inevitably lead to modification of the recharge rate. In general, urbanization will have an impact of groundwater recharge, which magnitude and even the sign will depend on site-specific conditions such as extent of surface sealing by urban infrastructure (Lerner and Harris, 2009), density and intensification of urban drainage network (Deal and Schunk, 2004), or degree of leakages from water mains and sewing systems. Leakages from the sewing systems may also pose serious problems for groundwater quality of neighboring aquifers (Chisala and Lerner, 2008). It should be noted that the above-mentioned processes and mechanisms which affect natural groundwater recharge rate have unintentional character i.e. they are usually a by-product of anthropogenic activities of various nature.

Another category of human impact on natural recharge mechanisms is artificial recharge. Here, often large-scale, extensive measures are undertaken to increase the natural recharge by technological means. They include among others: (i) irrigation, (ii) bank filtration and artificial infiltration ponds, (iii) increasing groundwater storage after overexploitation by direct injection of water to the system (aquifer storage recovery – ASR). Obvious rationale for artificial recharge comes from deficit of water, either for direct human use or for agriculture, persisting in many countries.

Artificial recharge will inevitably lead to intensification of groundwater renewal (e.g. Alley et al., 1999). Fig. 4.5 illustrates how water withdrawal for irrigation and return flow enhance water circulation within intensively exploited aquifer located in southern High Plains (USA). Although recharge has increased due to irrigation more than 10 times, natural discharge from the system was affected only marginally.

Intensification of groundwater renewal often leads to deterioration of groundwater quality (e.g. Aiken and Kuniansky, 2002; Herczeg et al., 2004).The most common problem is gradual salinization of groundwater induced by irrigation.

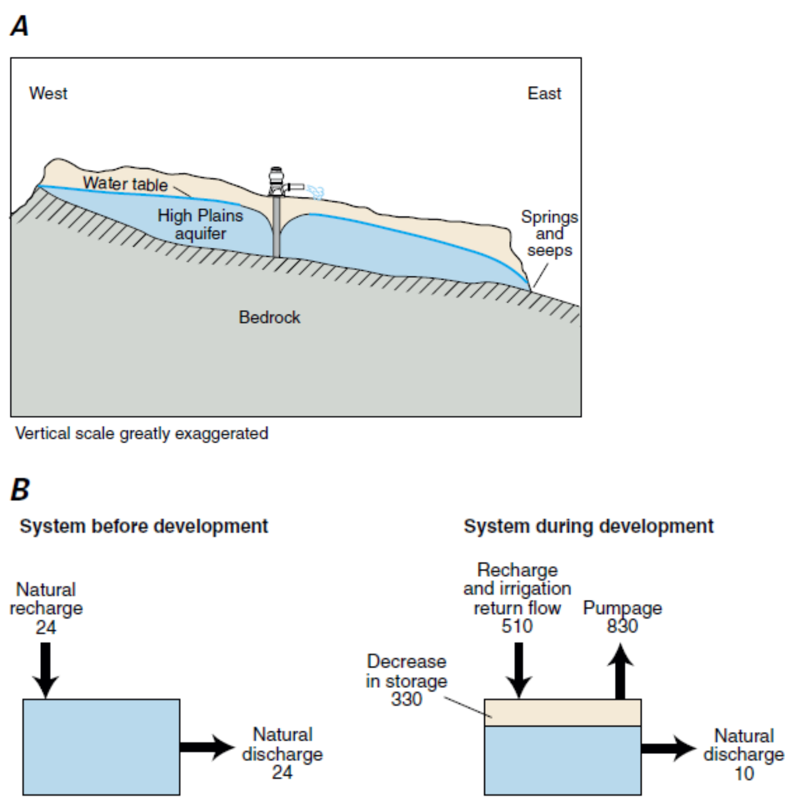


Fig. 4.5 Schematic illustration of a groundwater system (High Plains aquifer, USA) developed for irrigation purposes (A). Impact of irrigation scheme on water fluxes within the system (B) After Alley et al, 1999 (Modified from Lohman, 1972).

Some countries impose limits on artificial enhancing of groundwater renewal. For instance, Polish guidelines for groundwater usage propose Groundwater Renewal Index (GRI) as a measure of human intervention into groundwater renewal (Paczynski et al, 1996). GRI is defined in terms of mean groundwater age within the considered portion of the system:

$$GRI = \frac{MRT_N}{MRT_{IM}}$$

where MRT_N is the mean residence time (age) of water under natural conditions and MRT_{IM} is the expected new mean residence time after imposing technical measures enhancing groundwater renewal. If GRI is larger than 2.5, additional studies should be performed before enhancing scheme is allowed.

4.2 Sustainability of groundwater resources, groundwater mining

Todd (1959) defines safe yield of groundwater as "the amount of water which can be withdrawn from a groundwater basin annually without producing an undesirable result". Undesirable results may include reduction of groundwater reserves, deterioration of chemical quality of groundwater, for instance due to changes of redox conditions (Apello and Postma, 2005), intrusion of water of poor quality (e.g. sea-water instrusion), the contravention of existing water rights, deterioration of the economic advantages of pumping (Domenico, 1972) and impact on groundwater dependent ecosystems Klove et al. (2011). Freeze and Cherry (1979) suggested to include the excessive depletion of stream flow by induced infiltration and land subsidence as undesirable results. The challenge is to link the envisaged changes of groundwater levels, flows and quality indicators as a result of exploitation, to the expected impacts on ecosystems and social benefits (Alley and Leake, 2004, Sophocleous, 2007, Zhou, 2009).

A common misperception is that the development of a groundwater system is "safe" if the average annual rate of groundwater withdrawal does not exceed the average annual rate of natural recharge. his simple concept evolved with time to include economic, legal, and water quality considerations. In parallel, sustainability concept was introduced which was based on the principle that no single environmental issue can be addressed in isolation. Thus, sustainable development encourages integrated water management approaches and sustainable usage of water such as artificial recharge, conjunctive use of surface water and groundwater, and use of recycled water, always taking into account possible limitations of such development due to environmental constraints (Alley and Leaky, 2004).

Water Framework Directive of EU (WFD, 2000) considers surface waters and groundwater as renewable natural resources. The task of ensuring good status of groundwater requires early action and stable, long-term planning of protective measures owing to considerable timescales of groundwater formation and renewal. Therefore, these timescales should be taken into account when timetable of adequate measures aimed at timely achievement of good status of groundwater and reversing any significant and sustained upward trend in the concentration of any pollutant in groundwater is established. Article 11 of the WFD (Programme of measures (3f)) includes a requirement for prior authorization of artificial recharge or augmentation of groundwater bodies. It states that “The water used for this purpose may be derived from any surface water or groundwater, provided that the use of the source does not compromise the achievement of the environmental objectives established for the source or the recharged or augmented body of groundwater. These controls shall be periodically reviewed and, where necessary, updated”.

Quantification of environmental water requirements (EWRs) is a promising new concept devised to ensure sustained streams of ecosystem goods and services related to water quantity and quality at safe minimum standards for the protection of ecosystem structure and function in both natural and socio-economic systems (Klove et al., 2011). In relation to groundwater-dependent terrestrial ecosystems, EWR signifies the minimum amount of water in terms of quantity and quality, to maintain basic functions of the given Groundwater Dependent Ecosystem (GDE)

Fig. 2.1 illustrates conflict which may arise over groundwater resources between the EWR of GDE and potable water requirements of local population. The aquifer located in southern Poland being studied in the framework of GENESIS project consists of two water-bearing strata separated by Badenian clays. The principal economic role of the deeper aquifer, is to provide potable water for public and private users. Estimated disposable resources are 40,000 m^3/d with typical well capacities of 4 to 200 m^3/h (Witczak et al., 2008). Hospitals and food processing plants also exploit some wells. The yield of the aquifer is insufficient to meet all the needs and, as a consequence, licensing conflicts arise between water supply companies and industry over the amount of water available for safe exploitation. Wola Batorska well-field recently established north of Niepolomice Forest area may lead to lowering of water table and threaten the functioning of GDE.

Under natural conditions, groundwater systems are in a dynamic equilibrium in which long-term average recharge equals long-term average discharge. Pumping groundwater will inevitably cause the decrease of groundwater levels which in turn induce new recharge and reduce natural discharge. It has been demonstrated that pumping initially removes water from storage, but over time is increasingly derived from decreased discharge and/or increased recharge (Theis,1940). When a new equilibrium is reached, no additional water is removed from storage. In cases of fossil or compacting aquifers, where recharge is either unavailable or unable to refill drained pore spaces, depletion effectively constitutes permanent groundwater mining. In renewable aquifers, depletion is indicated by persistent and substantial head declines (Konikov and Kendy, 2005, Vrba and van der Gun , 2004)

4.3 Overview of tools assessing renewal rates of groundwater

Over the years a number of methods for assessing renewal rates of groundwater has been devised and tested (Healy, 2010, Scanlon, Cook, 2002). They can be separated into several categories with respect to the tools used and portions of the system which are being assessed from this perspective. Water budget methods are aimed at constructing water balance on catchment scale and separating the recharge component from it (Healy, 2010). Quality of the results critically depends on the knowledge of individual elements of the balance.

Modeling methods are based on budgeting of flow through the given groundwater system (Healy, 2010, Zhou, 2009) They allow verification and combining of individual elements of the budget. However, great care is required when individual fluxes are manipulated in the model; recharge rates can be obtained through modification of hydraulic conductivity of the matrix which is equally poorly constrained. Moreover, the simulated heads are only sensitive to the ratios of recharge and hydraulic conductivity and, therefore, good fitting can be obtained for different combinations of both parameters (Zhu, 2000).

Methods based on surface-water data are aimed at deriving groundwater discharge to rivers and streams (Buss et al., 2009, Chapman, 1999, Healy, 2010). They rely mostly on hydrograph separation. Stream water-budget methods and seepage measurements usually provide estimates of focused recharge or exchange of groundwater an surface water. They are particularly well-suited for hyporeic zone (Berryman, 2001).

Physical methods (unsaturated zone) are aimed at assessing effective infiltration in the unsaturated zone. Budgeting methods taking into account inputs and outputs of water from unsaturated zone are widely used here (Healy, 2010). A wide range of possible techniques for soil water extraction is provided. Advantages and disadvantages of these methods are given by Weihermueller et al. (2007). Multiple tracer approaches probably offer the best potential for point estimates of recharge rates, although data must be interpreted with care in areas with multi-modal flow in the vadose zone (e.g. Vries and Simmers, 2002). Chloride is particularly useful for quantifying low recharge rates in arid and semiarid regions (Edmunds and Tyler, 2002). The issues of localized recharge and spatial variability need not be a problem if concern is with regional estimates. The combination of reliable local data, remote sensing, and GIS technology is recommended for recharge estimates over large areas.

Physical methods (saturated zone) rely on analysis of fluctuations of water table as an indicator of effective recharge of the system (Healy, 2010, Schicht, Walton, 1961). Main disadvantage of these methods is poor representation of lateral flow in the assessed system (e.g. Asmuth, 2012).

4.4 Challenges

In light of ever-growing anthropogenic pressure on groundwater resources, both with respect to quantity and quality, cost-effective and accurate assessment of groundwater renewal gains in weight particularly in regions where demand exceeds supply. Groundwater mining is a burning issue in many parts of the world.

In the past decades an array of methods for assessing renewal rates of groundwater has been devised and tested. It seems that future lies here in the integration of diverse instrumental approaches with adequate modeling tools and GIS technology. Also, devising new methods of up-scaling local estimates of recharge rates on larger areas will be important from this perspective.

Sustainable exploitation of groundwater resources on local and global scales requires not only maintaining withdrawals of water by man at safe levels guarantying adequate renewal of groundwater systems and keeping quality of water at acceptable limits, but also respecting rights of groundwater dependent ecosystems as equally important users of this precious resource.

5 Impact of climate and land-use changes on flow-path structure and transport in groundwater systems

5.1 Impacts of climate change on groundwater resources

Climate changes, which encompass changes in precipitation, temperature and evapotranspiration, can affect groundwater systems in many ways; it can change the interactions between groundwater and surface waters and may imply changes in use related to irrigation. Impacts on groundwater systems cannot be studied in isolation, as various and complex interaction in the hydrological cycle will be critical to our understanding of the land-atmosphere coupling. Groundwater flow and storage are changing in response not only to climatic changes but also to human impacts.

A groundwater system comprises the subsurface water, the geologic media containing the water, flow boundaries, sources and sinks. Water flows through and is stored within the system. Climate change can impact the groundwater levels and flow through various processes that affect the water balance. The hydrological water balance for a catchment can be written as:

$$P = ET + D + Q + \Delta S \qquad (1)$$

where P is precipitation [L^3T^{-1}], ET is evapotranspiration [L^3T^{-1}], D is discharge [L^3T^{-1}], Q is water extraction [L^3T^{-1}] and ΔS is change in storage [L^3T^{-1}]. Climate change can affect all the components of the water balance, precipitation, evapotranspiration, discharge, water extraction and storage. Changes in storage affect the unsaturated and saturated zones and storage in the form of snow and ice. If we consider the storage changes for an aquifer, the interactions with the other hydrological compartments also have to be considered. Changing interactions with surface water bodies have a significant impact on changes in aquifer storage and should be included in the aquifer water balance:

$$\Delta S_{aqui} = \Delta P - \Delta ET - \Delta R - \Delta Q + (\Delta L_{in} - \Delta L_{out}) \qquad (2)$$

where L_{in} are the fluxes from the surface to the aquifer [L^3T^{-1}], L_{out} are the fluxes from the aquifer to the surface water bodies [L^3T^{-1}]. Climate change assessment studies for groundwater solve normally a distributed form of equation (2). However, ΔP and ΔET are normally taken from climate simulations, and only if integrative hydrological models are used, the other terms on the right-hand side of equation (2) are explicitly solved (Hendricks, 2009).

Groundwater can discharge to surface waters, atmosphere and to the ocean. Groundwater discharge includes springs, rivers, lakes, oceans, evaporation of soil moisture and transpiration by phreatophytic vegetation that draws its water from the water table. Furthermore, groundwater discharges also includes pumping activities by humankind. Groundwater discharge is a key factor controlling water table conditions, surface and groundwater quality, lake levels, baseflow of rivers and streams, and terrestrial and aquatic ecosystems, notably in riparian zones and wetlands (UNESCO, 2006). Enhanced groundwater discharge by abstraction and land drainage can moreover lead to land subsidence, which is particularly a concern in low-lying coastal areas. Alterations on recharge due to climate change can affect groundwater discharge, and all its interactions. A more detailed description of surface water – groundwater interaction can be found in Deliverable 4.2.

Variations in temperature and precipitation during the year may have a direct impact on changes in groundwater levels, reserves and quality. Indirectly, climate change may also have effects on land management practices, land use and agricultural practices such as irrigation with water extracted from aquifers, which could also alter hydrological systems (Brouyere et al., 2004). The direct effect of climate change on groundwater resources depends upon the change in the volume and distribution of groundwater recharge. Therefore, quantifying the impact of climate change on groundwater resources requires not only reliable forecasting of changes in the major climatic variables, but also accurate estimation of groundwater recharge (Singh and Kumar, 2010).

Aquifers react much slower to climate change than surface water bodies, but on the long-term the average groundwater level might be much lower or higher than under the current conditions, with serious implications for drinking water supply and groundwater dependent ecosystems. The time of travel through the system depends on the spatial and temporal gradients of hydraulic head, hydraulic conductivity, and porosity of the system. The time of travel of water is important in determining the movement of contaminants within a groundwater system (Alley et al., 2002).

Solute transport in groundwater depends on a range of fate and transport process, including advection, dilution, dispersion, diffusion, sorption, degradation and volatilisation. The influence of climate change on fate and transport processes is difficult to assess because it is intimately linked to the hydrogeological context and larger scale hydrogeological processes, such as climate-induced changes in groundwater levels, hydraulic gradients, groundwater fluxes and water quality, and because the processes do not operate in isolation (Bloomfield et al., 2006). Advective transport in aquifers is driven by hydraulic gradients and the rate of transport is a function of aquifer hydraulic conductivity and porosity. In dual porosity aquifers there is the potential for rapid flow through the fracture network. Dispersion results in the reduction of solute concentration through mechanical mixing or dilution along groundwater flow paths. Diffusion results in the movement of solutes from regions of high concentration to regions of lower concentration. Solute concentrations may also be reduced by volatilisation in the unsaturated zone, and by degradation and sorption. The most significant climatic impacts on groundwater systems may be due to changes in recharge, moisture content of the unsaturated zone, and groundwater levels. More frequent and intense storm events will affect groundwater recharge and influence the solute transport to the unsaturated and saturated zone.

Change in climate will affect the soil moisture, groundwater recharge and frequency of flood or drought episodes and finally groundwater level in different areas. In a number of studies, it is projected that increasing temperature and decline in rainfall may reduce net recharge and affect groundwater levels (Singh and Kumar, 2010). Changes in regional temperature and precipitation have important implications for all aspects of the hydrologic cycle. Variations in these parameters determine the amount of water that reaches the surface, evaporates or transpires back to the atmosphere, becomes stored as snow or ice, infiltrates into the groundwater system, runs off the land, and ultimately becomes baseflow to streams and rivers (Allen, 2004).

The most relevant climate variables with respect to groundwater are precipitation, temperature and evapotranspiration. We need those variables from climate models. Climate-change scenarios are normally expressed in terms of changes in temperature and precipitation. Consequently, the effects of climate change on potential evaporation or even on evapotranspiration are not simple to estimate. However, in order to assess the impact of climate change on groundwater information on changes in evapotranspiration is required because it is a key component of the water balance. Climate change scenarios used in this project are explained in Deliverables 5.2 and 5.3.

5.1.1 Precipitation

Because groundwater aquifers are recharged mainly by precipitation or through interaction with surface water bodies, the direct influence of climate change on precipitation and surface water ultimately affects groundwater systems. Groundwater recharge and discharge conditions are reflection of the precipitation regime, climatic variables, landscape characteristics and human impacts such as agricultural drainage and flow regulation. In order to analyze the effects of changes on precipitation upon groundwater it is necessary to consider not only the change in the total amount of precipitation, but also in the distribution of the precipitation along the year and the intensity of the precipitation. The greater variability in rainfall could mean more frequent and prolonged periods of high or low groundwater levels.

Changes in precipitation can also have an important impact on groundwater quality. An increase in precipitation could increase dilution by greater river flow volume, as well as shorter residence times for in-stream nitrification. In contrast, increased nitrate content is caused by sustained droughts. Sequences of dry summers lead to the build up of nitrogen in the soil that is flushed from the land into streams when droughts break (Wilby et al, 2006). More frequent intense rainfall events may lead to more by-pass flow increasing the likelihood of rapid solute movement through aquifers. In the other hand, low rainfall can increase the solute concentration.

Soil hydraulic conductivities depend on moisture content and so water with pollutants may move more rapidly through soils, but they will also show enhanced degradation rates. High recharge rates can produce high groundwater levels which may intercept solutes in the unsaturated zone, reducing the time for degradation and leading to seasonal peaks in the solute concentration in groundwater (Bloomfiled et al., 2006).

Rapid transport of pollutants from the base of the soil zone into aquifers is sensitive to the intensity and seasonality of rainfall events. The increased seasonality of rainfall will affect seasonal variations in the moisture content of the unsaturated zone. As advection velocities increase at higher moisture contents, leaching of pollutants to the saturated zone may become more seasonal. High groundwater levels may occur more frequently due to higher winter rainfall. Periodic high groundwater levels can intercept pollutants in the unsaturated zone and soil zone, reducing the time for degradation and leading to seasonal increases in the concentration in groundwater.

Coastal aquifers are important sources of freshwater; however, salinity intrusion can be a major problem in these zones. Salinity intrusion refers to replacement of freshwater in coastal aquifers by saltwater, which leads to a reduction of available fresh groundwater resources. Changes in precipitation can significantly alter groundwater recharge rates for major aquifer systems and thus affect the availability of fresh groundwater. Salinisation of coastal aquifers is a function of the reduction of groundwater recharge and results in a reduction of fresh groundwater resources (Singh and Kumar, 2010).

5.1.2 Temperature

Rise in temperature associated with climate change leads to a general reduction in the proportion of precipitation falling as snow, and a consequent reduction in many areas in the duration of snow cover. This has implications for the timing of streamflow in such regions, with a shift from spring snow melt to winter runoff (Arnell, 1999). This could potentially lead to higher winter flows and more frequent flooding, especially in rain-dominated systems along the coast.

Many rivers and streams that are now fed by glacier runoff could be significantly impacted as a result of climate change. As glacier retreat accelerates, increased summer runoff could occur. However, when the glaciers have largely melted, the present late summer and fall glacial input into streams and rivers will be lost, resulting in a significant reduction in flow in some cases (Brugman et al., 1997).

Higher temperatures could increase the volatilisation and degradation of pollutants in the soil and surface waters. Pesticide concentrations may be reduced by increased volatilisation and degradation rates in the shallow unsaturated zone but there will be no influence in the deeper unsaturated and saturated zones (Bloomfiled et al., 2006). Higher temperatures during the summer will lead to increased potential for pesticide degradation and so have an opposite effect on pesticide concentrations. Warmer drier summers may lead to cracking of soils increasing the potential for by-pass flow. Climate-induced changes in the temperature of the shallow unsaturated zone may affect pesticide volatilisation and degradation as already noted. However, climate induced changes in the temperature of the deeper unsaturated and saturated zone of aquifers will be negligible.

5.1.3 Evapotranspiration

Hydrological impact assessments of watersheds and aquifers require information on changes in evapotranspiration because it is a key component of the water balance. Changes in evapotranspiration will affect the amount of water that recharges the aquifers. However, climate-change scenarios tend to be expressed in terms of changes in temperature and precipitation. Consequently, the effects of global warming on potential evaporation (or more inclusively, evapotranspiration) are not simple to estimate (Allen et al., 2004).

Evapotranspiration is directly accounted into the balance equation; however, it is closely related to precipitation and temperature, temperature increase can increase the ET and then decrease the recharge. For example, Potential evaporation is higher under HadCM3 simulations for several reasons: the temperature increase is greater in many regions, the vapour pressure increase is generally smaller (leading to a greater increase in vapour pressure deficits), windspeeds are slightly higher, and the patterns of net radiation change are different, reflecting the different spatial patterns of precipitation change (Arnell, 1999).

Climate is probably the most important factor in determining the types of crops that are grown within a particular location. Climate change can force to a shift on crops Changes to cropping patterns involving a geographical shift in the distribution of existing crops, which can make changes on land use.

5.1.4 Sources of uncertainty

Climate change impact assessment involves many uncertainties. First, there are uncertainties linked to general circulation models (GCMs). Second, there are uncertainties in the representation of climatology at regional scales, including differences between dynamical and statistical downscaling methods. Third, there are parameter and structural uncertainties in the hydrological models used for impact assessment.

Regarding the GCMs, the sources of uncertainties can by related to the prediction of: (i) future emissions of greenhouse gases, (ii) their conversion into atmospheric concentrations and (iii) subsequent radiative forcing. Air temperature and precipitation are the two climatic variables that are most relevant to hydrologic predictions.

Precipitation is commonly downscaled in climate change impact studies; however, the reliability of the downscaled result is often poor or unreliable

Uncertainty is embedded in model parameters, structure and driving force of the hydrological cycle. Predicting the long-term effect of a dynamic system is very difficult because of limitations inherent in the models, and the unpredictability of the forces that drive the earth.

Although uncertainties are inevitable, new response strategies in water resource management based on the model may be useful.

5.1.5 Estimation of climate change impacts on groundwater. Integrated analysis

It is very difficult to analyse the influence of each variable of climate change upon groundwater resources. In order to properly estimate the effects of climate change it is necessary to analyse all the variables in an integrated manner, taking into account their feedbacks. As climate changes can have different impacts on different regions, there is no a straightforward way to quantify those impacts. The use of integrated modelling is thus crucial and the identification of the interrelations between different processes. Climate change can affect the stream flows, which would modify the recharge to groundwater. River–aquifer interactions may be largely influenced by climate conditions occurring in the headwaters of the basin. Brouyere et al. (2004) from a study in the Geer basin in Belgium, conclude that the evaluation of the impact of climate change on groundwater reserves and on base flow is not straightforward. On a multi-annual basis most tested scenarios predict a decrease in groundwater levels; at the same time, the tested scenarios do not show enhancement of the seasonal variations in groundwater levels. Eckhardt and Ulbricht (2003) simulated relatively small effects on mean annual recharge in central Europe. Even so, the seasonality of groundwater recharge and stream flow were sensitive to climate change. They included the joint effects of atmospheric CO_2 concentrations on carbon assimilation rates and the stomatal conductance of plants. For the Grand Forks aquifer in Canada, Allen et al. (2004) estimated very small changes in the overall configuration of the water table and general direction of groundwater flow for different scenarios of high and low recharge. However, they found changes in the water-balance output which account for the redistribution of water within the system in response to varying recharge under steady-state conditions. On the other hand, the aquifer showed to be highly sensitive to changes in river stage compared with changes in recharge. De Wit et al. (2001) studied the impact of climate change on the hydrology of the river Meuse. Their general conclusion is that catchments with dominance of the fast runoff component over groundwater base flow are more sensitive to climate change than others. Loaiciga et al. (2000) studied the impact of climate change on the groundwater resources of the Edward BFZ regional karst aquifer in Texas. They draw the conclusion that the groundwater resource in this aquifer could be strongly impacted under a warmer climate.

Singh and Kumar (2010).mentioned that rising sea levels may lead to increased saline intrusion into coastal and island aquifers, while increased frequency and severity of floods may affect groundwater quality in alluvial aquifers. Sea-level rise leads to intrusion of saline water into the fresh groundwater in coastal aquifers and thus adversely affects groundwater resources.

Bloomfield et al. (2006).conclude that the main effects of climate change on groundwater pollution by pesticides are likely to be (i) an increase in the seasonality of pesticide concentrations arriving at the water table, (ii) an increase in the frequency of high pesticide concentrations at the water table in response to individual storm (by-pass flow) events particularly in the late winter and spring, and (iii) an increase in the frequency of seasonally high pesticide concentrations at the water table associated with high interannual groundwater levels.

Regarding irrigation water (Singh and Kurmar,(2010) mentioned that a change in field-level climate may alter the need and timing of irrigation, an increased dryness may lead to increased demand, but demand could be reduced if soil moisture content rises at critical times of the year. It is projected that most irrigated areas in India would require more water around 2025 and global net irrigation requirements would increase relative to the situation without climate change by 3.5–5% by 2025 and 6–8% by 2075. In India, roughly 52% of irrigation consumption across the country is extracted from groundwater; therefore, it can be an alarming situation with decline in groundwater and increase in irrigation requirements due to climate change

5.2 Impact of land use changes

Land use changes are driving forces that alter the hydrological processes intervening in all components of the water budget in the hydrogeological systems. In that way, land uses change the natural evapotranspiration, infiltration and surface runoff processes as well as the surface and groundwater storage. Although precipitation is considered to be a factor not directly influenced by land uses, it is affected by climate changes which are also related to land uses. The present chapter aims at describing the modifications caused by the various land uses in each component of the water budget and determine the importance of each one in the dynamics of the hydrogeological systems.

5.2.1 Land use effects on evapotranspiration

Evapotranspiration (ET) is the factor of the water budget that consumes the majority of water within a catchment area except in the case of very humid and cold climates. It is estimated that global land ET returns about 60% of annual land precipitation to the atmosphere (Oki, T. and Kanae, 2006; Jung et al., 2010). Based on recent global research (Jung et al., 2010) suggested that the rate of land ET increased from the early 1980s to the late 1990s whereas a declining trend was observed in global ET since 1998. This decline was attributed to limited moisture supply and to a lower extent to stomata closure caused by increasing CO_2 concentrations, land-use changes, or decreasing wind speed. At the regional level, for a given rainfall regime and soil moisture capacity, evapotranspiration is controlled be crop types. Lerner and Harris (2009) pointed out the significant difference of evapotranspiration and consequently on groundwater recharge, between trees and woody shrubs on one hand and crops and pasture on the other. In general, evapotranspiration demands are much higher in areas of original native forests. It should also be noted herein that evapotranspiration is also affected by the irrigation techniques and scheduling. Qiu et al. (2011) showed that total evapotranspiration of hot pepper cultivation in greenhouse increased by 55.5% using furrow irrigation compared to drip irrigation. Vieira de Azevedo et al., (2008) conducted a study on "Superior" grapevines in Brazil and showed that increased evapotranspiration was observed when increasing the irrigation time interval.

Wegehenkel (2002) examined the scenario of afforestation in Stobber-catchment located in Brandenburg, Germany, applying the hydrologic model THESEUS. The results of this research showed that an increase of the forest area from 34% to 80% would result in approximately 18% increase of evapotranspiration and a reduction of the river discharge from 39–41%.

Analogous to the previous study are the results obtained by Krause (2002), who applied the J2000 hydrologic modelling system in Mulde catchment in Germany. His results showed that the increase of forested areas resulted in increase of evapotranspiration and reduction of surface runoff and percolation to groundwater.

Besides the impact of crop type and irrigation techniques, evapotranspiration is also affected by other land uses such as urbanization. Haase (2009) conducted a study on the long term effects of urbanization on the water balance in the city of Leipzig in Germany and showed that the actual evapotranspiration decreases with the proportion of impervious land. In this case study it was found that in areas with a proportion of impervious land of >20–40%, evapotranspiration declines by 100 – 150 mm/a, whereas in areas with very high proportion of imperviousness (>80–100%), evapotranspiration diminishes by 450 mm/a. However, it seems that evapotranspiration diminishes in favour of direct run off, that seems to prevail in an urban environment.

5.2.2 Modifications of surface runoff due to land use changes

Modifications of surface runoff are expected due to various land uses. Agricultural activities cause a direct intervention to surface runoff modifying the stream network of a regime by the construction of drainage and irrigation networks and levees based on farmers' needs. Additionally, agricultural techniques such as tillage alter the natural runoff potential of an area. Infrastructures usually cause important runoff alterations. During the last decades the construction of large motor ways has become very frequent. Those constructions, usually act as barriers to surface runoff and in the majority of cases great interventions to the hydrologic regime are required in order to divert runoff and prevent flooding. Construction of dams for various purposes such as irrigation, power production or even flow regulation change the hydrologic status but also influence to a great extent the wetlands which are usually formed in the delta areas of rivers. Typical example is the Lule river in northern Sweden, strongly regulated with 15 hydro power stations that altered the natural water regime and caused groundwater deterioration.

Mining activities in the form of quarries, open cast and deep mines are also known to have an important impact on surface and ground waters as their operation requires surface water diversion and drainage of usable water from shallow aquifers. This usually results in lowering of water levels in adjacent areas and changes in flow directions within aquifers. Numerous studies concerning mine dewatering processes and their impacts on ground waters are found in relevant literature (Kavvadas and Marinos, 1994; Zipper et al., 1997; Li and Zhou, 2006; Wu et al., 2006; Panilas et al., 2007), highlighting the major disruptions in ground water regimes, both in the change of groundwater flows, recharge and discharge areas and the consequent effects such as the drying up of the associated springs. Contamination of waters due to mining activities is also regarded as a very serious aspect which is analysed in a following section. Panilas et al. (2007) used hydrogeological modelling in order to predict the possible hydrologic effects of the proposed lignite open-cast mining in Drama lignite field in northern Greece. They found that close to the mine area, the dewatering processes will result in the abandonment of the shallow wells as well as the decrease of the ground water pumping rates of the deep wells. In the broader area, the surrounding ditches and streams are expected to be affected from the mine drainage. Thus, the aquifer discharge towards the ditches will cease, while there will be an inversion of the ground water flow of the ditches towards the underlying aquifer. Also minor subsidence phenomena are expected due to groundwater level decrease. Another case is the Rokua esker field site within Genesis project, located in Northern Finland which is connected to small "kettle" lakes situated within the esker area. Most of these lakes have no outlet or inlet: the water level is dependent on the ground water level of the esker. Water levels of the kettle lakes have been declining for the past decades but the reason is still uncertain. Among the most probable reasons is the intensive peatland drainage mainly for forestry, but to some extent also for agriculture and peat harvesting that has been carried out in the surrounding wetlands since 1940's.

Several examples of ecosystems influenced by modification of surface runoff are found in the literature. The effects might be positive or negative depending on the specific case. In the past several drainage schemes have taken place in order to drain lakes and their wetland areas merely for providing fertile land to farmers and to stop the evolution of malaria. Several such cases exist, e.g the lake Kopaida and the lake Karla in Central Greece that were both drained during the last century. However the long term effects of those interventions, although for lake Kopaida are still believed to be positive, for lake Karla, on the contrary, the adverse effects on the surrounding ecosystems and groundwaters compared to the benefits are now regarded as severe and currently an attempt to restore the lake is taking place. The most famous, however, example of adversely impacted wetland area is the draining and development of the Everglades which dates back to the 19th century, aiming mainly in providing agricultural land. This in turn led to the introduction of large amounts of fertilizers which changed the natural ecology of the area. From 1970s' restoration of the Everglades became an international priority.

There should however be mentioned herein the positive effects brought in many cases by the construction of dams and the associated artificial lakes. Such lakes, among numerous others, are the Plastira lake in central Greece, formed in 1959 both for hydroelectric power production and for irrigation purposes. Over the years a very important ecosystem was developed within and around the lake, and the region is ever since one of the most popular summer and winter destinations in Greece. An analogous case is the one of Kerkini lake, formed during 1930s' in northern Greece, after the construction of a dam in Strymonas river. Today, the area is a unique wetland which is protected by the Ramsar Convention on Wetlands.

Stanzel et al. (2002) examined the changes expected to occur in hydrology of the Karagan lagoon after expansion of the irrigation scheme in the Uda Walawe basin in Sri Lanka. They applied two hydrologic models with very little input data and they found out that that drainage flows from the extended Uda Walawe scheme would lead to a significant rise in water level at the Karagan Lagoon throughout the year, preventing its drying up in summer and changing its characteristics from a seasonally hyper-saline to a freshwater wetland.

Regarding the effects of urban sprawls on surface runoff, Haase (2009) conducted a thorough study and concluded that the water regime in urban areas is shifting towards a direct run-off due to surfacing and sealing of open land. In the same study it is also pointed out the increased flooding risk mainly due to the increased release of water out of the urban system. Other effects of urbanization pointed out in relevant literature are the decline in the water retention and filtering capacity of soils and surfaces for pollutants (Collin and Melloul, 2003; Emmerling and Udelhoven, 2002).The long term effects, however, are related to the distribution and spatial pattern of converted land and its previous quality (Newman, 2000; Burchell and Mukherji, 2003; Nuissl et al., 2008).

5.2.3 Land use effects on groundwater recharge and groundwater storage

It is commonly accepted that almost all human activities interact with groundwater resources, either modifying the recharge quality and quantity or even altering the groundwater storage and flow patterns. Taking into account that many important ecosystems are groundwater dependent, it is easily appreciated how a modification in the natural chain of water resources may easily cause dramatic and even unpredictable effects on ecosystems.

Typical examples of groundwater recharge reduction are examined within the FP7 GENESIS project. The Kromme Rijn site, located in central Netherlands, is one of them, where groundwater abstractions in the upland areas for domestic supply in combination with water use for irrigation and changes of discharge characteristics of the river Rhine caused a decline in associated groundwater levels in this pilot area. The Mancha Oriental aquifer system, located in south-east Spain, provides water for 80,000 hectares of irrigated agriculture. The considerable development of irrigation systems during the 1975-2000 period has caused a significant decrease in the piezometric levels of this aquifer, provoking a serious streamflow depletion in the connected Jucar river. Vosvozis river basin, located in north east Greece, is another test site within GENESIS project which can be considered as typical of the human intervention on its water regime. Unsuccessful attempts to dewater the area through channels to the sea, let seawater enter the coastal wetland area. Intensive pumping for irrigation changed the natural groundwater flow from the aquifer to the coastal area, intruding thus seawater from the coastal wetland to the freshwater aquifer and causing groundwater quality deterioration.

The Zagreb aquifer in Croatia is also known to be affected by the adverse effects of overexploitation, where groundwater abstractions for domestic, agricultural and industrial uses caused serious ground water level drawdown which have already reached minimum on some well fields, leading to water scarcity during droughts.

Whether, however, recharge will be decreased or increased is really dependent on the type of land use compared to its previous status. A recent global review found that recharge is two orders of magnitude higher through crops than through original native forests (Scanlon et al., 2007; Lerner and Harris, 2009). The results of the previous research are in agreement with a study of 50 years of the Mississippi River. During this period much of the perennial vegetation has been replaced by seasonal crops such as soybeans. At the same period baseflow has increased significantly (Zhang and Schilling, 2006; Lerner and Harris, 2009). Those effects might be attributed to the increased evapotranspiration demands which are found to be much higher in areas of original native forests (Lerner and Harris, 2009).

Another interesting aspect is quoted in the work published by Lerner and Harris (2009) concerning the effects of urbanization on groundwater recharge. As a great portion of the urban areas are converted to impermeable surfaces, one could expect that with less precipitation infiltration, a decreased amount of recharge would take place compared to rural areas. Deal and Schunk (2004) argue that surfacing open land, especially in connection with the density and intensification of the urban drainage network, results in higher and accelerated direct runoff flows and in a direct fall in the groundwater recharge rates and subsequently also in the low-water flow of receiving water. The situation seems however to be a bit different as described by Lerner (2002) and others as well, that showed that urban recharge is similar or even higher than rural recharge because: a) rainwater is usually routed from the urban draining system to the groundwater, whereas not all urban surfaces are impermeable and b) large volumes of water (typically 25% of the urban water supply) are returned to groundwater through leakages from water mains and the sewing systems of the urban areas. Nevertheless, leakages from the sewing systems may also pose serious quality problems to groundwaters (Chisala and Lerner, 2008). Based on the above, urbanization may have an impact on groundwater recharge, which is related to the degree of imperviousness of the urban surfaces and the quality and density of the drainage and sewing network. It is believed that in order to reach a sound conclusion, each specific case should be examined separately as there is no general rule.

5.2.4 Quality issues from land use changes

After water reaches earth's surface or enters the substrate as recharge, it is subjected to natural interactions with the surrounding geological formations which alter its chemical composition. This chemical composition is usually referred as baseline concentration or natural background level (NBL). It is thus true that water quality is naturally highly variable and it is very essential to know the natural composition of water in order to understand the trends and impacts of contaminants introduced by human activities. According to the Article 3 (5) of the Groundwater Directive (GWD) (GWD 2006/118/EC) Member States were obliged to establish groundwater threshold values (TVs) by the end of 2008 and to publish them in the Water Framework Directive (WFD) (WFD 2000/60/EC)) river basin management plans. Although GWD does not provide specific guidelines for TVs determination, various approaches exist which are described in the Publishable Final Activity Report of the BRIDGE project (BRIDGE 2009). Based on this methodology groundwater threshold values are assessed based on Environmental Quality Standards (EQS) regarding groundwater as 1) a resource, 2) groundwater 'itself', or 3) an ecosystem. The final BRIDGE methodology proposes a combination of NBLs and EQS for the determination of groundwater threshold values.

Besides the natural processes that alter the chemical composition of water and should be taken into account, it is beyond any dispute that human activities pose a serious threat on water quality.

Groundwaters are sensitive to both point and non-point (diffuse) sources of pollution. Many groundwater vulnerability assessment methods appeared in the relevant literature. The most common ones are the DRASTIC system (Aller et al., 1987), the GOD system (Foster 1987), the AVI rating system (Van Stempvoort et al., 1993), the SINTACS method (Civita 1994), the ISIS method (Civita and De Regibus 1995), the Irish perspective (Daly et al. 2002), the German method (Von Hoyer and Sofner 1998), the EPIK (Doerfliger et al., 1999) as well as the methodologies presented by Dixon et al. (2002), Dixon (2005) and Gemitzi et al. (2006). As stated by Gogu and Dassargues (2000) and Gemitzi et al. (2006), the vulnerability of groundwater to pollution includes two basic parameters: a) intrinsic vulnerability i.e, the vulnerability of groundwater to contaminants generated by human activities, taking into account only the inherent hydrogeological characteristics of the area, and is independent of the nature of the contaminants and b) specific vulnerability which is specified for a particular contaminant or group of contaminants. The latter is related directly to various land uses as those will determine the specific contaminants released to the environment. How easy each pollutant will travel from its release to the final discharge point is mainly dependent on the intrinsic aquifer properties. Therefore it is essential to have detailed hydrogeological information in order to assess the potential for pollution and to estimate the fate of pollutants.

The most common pollutants are nitrates which are related to the application of both inorganic and organic fertilizers in agricultural areas and form a diffuse source of pollution. Nitrates in combination with phosphates cause eutrophication to surface water ecosystems. Nitrates however may also be the product of point sources of pollution, originating mainly from livestock farms. Wakida and Lerner (2005) point out the significant nitrate concentrations, similar to those in agricultural areas, which occur in aquifers beneath cities from leaking sewers, contaminated land and landfill leachates. Numerous aquifers and ecosystems all over the world suffer from nitrate pollution. Typical cases are examined within Genesis project such as the Po river valley in Italy, the Mancha Oriental aquifer system in Spain, the Czestochowa aquifer in Poland, the Vosvozis river site in Greece, the Grue site in Norway, the Kromme Rijn site in Netherlands.

Microbiological pollution is also a very serious threat, originating from leaking sewing systems, septic tanks or accumulation of manure. A crucial parameter while examining the possible impacts of the microbiological pollution is the travel time of the pollutant to the discharge point. If the travel time is long enough for the biodegradation processes to diminish the pollution, no risk to human health is expected. Special attention should be paid to karst aquifers, as the high groundwater velocities may result in increased risk for public health. Such a case is observed in Areuse spring in Switzerland, where indicators of contamination with faecal matter are regularly detected at the spring during flood events.

Agricultural land uses are also related to high pesticide concentrations. They are regarded as very harmful for human health, thus drinking water standards for pesticides are set very low (0.1μg/l) for each individual pesticide. However, their metabolites also pose an unquantifiable threat, since they are seldom analyzed (Lerner and Harris, 2009). Pesticides may also originate from point sources of pollution. Such is the case of Bitterfeld in Germany, a huge former industrial area located at the flood plains of the Mulde. One former open pit mine was used as an industrial dump site and was filled with waste of the production of Lindane and other pesticides, which are now forming huge contamination plumes and are partly leaking into open water bodies functioning as principle draining systems.

Over pumping of coastal aquifers for irrigation or domestic uses may lead to salt water intrusion and a subsequent deterioration in groundwater quality. High salinity values are also related to the use of salt in roads in order to remove ice, especially in northern countries.

Mining industry is known for its contribution to water pollution mainly with heavy metals and in the form of acid mine drainage in areas where sulphide minerals are present. Mining activities are not the sole source of heavy metals which may originate from other industrial activities and from landfills as well.

In fact, almost all processes related to manufacturing, handling and storing of chemicals may cause water pollution in the surrounding areas. Lerner and Harris (2009) state that amongst the most frequent pollutants are the chlorinated hydrocarbons (DNAPL) and the petroleum hydrocarbons (LNAPL) which are related to the most common chemicals. They originate from the storage and use of petroleum based fuels (airports, military bases, petrochemical industry, etc) and industrial chemicals used in the manufacturing industry.

Recently, much research is focused on Organic Wastewater Contaminants (OWC), also known as emerging pollutants and comprise all the trace organic compounds that can reach waters via sewage systems (Daughton, 2004; Focazio et al., 2008; García et al., 2010; Balderacchi et al., 2011). The United States Geological Survey includes in this list: pharmaceuticals, surfactants, flame retardants, plasticizers and sterols. A problem related to those substances is that they are not eliminated in the wastewater treatment plants, therefore the most frequent sources of those pollutants are the sewage-system leaching and sewage system and treatment plants for human pharmaceuticals and manure and sewage sludge in agriculture (Balderacchi et al., 2011).

Radionuclides are perhaps the most harmful pollutants. Nuclear power plants manufacturing industry, hospitals, application and disposal of man-made radionuclides are the main anthropogenic sources of those substances in the environment. Under normal conditions and because all the previously mentioned activities are subject to strict regulatory controls only minute amounts of radioactivity are released to the environment (Balderacchi et al., 2011). However, nuclear accidents such as the Chernobyl and the Fukushima, provided really bitter experiences to humanity.

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