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# On some methodological problems in the use of environmental tracers to estimate hydrogeologic parameters and to calibrate flow and transport models

Andrzej Zuber · Kazimierz Róžański ·  
Jarosław Kania · Roland Purtschert

**Abstract** Environmental tracers are used qualitatively for a better formulation of conceptual models and quantitatively for assessing groundwater ages with the aid of box models or for calibrating numerical transport models. Unfortunately, tracers often yield different ages that do not represent uniquely the water ages. Difficulties result also from different definitions of age, e.g. water age, advective age, tracer age, or radiometric tracer age, that are measured differently and depend on aquifer parameters and characteristics of particular tracers. Even the movement of an ideal tracer can be delayed with respect to the advective movement of water due to diffusion exchange between mobile and immobile water zones, which for fissured rocks or thin aquifers, may lead to significant differences between advective and tracer ages, i.e. also between advective and tracer velocities. The advective

velocity is of importance in water resources considerations as being related to Darcy velocity, whereas the tracer velocity is a more useful term for the prediction of pollutant transport. When a groundwater system changes from one hydrodynamic steady state to another, environmental tracers need much more time to reach a new steady state. Several tracer studies are recalled as examples of tracer-specific effects on the estimations of groundwater age.

**Keywords** Environmental tracers · Groundwater age · Tracer age · Hydrodynamic age · Numerical modeling

## Introduction

Tracer methods found numerous applications in groundwater hydrology, being particularly useful at the initial stages of investigations for determining the origin of water as well as for identifying recharge areas, mixing patterns and other parameters needed for the formulation of adequate conceptual models of the studied systems.

Nowadays, two tracer-based approaches aimed at quantitative determination of flow and transport parameters in active groundwater systems are in common use. In the first approach, tracer data serve as a tool for quantifying the age of water, which in turn can be used for calculating some parameters related to the studied groundwater system such as recharge rate, flow velocity and hydraulic conductivity or for the estimation of its vulnerability to potential pollutants. In the second approach, the measured concentrations of tracer(s) are used for calibration or validation of transport and flow models, and, if necessary, for correction of the conceptual model. Recently, more common is the second approach in which numerical transport models are fitted to spatial and temporal distributions of tracers.

The first approach is applied when tracer data are to be interpreted in terms of groundwater age (other terms like turnover time, residence time, timescale or transit time are

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A. Zuber  
Carpathian Branch,  
Polish Geological Institute,  
ul. Skrzatów 1, 31560, Kraków, Poland  
e-mail: andrzej.zuber@pgi.gov.pl

K. Róžański  
Faculty of Physics and Applied Computer Sciences,  
AGH–University of Science and Technology,  
Al. Mickiewicza 30, 30059, Kraków, Poland  
e-mail: rozanski@novell.ftj.agh.edu.pl

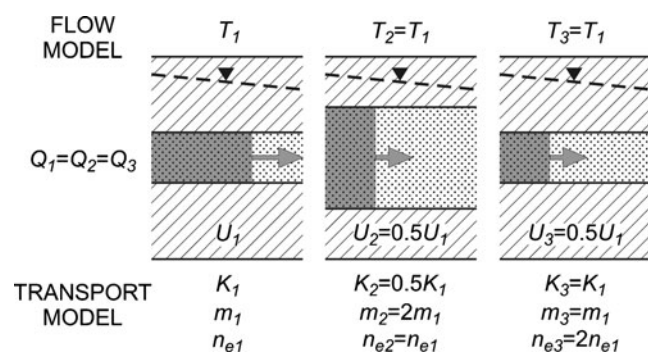
J. Kania (✉)  
Faculty of Geology, Geophysics and Environmental Protection,  
AGH–University of Science and Technology,  
Al. Mickiewicza 30, 30059, Kraków, Poland  
e-mail: jkania@agh.edu.pl

R. Purtschert  
Physics Institute,  
University of Bern,  
Sidlerstrasse 5, 3012, Bern, Switzerland  
e-mail: purtschert@climate.unibe.ch

in common use). For stagnant and active groundwater systems, the age of water is the time span since its last contact with the atmosphere. However, for active systems, especially those containing young waters, different methods are in use to quantify that important parameter (e.g. Solomon et al. 2006; Kazemi et al. 2006); some of these methods are discussed further. Lumped-parameter models (box models) are often used for the determination of groundwater age; the expected distribution of flow lines and the hydrologic situation usually guide the selection of the appropriate category of the model.

In the second approach, tracers are needed because numerical transport models based on flow models, even if properly calibrated by common procedures (fitting the distribution of water heads and balancing the volumetric flow rates), are insufficient to describe adequately the velocity (or age) of water, which is the governing parameter of solute (tracer, pollutant) migration. Figure 1 illustrates schematically the fact that transmissivity and volumetric flow rates obtained from numerical flow models do not define the flow velocity in a unique way, even for a homogeneous medium where the flow velocity is the governing parameter of solute (tracer) migration. For known transmissivity and volumetric flow rate, the flow velocity can be over- or underestimated depending on the hydraulic conductivity, the aquifer thickness and/or the effective porosity. Under favorable conditions, environmental tracers supply information on water age, hence on the flow velocity which is the governing transport parameter. The knowledge of that parameter often leads to the recalibration of the flow model and/or to corrections of the conceptual model.

The dispersivity is another important aquifer parameter for the prediction of pollutant migration that can in some cases be estimated either theoretically or from data in the literature; its direct determination is possible with the aid of suitable artificial-tracer methods. In some cases environmental tracers can also supply information on the dispersivity in the studied systems.



**Fig. 1** A schematic example presenting differences between governing parameters of flow and transport models in porous aquifers ( $T$  transmissivity;  $Q$  volumetric flow rate;  $U$  interstitial flow velocity;  $K$  hydraulic conductivity;  $m$  aquifer thickness;  $n_e$  effective porosity)

Numerous examples illustrating the use of environmental tracers in the context of box models (nearly all applications of  $^{14}\text{C}$ ; for transient tracers, see e.g. Małozewski and Zuber 1982, 1996; Zuber 1986a; Kendall and McDonnell 1998), and at different stages of numerical flow and transport modeling, are available in the literature (e.g. Robertson and Cherry 1989; Barmen 1994; Voss and Wood 1994; Engesgaard et al. 1996; Castro et al. 1998; Castro and Goblet 2003; Zoelmann et al. 2001; Bauer et al. 2001; Mattle et al. 2001; Izbickei et al. 2004; Troldborg et al. 2007; Stichler et al. 2008).

Difficulties in the use of environmental tracers result from potential differences in their transport characteristics in relation to water, like exchange with immobile reservoirs (diffusion into immobile water zones and, in case of  $^{14}\text{C}$ , possible interaction with solid carbonates), input functions difficult to reconstruct (e.g. seasonally variable  $^3\text{H}$ ), possible diffusion exchange of gaseous tracers with the atmosphere through the unsaturated zone, underground production ( $^{39}\text{Ar}$ ,  $^{36}\text{Cl}$ ), contamination (chlorofluorocarbons), and others. Although available tracers and their characteristics are thoroughly described in the literature (e.g. Clark and Fritz 1997; Cook and Herczeg 2000; Mook 2001; IAEA 2006), the choice of adequate tracer(s) and appropriate sampling strategies is not straightforward, particularly in early stages of investigations when timescales of the studied aquifer are not well known. The wide range of possible groundwater ages requires a corresponding set of tracers with suitable characteristics, which are not always available.

The aim of this contribution is to discuss some complications encountered in the use of the most common environmental tracer methods for quantifying the hydrogeologic parameters of active groundwater systems with the aid of the lumped-parameter and numerical models. For a better understanding of the behavior of environmental tracers, some basic principles well known in artificial tracing are recalled. The discussion is mainly based on the authors' personal experience and is aimed at the wide readership of field hydrogeologists, though some aspects can be also of interest to researchers.

## Definitions of water age

Groundwater dating is a broad subject with a well-developed theoretical basis (e.g. Cornaton and Perrochet 2005; Castro and Goblet 2005; Solomon et al. 2006; Kazemi et al. 2006; Varni and Carrera 1998). However, an ordinary user of the tracer methods is usually not familiar with all theoretical problems of groundwater dating. Therefore, within this section, some basic definitions and concepts related to groundwater age are recalled.

Generally, groundwater age is defined as the time span since the last contact of water with the atmosphere, as discussed in the previous, and that definition is valid for both stagnant and active groundwater systems. For stagnant (buried) systems, the age is usually evenly distributed within the system due to the long-lasting

effects of molecular diffusion. In active systems, water flows along different flow lines; thus, its ages are distributed within the system and at sampling sites where different flow lines converge. Stagnant water systems, as well as the spatial distributions of ages within the active systems, are excluded from further discussion. The reader interested in the latter subject is referred to Cornaton and Perrochet (2005), Solomon et al. (2006) and Kazemi et al. (2006).

Quantitative determination of the groundwater age at the outlet (drainage area) or at a given site in the system (sampled well) depends on either the measurement method or the interpretation model. Travel (transit) time can be used as the synonym of age, whereas for the known flow distance, the term groundwater velocity can be used.

The advective age is defined by pore water velocity (advective velocity,  $U$ ) which results from the Darcy velocity ( $q$ ) divided by effective porosity ( $n_e$ ), i.e., the porosity in which the movement of water takes place. For fissured rocks, the effective porosity is usually nearly equal to the fissure porosity ( $n_f$ ). The advective age of individual flow lines ( $t_{ad}$ ) is given by Eq. 1 (e.g. Varni and Carrera 1998; Castro and Goblet 2005):

$$t_{ad} = \int_{x_0}^{x_1} \frac{dx}{U(x)} = \int_{x_0}^{x_1} n_e(x) \frac{dx}{q(x)} \quad (1)$$

where  $x_0$  is the beginning of the flow line in the recharge area, and  $x_1$  is the observation point on the trajectory of that line. That definition also applies to whole systems that can be approximated by the piston flow model, i.e. by flow lines of equal length and velocity, with no longitudinal dispersion. The mean advective age can also be 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. Other terms in use for the advective age are the hydrodynamic age, kinematic age, and mobile water age.

In the reservoir theory, the exit age distribution function ( $E$ ) represents the exit distribution of the medium (water) flowing through the investigated system. That function can be described as the exit distribution of the normalized concentration of a conservative tracer ( $C_1$ ) instantaneously injected at the entrance to the system:

$$E(t) = \frac{C_1(t)}{\int_0^{\infty} C_1(t) dt} \quad (2)$$

If there is no diffusive or dispersive exchange of the tracer between flow lines, that equation also represents the exit distribution of flow lines, i.e., the distribution of advective ages. In the case of exchange of tracer between the flow lines, the tracer distribution is governed by both the flow lines and exchange effects. However, if the exchange rate of tracer molecules differs from that of

water molecules, the distribution of tracer may differ from that of water. If stagnant water zones are present in the system, and the tracer exchanges by diffusion between the advective and stagnant zones, the observed tracer distribution becomes delayed in relation to the advective distribution. Thus, the exit tracer distribution may differ from the exit distribution of active flow lines and from the exit distribution of water molecules, the last one being understood as the distribution of exit water age.

For systems in the hydrodynamic steady-state, the mean value of the age (transit time) can be derived from the  $E(t)$ -function as:

$$t_t = \int_0^{\infty} tE(t) dt = \frac{\int_0^{\infty} tC_1(t) dt}{\int_0^{\infty} C_1(t) dt} \quad (3)$$

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 ( $t_{ad}$ ), independently of the exchange between the flow lines. In the case of exchange with stagnant zones, both ages are larger than the mean advective age and may differ, if water molecules exchange differently then tracer molecules due to different coefficients of molecular diffusion or due to differences in size, which make some small-size stagnant zones (micro-pores) non-accessible for molecules that are too large.

Equation 3 is formulated for the outlet of the system but it can also be used at any point within the system, and represents the basic concept in the use of box models for the interpretation of tracer data in hydrogeology in terms of groundwater age, where the continuous appearance of an environmental tracer at the inlet to the system (recharge area) is taken into account by the convolution integral, when calculating tracer concentration at the outlet of the system (e.g. Małozzewski and Zuber 1982, 1996; Zuber 1986a). If stagnant water zones accessible to tracer are present in the investigated system, the advective age is not measurable, whereas the tracer age will represent the water age, with some limitations previously mentioned and also discussed in section [Relations between the movement of water and tracers](#).

The groundwater age can be simulated directly when the concentration in the transport equation is replaced by the product of water mass and age (Goode 1996; Castro and Goblet 2005). If the exchange with stagnant zones is neglected in the transport equation, then the advective age is obtained. However, if the stagnant zones are properly accounted for in the transport equation, the water age of the whole system is obtained. Similarly, the distributions of water ages or advective ages can be obtained from adequate numerical codes of the transport equation, if an instantaneous injection of a conservative tracer is applied over the whole recharge area. Then, the temporal tracer distribution calculated for any site will represent the required age distribution, whereas the mean age is obtainable from Eq. 3. Numerical age simulations require

a good knowledge on the values of a number of transport parameters which is seldom the case; thus, they cannot replace the use of tracer methods.

Changes in the concentration of radioactive tracers with a constant, or quasi constant, input are interpretable in terms of age. In common use is the radiometric age ( $t_a$ ), defined by Eq. 4 for piston flow systems, whereas for systems with an exponential distribution of flow lines and without mixing between the lines Eq. 5 applies:

$$t_a = \frac{1}{\lambda} \ln\left(\frac{c_0}{c}\right) \quad (4)$$

$$t_a = \left(\frac{c_0}{c} - 1\right) / \lambda \quad (5)$$

where  $c$  and  $c_0$  are the measured and initial concentrations, respectively, and  $\lambda = \ln 2 / T_{1/2}$  is the radioactive decay constant. When the  $c_0/c$  ratio is close to one, both models yield similar age values. In general, the larger the  $c_0/c$  ratio, the older the ages, with those yielded by Eq. 5 becoming older than those yielded by Eq. 4. It is evident from the preceding discussion that different age definitions are in use, and that measured tracer ages may differ from the sought quantity, i.e., the water or advective age.

## Conceptual models

Discussion of the definition of a conceptual model, though trivial, appears to be justified considering numerous options existing in the literature. A general definition adequate for all kinds of groundwater studies is recommended here as also adequate for modeling tracer data (NEA 1990; Małoszewski and Zuber 1992, 1993). According to that definition, a conceptual model is “a qualitative description of a groundwater system and its representation (e.g. geometry, lithology, hydrogeologic parameters, initial and boundary conditions, and hydro-geochemical and/or hydrobiochemical reactions) relevant to the intended use of the model”. The conceptual model is derived from available data and contains theoretical variables and hypotheses relevant to the planned investigations. The conceptual model can be presented as a written description and/or graphically as a map, cross-section or block-diagram; its development is a must for any kind of hydrogeologic, hydrochemical and tracer investigation, and especially also for numerical modeling.

Because of the inherent spatial and temporal averaging properties of environmental tracers, the use of such tracers provides insight on the flow and transport dynamics in aquifers on temporal and spatial scales, related to the timescales of the used tracers, which cannot be obtained by other methods. Environmental tracers may supply information on the presence of heterogeneities of geological structures, which are difficult to recognize and/or to describe quantitatively (Harrar et al. 2003; Poeter

2007). For instance, Troldborg et al. (2007) showed that four different conceptual models of a multilayered Quaternary aquifer yielded quasi-identical head distributions but different ages and different concentration distributions of transient tracers. Thus, tracers may help to construct an adequate conceptual model.

## Quantitative modeling approaches

### Box models

Box models are the simplest mathematical models commonly used to interpret tracer data in terms of groundwater age. For environmental tracers, the model type usually defines the age distribution of tracer, which mainly stems from the age distribution of flow lines. This is in contrast to artificial tracing where the tracer age distribution (breakthrough curve) resulting from an instantaneous point injection usually depends mainly on the hydrodynamic dispersivity and the dispersion caused by matrix diffusion (e.g. Małoszewski and Zuber 1985).

The most typical distributions of flow times and ages in homogeneous groundwater systems are represented by several categories of box models that can be chosen according to one of the simplest conceptual models of a flow system, i.e. single parameter piston-flow model (PFM) and exponential model (EM), and two-parameter models, like the piston-flow and exponential models connected in line (EPM), and the dispersion model (DM) (e.g. Małoszewski and Zuber 1982; Zuber 1986a). In the piston flow model, dispersion is neglected and all the flow lines have the same travel time. In the exponential model, the ages of flow lines are distributed exponentially, i.e. from zero to infinity, and the exchange of tracer between flow lines is neglected. The EPM, which combines the PFM and EM in line, is more realistic as the zero-age flow-lines are excluded. The ratio of the total volume to the exponential flow volume is, besides the mean age, the second parameter of that model. The dispersion model is the most flexible of all available categories of box models because its second parameter, the dispersion parameter, represents both the age distribution of flow lines and the dispersivity caused by heterogeneity, hydrodynamic dispersion and matrix diffusion effects. Other available categories of models do not offer much wider interpretation possibilities (e.g. Amin and Campana 1996).

For all models, it is possible to assume or fit an additional parameter that represents a tracer-free component (Małoszewski and Zuber 1996). If that component is of different origin than the main component, its fraction can be determined with the aid of stable isotopes (e.g. Małoszewski et al. 1990). Other tracers that date older waters (e.g.  $^{14}\text{C}$  or  $^4\text{He}$ ) can also be helpful in identifying the presence of an old water component in modern water (e.g. Zuber et al. 2004).

For reliable age interpretation, a long time series of the data should be available. However, even if the available series are several years long, several models with contrasting age values can yield equally good or equally

poor fit. Then, if possible, other constraints (e.g. depth of sampling) have to be taken into consideration for the final selection of the model.

Tracer investigations of small and medium-size aquifers usually have to be concluded in 1 or 2 years. In such cases, with the resulting short time series of tracer data, only the PFM and EM yield unique age results, which are often far from true values due to the simplified nature of these models. To improve the results of tracer dating in such cases, several transient tracers are simultaneously measured, and the data of selected pairs of tracers are compared in two-tracer plots with theoretical relations calculated for the PFMs and EMs. If no agreement between measured and calculated values is obtained, the presence of a tracer-free component is assumed, and the binary mixing models (BMM) are additionally used to interpret the data of selected tracer pairs (Loosli et al. 2000; Plummer et al. 2006). Then, the interpretation yields the PFM or EM tracer age for the tracer-containing flow component and the fraction of tracer-free water. The BMM represents nothing other than the option of the tracer-free component in other models discussed in the previous; however, a significant difference lies in their use for the interpretation of two-tracer plots, e.g. relations of  $^3\text{H}$  and  $^{85}\text{Kr}$  (Loosli et al. 2000) or CFC-12 and CFC-113 (Plummer et al. 2006).

If a sufficiently long time series of transient tracer data are available at chosen sampling sites like springs or abstraction wells, more sophisticated models can be used. Long time series of  $\delta^{18}\text{O}$  (or  $\delta^2\text{H}$ ) variations resulting from their seasonal variations in precipitation are easily available for systems with very young waters. Sometimes also tritium time series are available for systems which were investigated some time ago and were re-sampled more recently. Then, in addition to single-parameter models (like PFM and EM), two-parameter box models (like DM and EPM) can effectively be used, which supply more reliable information on both the mean age and the age distribution. The type of box-parameter model is either assumed a priori based on the hydrologic situation or selected from several available categories in the process of fitting (calibration).

Due to a short half-life (12.32 years, Lucas and Unterweger 2000), tritium accumulated in the environment as the result of nuclear bomb tests becomes nowadays less applicable than in the previous decades. Paradoxically, the box modeling of the tritium bomb peak would be much more useful if the half-life were much longer or even infinite because then its disappearance in groundwater systems would be caused only by dispersion. Theoretically, the sum of  $^3\text{H}$  and tritiogenic  $^3\text{He}$ , expressed in tritium units (TU), should represent such a pulse. However, if the thickness of the unsaturated zone is not negligible, the escape of  $^3\text{He}$  to the atmosphere makes that approach unreliable. An additional limitation of this approach, and also of the  $^3\text{H}/^3\text{He}$  method, results from significant uncertainties associated with the extraction of the tritiogenic  $^3\text{He}$  signal from the total measured  $^3\text{He}$ .

The tracer age obtained with the aid of a box model may differ considerably from the groundwater age due to differences between assumed and real distributions of the flow lines. Therefore, the model(s) should be chosen with care and their limitations kept in mind to avoid misinterpretation of the results. In that respect, it is important to remember that the EM requires the presence of infinitesimally short flow times (lines) which do not exist when the sampling is performed in wells screened at depth. However, they may exist when shallow groundwater systems are drained by springs, streams, or rivers (Małozzewski and Zuber 1982). Abstraction wells situated in or close to recharge areas are usually characterized by very wide age distributions which can be reasonably approximated by the EMs or EPMs. In homogeneous systems, at large distances from the recharge area, the age distributions of flow lines are narrow in relation to the mean age, which makes acceptable the application of the PFM to the interpretation of such radioactive tracers like  $^{39}\text{Ar}$  and  $^{14}\text{C}$ , characterized by constant or quasi-constant inputs. Possible influence of increasing hydrodynamic dispersion along flow paths is usually neglected in the age interpretation of these tracers when other uncertainties, particularly for radiocarbon, are considered. However, Castro and Goblet (2005) showed that for the heterogeneous systems, particularly in the cases of low flow velocity, both the longitudinal and lateral dispersion may significantly influence the  $^{14}\text{C}$  ages.

A box model may yield the mean age which is larger than the time span since the first appearance of an airborne tracer used in the modeling. Such situations occur at sampling sites with wide age distributions (e.g. exponential) where short flow lines contain transient tracers, whereas other lines are free of them (Zuber et al. 2005).

As a consequence of the inadequacy of some models to represent field situations, serious discrepancies may occur between tracer ages and water ages. To emphasize such possible discrepancies the term “apparent age” is common in relation to groundwater ages obtained with the aid of different interpretation methods of tracer data. As the interpretation methods often remain unreported in detail, in order to reduce possible misunderstandings, a more detailed description can be suggested, e.g. “ $^{14}\text{C}$  piston-flow age” (uncorrected or corrected), “ $\text{SF}_6$  piston-flow age”, or “ $\text{SF}_6$  exponential-flow age”, etc. Then, the reader will be informed which tracer and the type of approximation was used. A more comprehensive discussion on simple box models and their advantages and disadvantages in the interpretation of environmental tracer data can be found in Małozzewski and Zuber (1996).

### **Numerical models**

Numerical transport models are based on flow models which were calibrated to water table elevation and volumetric flow rates. The use of tracers to calibrate transport models and eventually to correct the flow and conceptual models can be therefore regarded as a second step in the process of model calibration (recalibration). Numerical models can, in principle, account for any heterogeneity of the studied system by using sufficiently

small computational cells. However, in practice, neither the knowledge of geology is complete nor the tracer data are of adequate resolution to supply sufficiently detailed information needed for the construction of a model that would account for all heterogeneities of the system under consideration. Uncertainties resulting from these limitations can be assessed and reduced to some extent by considering different conceptual models and/or by using stochastic approaches in which, instead of fixed values of the hydrologic parameters, their stochastic distributions are employed (e.g. Dagan 1983; Li et al. 2003; Neuman 2004), and random boundary conditions can be included (Shi et al. 2008). However, it seems that for numerical transport modeling, deterministic approaches are so far preferred by field hydrogeologists.

Tracer data are often scattered (both in space and time) in a way which is difficult to account for in the framework of the adopted conceptual and numerical models. Then, the modeler may either use their spatial averages as representative values for the mean migration patterns, or increase the number of cells in two or three dimensions to search for satisfactory agreement of the model with the data. In the first case, eventual disagreement between the model and available data may indicate the presence of some structure(s) unaccounted for by the conceptual model. In the second case, the modeler should be aware that in spite of a better fit, the number of free parameters may increase in an uncontrolled way, and still there is no guarantee that the solution obtained is representative and unique. Though the “best-fit” model is always sought, it is not necessarily the most adequate description of the system.

Numerical flow and transport modeling can be combined with box modeling. For instance, Stichler et al. (2008) showed that a numerical water flow model which was calibrated to the hydraulic heads only (with examined water balance) gave ambiguous results of the hydraulic conductivity (velocity) distributions in the area of a surface reservoir. This in turn yielded different capture zones of a production (pumping) well. Seasonal variations of the stable isotope data interpreted with the aid of box models yielded the values of hydraulic conductivities along particular flow lines, which were then used to (re-)calibrate the numerical flow and transport models. As a final result, a unique description of the capture zone was obtained.

### **Other modeling approaches**

Apart from the most common approaches described in the previous, there are two other important approaches towards modeling of environmental tracer data, which have different names but can collectively be described as multi-cell models and multi-cell multi-tracer models. They can be regarded as an intermediate approach between lumped-parameter modeling and fully distributed modeling. These multi-cell models are particularly useful for the interpretation of scarce data in large aquifers which cannot be approximated by lumped-parameter models due to the complexity of flow paths and mixing patterns. A complete description and some examples of such approaches can be found in Campana (2002). Some

modifications of the multi-cell approach are discussed by Tescan (2002). Modelers should be aware that the number of cells usually exceeds the number of data, and, as a consequence, the results of modeling in such cases can be ambiguous. The multi-cell and multi-tracer models which make use of isotope and chemical data assigned to each cell seem to be free of such ambiguities though their uncertainties may result from non-conservative behavior of the chemical constituents of the water. A description of that approach can be found in Adar and Kuell (2002) and Adar et al. (2002).

### **Model validation**

In the context of the modeling process, serious controversies and differences exist concerning the term ‘validation’. Some authors argue that validation is a false term because models cannot be validated but only invalidated (Bredehoeft and Konikow 1992; Oreskes et al. 1994; Konikow 1996). Bredehoeft (2003) even proposed to use the term ‘well-calibrated model’ instead of ‘validated model’. However, this term may also lead to misunderstandings. A good fit is a necessary condition for any model calibration but not a sufficient one to prove the adequacy of the model.

Validation can be understood as a practical term for describing a procedure which gives some kind of assurance that the chosen model satisfies the assumptions related to the process or system with the accuracy acceptable for the user. The validation process can be regarded as successful, if the calibrated model yields agreement with a new data set extended in space or time. The model can also be regarded as validated if the values of parameters resulting from the calibration process are in agreement with those obtained from other methods. Partial validation is achieved if the model describes satisfactorily only some parts of the system or selected processes; for instance, when the migration velocity is adequately represented by the model but not the dispersivity (Małozzewski and Zuber 1992, 1993).

In spite of serious objections to the meaning of the term ‘validation’, its use is quite common (e.g. Castro and Goblet 2003; Abbasi et al. 2004; Hasaan 2004a, b). The quality of the validation process strongly relies on experience and judgment of the modeler. Contrary to calibration, this is mainly a qualitative process. As “a geologic report is always a progress report” (N.W. Bass according to Bredehoeft 2003, 2005), with the availability of new data, the conceptual and mathematical models usually require adjustments.

### **Relations between the movement of water and tracers**

#### **Exchange of tracer between mobile and immobile reservoirs of water**

An ideal tracer is a substance that behaves exactly as the traced medium and has one property that distinguishes it from the traced material. The most ideal tracers of water

( $^3\text{H}$ ,  $^2\text{H}$  and  $^{18}\text{O}$ ) trace the water molecules, but not the volumetric flow which is of interest in water resources considerations. Some limitations of the tracer methods resulting from the lack of ideal substances to trace the mass transport of water are discussed in the following.

In fissured aquifers, the movement of tracers is delayed with respect to the movement of advective water due to diffusion exchange between advective water in fissures and stagnant water in the microporous rock matrix, as pointed out in the early works of Foster (1975), Freeze and Cherry (1979) and Neretnieks (1980). The tracer age in fissured aquifers with a porous matrix is related to the advective water age by the diffusion retardation factor, i.e., the mean advective water velocity is equal to the mean tracer velocity multiplied by that factor. For densely fissured rocks, with matrix porosity as the only stagnant water reservoir which is fully penetrated by the tracer, that factor is in a good approximation equal to the ratio of total porosity to the fissure porosity, which means that the tracer moves as if the water flow were through the whole open porosity, whereas, in fact, the mass transport of water (advective flow) usually takes place only in the fissure space (Neretnieks 1981; Małozzewski and Zuber 1985, 1991). Matrix porosity ( $n_p$ ) is usually much larger than fissure porosity ( $n_f$ , usually equal to effective porosity), which leads to the retardation factors of the order of 10–100, with the largest values in fissured chalks and marls (Zuber and Motyka 1994; Zuber et al. 2001). The mean tracer age ( $t_t$ ) is a particularly useful term for densely fissured aquifers where the following approximation is applicable:

$$q = n_e U \approx n_f U = n_f \frac{n_p + n_f}{n_f} v_t \approx n_p v_t = n_p x / t_t \quad (6)$$

which means that Darcy velocity and, thus, the hydraulic conductivity can be assessed from the tracer age and matrix porosity, the latter being easily measurable in the laboratory on rock samples (Zuber and Motyka 1994). For large timescales, such assessments may cover structural obstacles to flow, like faults and horsts.

It is not clear if a similar porosity relation holds for tracers that accumulate in water with age, like  $^4\text{He}$ . That problem requires theoretical and experimental clarification. However, if an accumulating tracer yields the same water age as an ideal airborne tracer, Eq. 6 should also apply in this case.

Travel times of tracers in karstic channels are usually little influenced by matrix diffusion, which explains large differences observed between them and the tracer ages obtained for the whole rock massifs (e.g. Małozzewski et al. 2002).

For radioactive tracers in scarcely fissured rocks, the retardation factor can be smaller than the porosity ratio, if the airborne tracer is unable to penetrate the whole porous space of the matrix due to the decay (Małozzewski and Zuber 1984). Then, the tracer age differs from the water age, and both differ from the advective age. Similarly, solutes characterized by large molecules can be unable to penetrate the whole microporous space; then, also in this

case the delay factor becomes smaller than the porosity ratio (Motyka et al. 1994). Igneous and metamorphic rocks are usually characterized by low matrix porosity; however, if the fissure porosity is lower, the diffusion exchange with the matrix may still lead to significantly large values for the retardation factor (Zuber et al. 1995; Zuber and Cieřkowski 1997).

Diffusion exchange may also occur between the mobile water in an aquifer and stagnant water in porous confining layers and/or between significantly permeable zones and interbeds of low permeability, as described in Sudicky and Frind (1981) and Sanford (1997). Though these two works were focused on the  $^{14}\text{C}$  method, all solutes are subject to similar delays caused by diffusion exchange between advective and stagnant or quasi-stagnant water zones.

### Exchange of tracers between water and solid interface

Kaufman and Orlob (1956) and Knutsson and Forsberg (1967) showed very early that even tritium, though being a part of the water molecule, can be delayed with respect to pore water (advective) velocity due to the exchange of traced molecules with bound water in clay minerals.

The transport of traced solute which exchanges with the solid phase can be even more complex. For instance, Małozzewski et al. (1980) showed that mass transport of  $\text{Ca}^{2+}$  determined chemically may greatly differ from that determined with the aid of a radioactive tracer,  $^{45}\text{Ca}^{2+}$ . If  $\text{Ca}^{2+}$  ions dissolved in water exchange with the solid material for the same ions (i.e. the net exchange flux is zero), their mass transport remains unaffected, whereas  $^{45}\text{Ca}^{2+}$  ions transferred to the solid phase remain there for some time and become delayed with respect to the water velocity. In that case,  $\text{Ca}^{2+}$  ions correctly traced the mass transport of water, whereas  $^{45}\text{Ca}^{2+}$  ions traced the cation exchange effect.

The transport of  $^{14}\text{C}$  can significantly be delayed with respect to the movement of water by reversible isotopic exchange with carbonate minerals, both in granular aquifers rich in carbonate material (Clark et al. 1997; Hinsby et al. 2002; Witczak et al. 2008) and in fissured carbonate aquifers, where the exchange is particularly effective due to the large area available for the exchange in the microporous matrix (Małozzewski and Zuber 1991). This removal process, if occurring along the entire flow path, can be expressed as an additional decay constant, leading to an effective half-life of the  $^{14}\text{C}$  contained in water, which is significantly shorter than the radioactive half-life (Gonfiantini and Zuppi 2003; Witczak et al. 2008).

### Injection-detection modes

In dispersive systems without stagnant water zones, the mean velocity of a conservative tracer may differ from the mean velocity of water, depending on the injection and detection modes. The residence time distributions of a conservative solute (tracer) and water in single-porosity systems without stagnant zones are identical if the solute

is injected and measured proportionally to the volumetric flow rates of particular flow lines (Kreft and Zuber 1978; Zuber 1986a, b; Małozzewski and Zuber 1996). If a solute is injected and/or measured proportionally to the inlet and outlet areas, the mean travel time (age) of tracers usually differs from the mean travel time of water. This effect is of particular importance when artificial tracers are used; however, in considerations related to environmental tracer methods, it is commonly regarded as negligible in comparison with other uncertainties resulting from the approximate character of models, differences in input functions, unsteady-state conditions and others.

The simplest flow system, i.e., a laminar flow through a capillary, is helpful for a better understanding of possible differences between the movement of an ideal tracer and water. If the flow distance is short, the molecular diffusion has no time to influence the tracer distribution as described by Zuber (1986b) and Małozzewski and Zuber (1996). Five different time distributions of the outflow tracer concentration (tracer age) result from differences in the injection-detection modes and flow distance.

Tritium is injected naturally to groundwater systems in quantities proportional to the infiltration rates in recharge areas. Gaseous tracers such as  $^3\text{He}$ ,  $^{85}\text{Kr}$ ,  $\text{SF}_6$ , chlorofluorocarbons and  $^{39}\text{Ar}$  can also be regarded in approximation as injected proportionally to the volumetric flow rates. However, they differ from tritium because their travel time through the unsaturated zone is often negligible due to a relatively fast migration by diffusion in pores occupied by air (Weise et al. 1992; Cook and Solomon 1995; Corcho et al. 2007).

A specific difficulty may exist for  $^{14}\text{C}$ , if the recharge area is partly covered by bare soil and partly by dense plant cover. In a bare area, the infiltration rates are higher and the supply of bicarbonates and  $^{14}\text{C}$  are reduced due to the absence of autotrophic respiration flux. In the plant covered part, the infiltration rate is reduced by evapotranspiration, whereas the supply of  $^{14}\text{C}$  is higher. As a consequence, the amounts of  $^{14}\text{C}$  entering the groundwater system are not proportional to the volumetric flow rates of particular flow paths. Such differences are most probably negligible in comparison with uncertainties associated with defining the initial concentrations of radiocarbon in the studied groundwater system. However, they can be of importance in attempts to use the bomb  $^{14}\text{C}$  for quantitative interpretation of ages in modern waters.

Tracers that are produced in situ and/or supplied by an external flux, like  $^4\text{He}$ , are not initially distributed proportionally to the flow velocity. Thus, they cannot ideally represent the mass movement of water and transport of solutes. In spite of these limitations,  $^4\text{He}$  is still very useful for dating old groundwater systems (Castro and Goblet 2003, 2005).

### **Binary mixing between waters of distinctly different ages**

Mixing between waters of distinctly different ages or origin usually leads to apparent age values. For instance,

the radiometric piston-flow age, calculated for the concentration measured in water resulting from binary mixture of two piston flows, is biased towards the age of the younger component because the tracer concentration follows a negative exponential trend with time (Geyh 2000; Bethke and Johnson 2002). For  $^{14}\text{C}$ , an additional difficulty occurs when the components which are mixed differ in TDIC (total dissolved inorganic carbon) content. Then, the  $^{14}\text{C}$  of the mixture should be calculated by taking into account both the  $^{14}\text{C}$  and TDIC values in the components subjected to mixing (Wigley et al. 1978). In the extreme case, if modern water mixes with much older water free of TDIC, the mixture will always yield the modern  $^{14}\text{C}$  age, independently of the proportions of mixed components. Similarly,  $^3\text{H}/^3\text{He}$  ages are highly non-linear with respect to mixing and are always weighted in favor of the water mass with the higher tritium concentration (Schlosser 1992).

### **Differences in age definitions**

Tracer data are commonly interpreted quantitatively by inverse modeling, i.e., the parameters of a groundwater system are to be determined from a model fitted to the data, where the main model parameter is the tracer age. However, though the tracer age derived from the concentration of tracer at a given sampling site is a useful term, it is not rigorous because of its dependence on the interpretation models (see section [Definitions of water age](#)) and tracer-specific effects (see section [Tracers and their specific properties](#)). As a consequence, a number of different estimates of the mean age and age distribution can be obtained for a given groundwater system.

Ideally, the tracer age distribution should reflect the flow line age distribution and the mean values of both should be the same. In reality, the diffusion exchange of tracer between mobile and immobile zones and mixing between different flow lines changes the relations between these two types of distributions as discussed in section [Definitions of water age](#).

Environmental tracers are the only tools for measuring the groundwater age; however, their measurements may yield results differing from simulations. For instance, direct simulations of ages performed by Zinn and Konikow (2007a) by the method of Goode (1996) for a hypothetical layered system demonstrated that significant changes in water ages and solute (tracer) transport can be caused by regional pumping.

Varni and Carrera (1998) showed that due to the dispersion and mixing between individual flow lines, advective ages and their distributions differ from the measured radioactive tracer ages in heterogeneous aquifers. They also mentioned that averaging of measured values depends on the measurement procedure (sampling mode), which may also lead to some differences.

Castro and Goblet (2005) compared simulated  $^{14}\text{C}$  and advective ages with direct simulations performed by the method of Goode (1996) for the Carrizo Aquifer, Texas (USA), by making use of the numerical model calibrated



earlier with the aid of  $^4\text{He}$  and  $^3\text{He}$  concentrations (Castro and Goblet 2003). They showed that these three dating methods yield significantly different results in the range of several ka to 60 ka. The differences were shown to be particularly large in heterogeneous zones and in the cases of low flow velocities. That study clearly showed that different estimates of groundwater age are available depending on the measurement and/or interpretation method.

### Steady and unsteady states

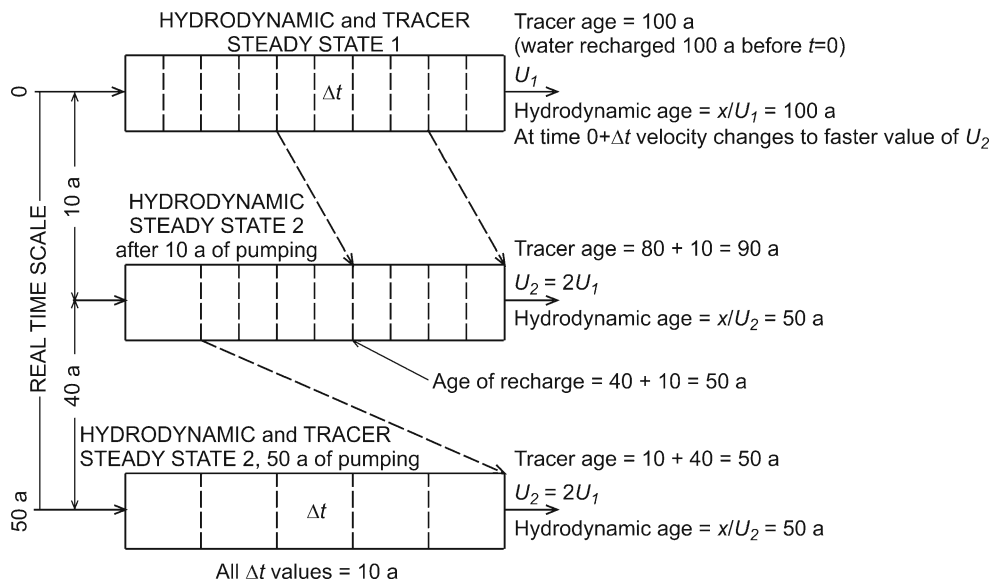
Tracer ages can be used directly for determining the hydraulic parameters, if the groundwater system or its investigated part remains in a hydrodynamic steady-state for the period comparable with mean ages of water at the sampling sites. Caution is required when interpreting the results obtained from the steady-state based models for a groundwater system that is evolving from one tracer steady-state to another one within the time span covered by the tracer data. Such a case is schematically shown in Fig. 2, where the system is initially in hydrologic and tracer steady states. The advective (hydrodynamic) and tracer (groundwater) ages of 100 years are assumed. A sudden change in flow velocity by a factor of 2 is imposed on the system; with the resulting fast transition to a new hydrologic steady state (such a situation will occur in systems with a fast propagation of water pressure). Ten years after the change, the new advective age is 50 years, whereas the tracer age is 90 years (water which now appears at the outlet, ten years earlier was already 80 years old). The new tracer steady-state is achieved 50 years after the change in the hydrodynamic conditions.

A typical field example related to the mechanism described in the previous is schematically shown in Fig. 3. In the initial pre-exploitation phase (Fig. 3a), the

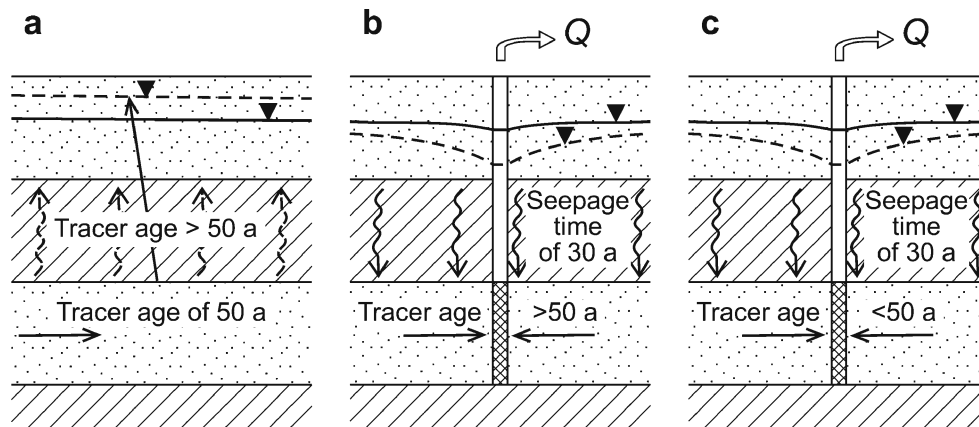
tracer age is assumed to be 50 years in the confined aquifer with a slow upward seepage to the upper unconfined aquifer with much younger water (a small contribution of upward seepage practically does not influence the mean age of that water). Installation of a well tapping the confined layer changes the hydraulic heads in the confined aquifer (Fig. 3b). At the beginning of pumping, the older water (>50 years) from the confining layer starts to flow back down to the pumping well (the flow time through the middle layer is assumed to be 30 years), which may temporarily lead to a tracer age even larger than in the pre-exploitation phase (>50 years). However, after a sufficiently long time, a new steady state is reached (Fig. 3c) and the tracer data will properly reflect a new steady-state age (<50 years) in the pumped well. Smaller ages can be observed even faster, without reaching the new steady state, if an erosion (a hydrogeologic) window and/or a thin aquitard are present, which enable a fast downward movement of very young water from the unconfined layer.

Qualitative effects demonstrated in Fig. 3 are in agreement with direct simulations of Zinn and Konikow (2007a), which show that age of pumped water initially considerably increases in comparison with the pre-exploitation steady-state stage. However, as the pumping increases, the volumetric flow rate through the investigated part of the groundwater system, the advective age during the period of pumping must be lower than that in the pre-exploitation era, which is neither indicated by tracers nor by direct simulation of groundwater age.

In general, for unsteady-state systems, the age is not a constant parameter. However, if the mean age is large in comparison with characteristic periods of hydrodynamic changes in the system, its value derived under the assumption of the hydrologic steady state can still be regarded as a representative parameter, as it was shown for a small



**Fig. 2** 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,  $a$  years



**Fig. 3** A hypothetical example showing three stages of a semi-confined aquifer with modern water in **a** the pre-exploitation stage, **b** at the start of abstraction, and **c** after sufficiently long time of operation; see text for details

mountain watershed in Harz Mounties (Germany) with a highly variable groundwater discharge (Zuber et al. 1986).

### **Disturbances caused by intra-well flows**

Disturbances of groundwater chemistry and concentrations of tracers caused by intra-well flows are known to exist in abandoned wells with leaky casings, in wells with long open intervals, or in monitoring wells with long screens. Zinn and Konikow (2007b) used numerical simulations to demonstrate quantitatively that intra-well flows influence the groundwater ages and solute concentrations. Such influence can be particularly significant for wells in and close to recharge areas where strong age stratification commonly exists (Corcho et al. 2009). Then, the tracer age may greatly differ from the water and advective ages, with uncertainties difficult to assess.

### **Tracers and their specific properties**

All dating methods are based on the assumption that input functions and processes altering the tracer concentration within the system are known and quantifiable. Some tracer-specific problems related to the inputs and the movements of tracers through the unsaturated zone are considered within this section.

The input function is defined as the flux of a tracer (mass per unit time) at the entrance to the system (beginning of the flow paths). For systems in a hydrodynamic steady state, the input function corresponds to the input concentration. For systems with variable recharge rates, the input function is represented by the product of the concentration and volumetric flow rate at the inlet to the system (Zuber 1986c).

### **Tritium**

The construction of an adequate tritium input function is difficult due to strong seasonal fluctuations of tritium content in precipitation. Attempts to construct a function which allows for yearly and seasonal variations of both

tritium concentration and infiltration rates were described by Andersen and Sevel (1974) and Przewłocki (1975). Davis et al. (1967) and Dincer et al. (1970) developed tritium input functions neglecting the contribution of summer months (April to September in the northern hemisphere), when the maximum tritium concentrations occur in the atmosphere. Grabczak et al. (1984) showed that, even if there is no summer net recharge, a fraction of water from summer rains with higher tritium concentrations reaches the water table. That effect is confirmed by the stable isotope composition of shallow groundwater, which in moderate and humid climates is close to the yearly mean value of precipitation even when summer evapotranspiration exceeds precipitation. This stems from the fact that summer evapotranspiration consumes in part both the summer and winter precipitation present in the root zone. The tritium input function accounting for this effect can be constructed by assuming that a fraction of summer precipitation reaches the water table. Under favorable conditions, that fraction can be estimated from the relation between the weighted mean stable isotope composition of precipitation and the composition of shallow groundwater (Grabczak et al. 1984; Małoszewski and Zuber 1996). However, the calculated tritium input function can considerably differ from the real one due to the presence of preferential flow paths in the unsaturated zone (e.g. Hinsby et al. 2002).

### **Gaseous transient tracers**

Gaseous tracers differ in mechanisms and travel times through the unsaturated zone from other tracers, which is of importance for groundwater systems containing modern waters. Basic assumptions behind the two-tracer plots mentioned in the section **Box models** is that both tracers are described by the same models, which means that they have to travel through the system in the same way. However, gaseous tracers quickly diffuse through air in the unsaturated zone. If a gaseous tracer is combined with tritium which slowly travels with percolating water, the mean ages differ and different types of age distributions are applicable (Corcho et al. 2004, 2007; Zuber et al.

2005). In addition, the dispersivity of the whole system strongly depends on the degree of heterogeneity of the unsaturated zone (Schwientek et al. 2009). Therefore, any gaseous transient tracer (e.g. tritiogenic  $^3\text{He}$ ,  $^{85}\text{Kr}$ ,  $\text{SF}_6$ , and chlorofluorocarbons) should not be used in a pair with tritium in the two-tracer plots, if the thickness of the unsaturated zone is not negligible.

Excess air (i.e. dissolved atmospheric gases in excess of equilibrium values) is ubiquitous in groundwater and is commonly attributed to partial or complete dissolution of entrapped air bubbles near the water table. This additional source of gas in groundwater is of particular importance for gases with low solubility such as  $\text{He}$  and  $\text{SF}_6$ . The air-excess effect can be corrected for by making use of measurements of dissolved atmospheric noble gases, particularly  $\text{Ne}$  (Heaton and Vogel 1981; Aeschbach-Hertig et al. 1999; Kipfer et al. 2002; Cook et al. 2006).

During groundwater flow in the saturated part of the aquifer, gases may be accumulated due to geochemical processes in the subsurface. The most common reactions are denitrification and methanogenesis under reducing conditions. Thereby, produced gases ( $\text{N}_2$ ,  $\text{CH}_4$  or/and  $\text{CO}_2$ ) are kept in solution as long as the local hydrostatic pressure exceeds the dissolved gas pressure. In the other case, the gas exsolves and bubbles are formed, which may escape from the sampled water. A correction for this degassing loss is only possible if either the depth of degassing can be reconstructed (Visser et al. 2007), or an equilibrium partitioning between the water and the gas phase can be assumed. For gaseous tracers which are accumulated in the subsurface like radiogenic helium, it is crucial to define the point in time when degassing occurred. No correction is required if degassing took place during the recharge, whereas the correction is largest if degassing occurred during sampling. The least complicated tracers with regards to excess air or degassing are noble gas radioisotopes such as  $^{85}\text{Kr}$ ,  $^{39}\text{Ar}$ , or  $^{81}\text{Kr}$  (Loosli et al. 2000; Collon et al. 2004; Corcho et al. 2009). Dating with these tracers is not based on concentration but on isotope ratios, e.g.  $^{39}\text{Ar}/\text{Ar}_{\text{total}}$ , which are rather insensitive to the recharge conditions or possible degassing processes.

Some transient tracers, especially chlorofluorocarbons, can also have elevated concentrations in groundwater due to local anthropogenic sources (Cook et al. 2006). It is therefore advisable to check local atmospheric concentrations of transient tracers and make appropriate corrections, if required. Some transient tracers, particularly  $\text{SF}_6$ , can have natural terrigenous sources and are released in some types of rocks (Busenberg and Plummer 2000), which limits the possibility of dating. The chlorofluorocarbons CFC-11 and CFC-113 and to a less extent also CFC-12 are degraded by microorganisms in most anaerobic waters and/or retarded by sorption processes.

### Radiocarbon

Radiocarbon is one of the most important tracers for dating groundwater systems with timescales between about 2 and 30 ka. In general, the interpretation of  $^{14}\text{C}$

in terms of groundwater age is difficult due to some specific effects, discussed in section [Binary mixing between waters of distinctly different ages](#), and a number of other reasons which are beyond the scope of the present work. Detailed discussion of the  $^{14}\text{C}$  and  $^{13}\text{C}$  hydrochemistry in relation to groundwater dating can be found in a number of text books and research papers (e.g. Wigley et al. 1978; Fontes and Garnier 1979; Plummer et al. 1994; Clark and Fritz 1997; Parkhurst and Appelo 1999; Kalin 1999; Plummer and Sprinkle 2001; Mook 2001, 2005; Kemp et al. 2002). Most of the authors apply available hydrochemical codes to account for the isotope exchange between dissolved and solid carbonates. However, some other authors consider the  $^{14}\text{C}$  method as unsuitable for quantitative dating in carbonate fissured aquifers or in granular aquifers rich in carbonates (Małozzewski and Zuber 1991; Clark et al. 1997; Hinsby et al. 2002; Witczak et al. 2008).

### Stable isotopes and noble gas temperatures

Seasonal variations of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  are mainly used for the investigation of small catchments with mean ages (turnover times) in the range of weeks to 2–4 years. In bank filtration studies, the surface-water tracer concentrations represent a well-defined input function (e.g. Stichler et al. 1986, 2008). Due to strong variations of the precipitation rate and its stable isotope composition, the construction of an adequate input function is not easy for infiltration studies through the unsaturated zone (e.g. McGuire et al. 2002; McGuire and McDonnell 2006; Małozzewski et al. 2006).

Changes in isotopic composition of infiltrating water, caused by the evaporation process in surface reservoirs, can serve for the investigation of flow patterns and mixing proportions in shallow groundwater systems (Yehdego et al. 1997) as well as for the calibration of numerical models (Stichler et al. 1986, 2008; Małozzewski et al. 1990).

For large aquifers with slow water movement, changes in the isotopic composition of water caused by climatic effects can also be used for calibration and/or validation of numerical models (e.g. Kirk and Campana 1990). Similarly, the recharge temperatures (NGT) determined from the concentrations of dissolved atmospheric gases ( $\text{Ne}$ ,  $\text{Ar}$ ,  $\text{Kr}$  and  $\text{Xe}$ ) act as time markers (Mazor 1972; Stute and Schlosser 1993; 2000; Aeschbach-Hertig et al. 1999, 2002), and can therefore be used for dating purposes.

### Other tracers

There are many other environmental tracers that are applicable in groundwater studies (e.g. Cook and Herczeg 2000). The accumulation of  $^4\text{He}$  (or in approximation total  $\text{He}$ ) in aquifers is used for groundwater dating in a wide range of timescales, while  $^{40}\text{Ar}$  is sometimes employed for dating very old waters with ages exceeding several tens of thousands of years (Torgersen and Clarke 1985; Torgersen and Ivey 1985; Solomon 2000; Ballentine and Burnard 2002). The accumulation of  $^4\text{He}$  usually results from in situ

production and/or from external diffusive or advective flux. Solomon et al. (1996) showed that  $^4\text{He}$  accumulated in the aquifer mineral phase in the course of its earlier geologic history as a hard rock, may exceed the in situ production for about 50 million years. The external flux may vary over wide ranges of magnitude, and, if present, may induce a strong vertical gradient of  $^4\text{He}$ , which requires adequate modeling (e.g. Castro et al. 2000). Very old waters can also be dated with the aid of  $^{36}\text{Cl}$  (e.g. Guendouz and Michelot 2006) and  $^{81}\text{Kr}$  (Sturchio et al. 2004).

### Examples of conflicting age estimates derived from different tracers and discrepancies between hydrologic and tracer data

While successful applications of the tracer methods are usually reported in the literature, the present contribution highlights some typical difficulties often encountered in the use of tracer methods. Several examples are presented in the following to demonstrate that even in the cases of successful applications, some significant discrepancies between particular tracers, and between tracers and other hydrologic estimates can sometimes be observed.

Loosli et al. (2000) described examples of the simultaneous use of  $^3\text{H}$  and  $^{85}\text{Kr}$ . The interpretation of the data of both tracers by box models yielded in some cases similar ages, whereas in some other cases very different values (2 years for  $^{85}\text{Kr}$  and 10–13 years for  $^3\text{H}$ ), as a result of longer travel time of tritium through the unsaturated zone.

Plummer and Busenberg (2000) described a study in which some sampled wells were characterized by high  $^3\text{H}$  contents without measurable chlorofluorocarbons, whereas some other wells with measurable chlorofluorocarbons were free of  $^3\text{H}$ . These discrepancies were probably caused by rather typical non-conservative behavior of chlorofluorocarbons and possible contamination. Successful applications of chlorofluorocarbons as tracers are usually based on a large number of sampled sites, where discrepancies observed at some sampling sites have limited influence on the general interpretation of the whole investigated system.

A different approach was presented by Zuber et al. (2005) who used both  $\text{SF}_6$  to calibrate the transport model for a sandy aquifer in southern Poland with modern waters, and time series of  $^3\text{H}$  data to validate partly the obtained transport model by comparing the data with the simulations performed for individual wells. For some wells, a good agreement was obtained, whereas for wells in some parts of the aquifer no satisfactory agreement could be reached, which was attributed to deficiencies in transport modeling resulting from a poor knowledge of aquifer parameters and variable withdrawal rates. Tritium data were also interpreted with the aid of box models, and the mean ages and age distributions at individual wells were compared with numerical simulations. The largest discrepancies between particular approaches were observed for one of the wells situated in the outcrop area, which remains unexploited. In the period 2000–2003, no

traces of  $^3\text{H}$  were found in that well, whereas two samplings yielded  $\text{SF}_6$  concentration of about 0.15 fmol/L. The lack of  $^3\text{H}$  in that well can be explained by the presence of a large sedimentary pocket with quasi-stagnant water, which was not discovered by conventional methods and, thus, unaccounted in numerical flow and transport modeling. In such a case, the significant concentration of  $\text{SF}_6$  is difficult to explain by quick diffusion through the unsaturated zone, though it cannot be definitely excluded. Whichever the reason, the large discrepancy between the  $^3\text{H}$  and  $\text{SF}_6$  data cannot be regarded in that case as accidental.

Zuber et al. (2001) used box models to estimate tritium ages in spring and well waters of an unconfined chalk aquifer in eastern Poland. Tracer ages obtained from the models were in the range of 29–380 years, due to large reservoirs of stagnant water in the microporous chalk. These age values were shown to be at least 70 times greater than the advective ages estimated from the hydraulic conductivities known from pumping tests, and the fissure porosities measured at the outcrops. It is worth mentioning that due to the effect of limited ability of tritium, as a relatively quickly decaying tracer, to penetrate fully the whole stagnant zone, the tracer ages were in this case perhaps somewhat lower than those expected from the retardation factor (see section [Exchange of tracer between mobile and immobile reservoirs of water](#)).

In an often cited work, Fontes and Garnier (1979) summarized several correction models based on carbon hydrochemistry and proposed their own model for finding the initial  $^{14}\text{C}$  content which is needed for piston flow  $^{14}\text{C}$  dating of groundwater. They also tried to corroborate their determinations of  $^{14}\text{C}$  ages in a fissured carbonate aquifer of northern France and Belgium by comparing the pore water (advective) velocity obtained from tracer data ( $v = \text{distance}/\text{age}$ ) with the Darcy velocity ( $q$ ) found from pumping tests. The pore-water velocity was, on average, three times lower than the Darcy velocity, whereas it should be larger by a factor equal to the reciprocal of the fissure porosity ( $v = q/n_c$ ). The effective porosity ( $n_c$ ) is usually equal to the fissure porosity ( $n_f$ ), which can be assumed to be of the order of 0.01. In such a case, the advective velocity found from tracer data was about 300 times lower than that estimated from pumping test data. Fontes and Garnier (1979) tried to explain the difference between the tracer and conventional data by possible inaccuracy of the latter. Małoszewski and Zuber (1991) presented a possible explanation by showing the potential influence of matrix diffusion and isotopic exchange between dissolved and solid carbonates, which are not taken into account in the hydrochemical models. No other explanation has been proposed so far.

A sandy aquifer of the Oligocene age in the Mazovian Basin, central Poland, may serve as an example of the influence of pumping on the differences between advective and tracer (water) ages. The aquifer is recharged indirectly from Quaternary sediments by downward seepage through Pliocene silts and several erosion windows in elevated areas, and discharged by upward seepage in river

valleys and local depressions (Fig. 4). The differences between particular tracer methods still remain unexplained. According to Zuber et al. (2000), the most reliable tracers suggest that the recharge took place mainly during the final stages of the last glacial period, i.e. about 10–15 ka BP, though other estimates, even of the order of 100 ka, are also available of (e.g. Dowgiałło et al. 1990). The numerical flow modeling leads to the estimates of the advective ages in the order of 0.8 ka in the central part of the basin as schematically shown in Fig. 4. The flow model was not independently confirmed and estimates of the advective ages based on that model may require some significant adjustments, but there is no doubt that tracer ages sharply disagree with the advective ages derived from the numerical hydrodynamic modeling, which can mainly be attributed to similar effects as those explained in Figs. 2 and 3 for smaller time scales.

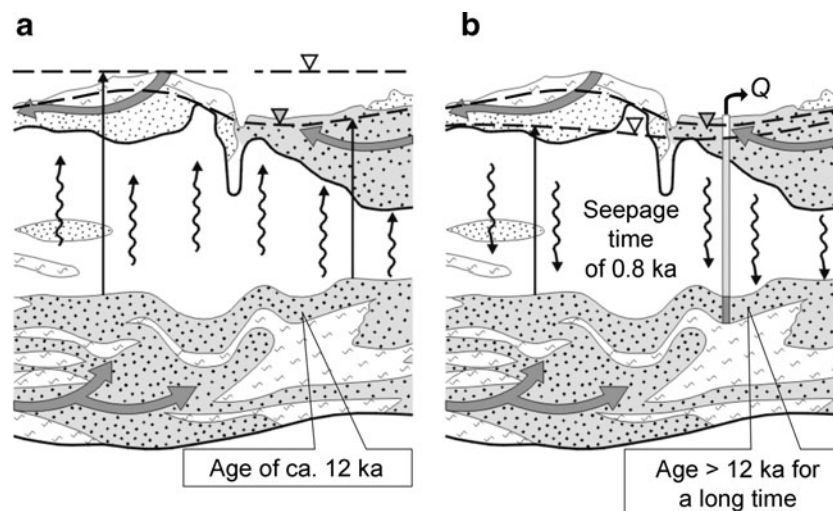
The Dogger aquifer of the Paris Basin (France) may serve as a particularly interesting case of conflicting age estimates, differing up to three orders of magnitude (Matray et al. 1994). That aquifer mainly consists of 200–300-m-thick limestones confined by Triassic and Callovian marls. Wei et al. (1990) calibrated flow and transport models of the Dogger aquifer with the aid of  $^{14}\text{C}$  and  $^4\text{He}$ , and obtained ages of ca. 100 ka. Marty et al. (1993), essentially on the basis of the same  $^4\text{He}$  data set, obtained an age of  $4 \pm 2$  Ma which was in qualitative agreement with  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  data of Matray et al. (1994) being characteristic of the pre-Pleistocene water, i.e. with the age greater than ca. 2 Ma. Castro et al. (1998) calibrated the flow model of the whole Paris Basin using a wide spectrum of noble gas data, and, for the Dogger aquifer, they obtained tracer ages in the range of 240–680 ka with an average of 460 ka. The reasons for such wide discrepancies remain so far unknown. Perhaps, they can partly be attributed to some tracer-specific effects, and partly to matrix diffusion effects.

## Conclusions

Tracer methods have found a permanent and unquestionable place in different kinds of groundwater investigations because they either supply information unavailable by other methods or confirm results which otherwise would be doubtful. Groundwater age is an important hydrologic parameter that is directly measurable only by tracer methods. However, the results offered by tracer methods depend on the characteristics of available tracers as well as on the aquifer type and dimensions, timescales of groundwater flow, accessible sampling sites and adopted sampling technique(s), length of available time series of tracer (s) data, and available funds. Due to these reasons, tracer methods are not free of limitations resulting from both the simplified nature of the interpretation methods and tracer-specific effects, whereas direct age simulations with the aid of numerical transport models depend on a number of parameters which usually are not sufficiently well known.

In each tracer-aided field study, a clear distinction should be made between the tracer age, groundwater age, and advective age. The tracer age is the quantity which is directly measured, and which, under favorable conditions, represents the groundwater age. The age of groundwater is of importance for all types of studies related to the transport of solutes in groundwater systems, whereas the advective age is of interest in the studies of water resources.

Box and numerical modeling represent the two most common approaches to quantitative interpretation of tracer data in terms of groundwater ages. Box models can be used for the interpretation of tracer data at individual sampling sites, either independently or as a complimentary tool to the numerical modeling of the whole system. As the groundwater age can be defined in different ways depending on the adopted calculation or measurement methods, in order to avoid misunderstandings, the adopted



**Fig. 4** A conceptual model of the evolution of groundwater age in the central part of the Mazovian Basin, central Poland, as a result of prolonged exploitation. **a** water in the main aquifer (Oligocene sands) was initially of pre-Holocene age (>12 ka); **b** intensive abstraction in the last several decades caused much faster horizontal flow and downward seepage in the central part of the aquifer. As a consequence, the advective age is estimated at ca. 0.8 ka, whereas the tracer age will remain above 10–12 ka for hundreds of years with a possible long-lasting tendency to even greater values due to the contribution of older water from the return seepage

definition of groundwater age and the measuring method should always be specified and the limitations of the chosen approach discussed and assessed.

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