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Principles and practice of calibration and validation of mathematical models for the interpretation of environmental tracer data in aquifers

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Calibration and validation processes of mathematical models applied to environmental tracer dating of groundwater are discussed and their importance exemplified by a number of case studies. The calibration procedures are shown to be often ambiguous due to the scarcity of data, approximate nature of models, and interplay of fitting parameters when their number is too large. A unique calibration is a necessary condition, though not sufficient, for validation. A satisfactory agreement of the values of parameters obtained by calibration with those known from independent methods may be regarded as an indirect validation. Direct or indirect validation is usually obtainable only with respect to some quantities or parameters and in such cases it should be regarded as a partial validation. Very often validation is unavailable, and, consequently, the model and the values of its parameters are questionable, but still can serve as starting points for further studies. Case studies discussed demonstrate that sometimes several properly calibrated and partly validated mathematical models, based on different conceptual models, can be used. In such cases the conceptual model of flow pattern and hydrochemistry remains unidentified.

Key words: model calibration, model validation, environmental tracers, tracer age water age.

INTRODUCTION

The paper is addressed to the modellers of environmental tracer data in groundwater systems and to all those who make use of the tracer data, but are not familiar with the limitations of the mathematical models developed so far for the interpretation of such data. It is hoped that the paper will clarify problems which are often omitted by the modellers and, which, consequently, escape the attention of the users of tracer data.

Environmental tracers in groundwater systems are used for a number of purposes as, for instance, determining the origin of water, supply of information on the vulnerability to pollution, calibration and validation of flow and pollutant transport models. Very often a qualitative approach is sufficient. However, for determining the parameters of the flow system, or for prediction of its response, a quantitative approach is needed and a mathematical model must be employed. The parameters of the model are related to the input–output tracer relations by making use of one, or more, of the following principles: (a) decrease of tracer concentration due to the radioactive decay along flow paths, (b) transfer of variable tracer input by the system, and (c) mass balance of flow and tracer(s) components. Principle (a) is usually employed when individual tracer determinations are available and the tracer input is constant. Principle (b) is employed for tracers with variable concentrations at the entry to a system.

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Principle (c) often in combination with (a) and (b), is particularly applicable when availability of a large number of tracer data distributed in space permits modelling of the structure of the system, e.g. by a network of cells or by analytical or numerical solutions to the solute transport equation(s). Models based on principles (a) and (b) are usually simple, especially when employed in solving the inverse problem, i.e. the values of parameters are sought by calibration (fitting). Models based on principle (c) are usually characterized by a large number of parameters. If the number of independent model equations is equal to the number of parameters, or if parameters can be determined by independent methods, their large number is to the advantage of the model. However, if the number of sought (fitted) parameters is larger than the number of independent equations a unique solution is not available, even if a good fit was obtained.

In the present paper the terminology developed within the Hydrocoin Project[55] for the flow and pollutant movement models, and adapted for the artificial tracer methods by Małoszewski & Zuber[46] is followed. The following terms were defined in the referred works: conceptual model, mathematical model, verification of a mathematical model, calibration, validation, and several other terms not discussed here. It is recalled that the *validation* is a process of obtaining assurance that a model is a correct representation of the process or system for which it is intended. Contrary to calibration, this process is qualitative and based on modeller's judgment and needs. *Partial validation* can be defined as the validation process performed in respect to some properties of a model.

Another useful term which can be used either instead of the validation or in addition to that term is *identifiability*. According to Kleissen *et al.*[39] several definitions of that term are available, but 'in essence, a lack of identifiability means that it is not possible to corroborate or refute all the constituent hypotheses of a model, given observed behaviour of the system. If a model cannot be identified... there will be little confidence in the estimates of the model's parameter values.' Identification of a proper model, i.e. selection of both a proper model and its parameters, can partly be based on a prior knowledge of a system, and is a part of the calibration and validation processes. It should be stressed that sensitivity analysis should be a part of the calibration process, i.e. the modeller should check how changes in the values of parameters influence the goodness of fit. If the boundary and initial conditions are not well defined and therefore have to be assumed, they should also be included in the sensitivity and calibration processes.

It should be mentioned that some authors (e.g. Konikow & Bredehoeft[40]) claim that flow models cannot be validated and the term 'validation' should be abandoned. In the opinion of the present authors a modeller should not avoid attempts at obtaining validation. In that process the operational identification of validation with calibration, mentioned by Konikow & Bredehoeft,[40] must not be employed.

The following sections are devoted to the discussion of different problems related to the calibration, validation and/or identifiability of mathematical models applied to environmental tracer dating. The discussion is based on published case studies, and extended to some aspects of interpretation not considered in the original papers. Of course, models and case studies familiar to the authors due to their personal involvement are discussed in more detail. Several terms which are important for understanding the relations between the parameters obtainable from the environmental tracer methods and those of flow systems are recalled first.

The *tracer method* is a technique for obtaining information about a system or some part of a system by observing the behaviour of a specific substance, the tracer, that has been added to the system.[27] In the case of environmental tracers they are added (injected) to the system by natural processes, whereas their production is either natural or results from the global activity of man.

An *ideal tracer* is a substance that behaves in the system exactly as the traced material as far as the sought parameters are concerned, and which has one property that distinguishes it from the traced material. This definition means that for an ideal tracer there should be neither sources nor sinks in the system other than those adherent to the sought parameters. In practice even substances which have other sources or sinks are regarded as tracers, if these sources and sinks can be properly accounted for, or if their influence is negligible within the measurement accuracy.[78] Hydrochemical models which are supposed to account for other sources and sinks are usually not well defined due to the complexity of natural systems and the lack of sufficient data. Discussion of such models is beyond the scope of the present work, but for the sake of the reader, references to papers dealing with the most important models are given.

The authors' experience is that a proper understanding and application of the tracer methods in groundwater systems require introduction of several definitions of ages. The definitions of the turnover time (water age), conservative tracer age, and radioisotope age are commonly accepted, though it is not necessarily always well understood when and why they are, or are not, compatible.

The *turnover time* of water (or *mean age* of water leaving a system, or *mean transit time of water*) is defined as:

$$t_o = V_m/Q \tag{1}$$

where Q is the volumetric flow rate through the system, V_m is the volume of mobile water. For unidimensional flow systems, which can be approximated by piston flow or dispersion model (discussed further), $t_o = x/v$, where x is the length of the system, and v is the mean transit velocity of water. The same relation holds if the age of water along a chosen flow line is considered. This latter definition of the water age is useful for direct comparisons with flow parameters available from conventional methods.

The *mean transit time* of a conservative tracer (t_t), or the *age of tracer leaving the system*, is defined by:

$$t_t = \int_0^\infty t c_I(t)dt \Big/ \int_0^\infty c_I(t)dt \qquad (2)$$

where $c_I(t)$ is the concentration of tracer resulting from its instantaneous injection at $t = 0$. The tracer age defined by eqn (2) is equal to the water age defined by eqn (1) for any model of flow, if the tracer is injected and measured in flux of water, i.e. if it is injected and measured proportionally to volumetric flow rates contributed to the total flow by individual flow paths[42,78], and if there are no stagnant zones accessible to the tracer.

Equation (2) is of basic importance in artificial tracing, whereas in environmental tracing it is of no operational use, but can be useful for a better understanding of some problems. For a radioisotope tracer, eqn (2) yields the same value of age as for a conservative tracer, if the correction factor for radioactive decay is introduced.

In the case of steady flow, the output concentration (c_{out}) can be related to the input concentration (c_{in}) of any tracer by the well-known convolution integral:

$$c_{\text{out}}(t) = \int_0^\infty c_{\text{in}}(t - t')\, g(t') \exp(-\lambda t')\, \mathrm{d}t' \qquad (3)$$

where $g(t')$ is the system response function ($g(t) = c_I(t)Q/M$, where M is the injected mass or activity of the tracer) which describes the residence time (t') distribution of tracer at the outlet,[42,78] and λ is the radioactive decay constant. The type of the model (e.g. the piston flow model, or dispersion model) is defined by the $g(t')$ function chosen by the investigator. The main parameter of any $g(t')$ function is the mean transit time of tracer (age) which is denoted here as t_t for both a conservative tracer and a decaying tracer corrected for the decay.

The *radioisotope age* (t_a) is usually defined by the radioactive decay equation for a system with a constant input concentration:

$$c/c_o = \exp(-\lambda t_a) \qquad (4)$$

where c and c_o are the measured and initial radioisotope tracer concentrations, respectively.

Equation (4) is meaningful only in two cases: (a) if a portion of water has been separated since the recharge time, and (b) if the piston flow model (PFM) can be accepted as a good approximation of flow in a given aquifer. Case (a) is self-evident, whereas in case (b) it can easily be shown from eqn (3) that $t_a = t_t = t_o$, if diffusion of tracer from mobile to stagnant water zones is negligible.

In unconfined homogeneous aquifers the transit times between the recharge area and discharge site along different flow lines have an exponential distribution. The radioisotope tracer age which is supposed to represent the mean transit time value is then:[20,23,78]

$$c/c_o = 1/(1 + \lambda t'_a) \qquad (5)$$

It may be shown again that $t'_a = t_t = t_o$, if diffusion is negligible. Evidently, the same c/c_o ratio yields different ages (t_a or t'_a) depending on the type of flow. It is also evident that the radioisotope age can be defined in different ways depending on the flow model. It is a common practice to regard eqn (4) as the definition of the radioisotope age, which differs from the water age when the piston flow model (PFM) does not apply. Even if the PFM is applicable, diffusion should be negligible as shown further. Therefore, it is strongly suggested that a radioisotope age, or more generally a tracer age, should be defined by both the tracer and the model employed. For instance, 'the piston flow ^{14}C age is... ', or 'the exponential model tritium age is... '. When a tracer age is reported without a reference to the model it is understood that eqn (4) was employed, but then the age value may have little meaning. Similarly, if the initial tracer concentration (c_o) is not directly measurable but estimated from a special model, and if that model is not reported, the age may also be of little value.

In the case of matrix diffusion the conservative tracer age is much greater than the water age, as shown by the following equation:[44,52]

$$R_p = t_t/t_o = (V_p + V_f)/V_f = \cong (n_p + n_f)/n_f \qquad (6)$$

where R_p is the retardation factor resulting from matrix diffusion, n_p and n_f are the matrix and fissure porosities, respectively; V_p and V_f are the stagnant water volume in the micropores of the matrix and the mobile water volume in fissures, respectively. According to eqn (6) the tracer age corresponds to the total water volume accessible to tracer, whereas the water age is defined by the mobile water volume, assumed to be in fissures only. If a non-ideal tracer exchanges with the solid matter, a large surface available for exchange in the matrix contributes to its increased delay and greater age as discussed further for the ^{14}C method.

Equation (6) holds for conservative substances but for other tracers its applicability is limited because decaying tracers are usually unable to penetrate the matrix far enough from the fissures to occupy homogeneously the whole matrix. The reader is referred to Neretnieks[52] and Małoszewski & Zuber[43] for derivations of formulae showing that $t_o < t_a < t_t$. It means that in fissured rocks the radioisotope tracer age (t_a) is always greater than the water age (t_o) but usually smaller than the conservative tracer age (t_t). For long-lived radioisotopes in densely fissured rocks (e.g. in the case of ^{14}C in rocks with several fissures per m^2), $t_a \cong t_t$ in a good approximation.[45] Theoretically, for short-lived radioisotopes, e.g. for the pre-bomb era tritium interpreted with the aid of eqns (4) or (5), t_a (or t'_a) is smaller than t_t and its relation to t_o is difficult to determine.[43]

From eqn (6) it follows that the Darcy velocity (v_f) is related to the conservative tracer velocity:[44]

$$v_f = n_f v = (n_p + n_f)v_t \cong n_p v_t \tag{7}$$

The simplified form of eqn(7) means that contrary to the flow of water the stagnant water in the matrix is the main reservoir for tracer transport.

It should be stressed that the tracer age models are commonly calibrated without taking into account eqn (6). The importance of that equation can be found out only in the process of validation. In general, a number of examples can be given to illustrate the importance of matrix diffusion for solute transport in fissured rocks. Its importance for age determinations and for the validation of the models employed has been exemplified in several recent studies.[17,79] Similarly, it seems that 'tracer ages that may exceed the computed hydrologic ages by orders of magnitude' reported by Mazor & Bosch,[49] and Mazor & Kroitoru[50] also result from the matrix diffusion, though the cited authors give other reasons. In any case, the cited works prove that the tracer ages and hydraulic ages may differ by orders of magnitudes, and therefore their definitions must be well understood, and the models employed for their determinations properly calibrated and validated. Unfortunately, the influence of matrix diffusion on the tracer ages, known since early works of Neretnieks[52] and Małoszewski & Zuber[43,44] and approximated for fissured rocks by eqns (6) and (7), is commonly neglected by modellers, which leads to serious errors in interpretation of tracer age determinations.

LUMPED-PARAMETER MODELS FOR A CONSTANT TRACER INPUT

General

In the lumped parameter approach for steady tracer input there are two models commonly used: the piston flow model (PFM), and the exponential model (EM). Both models are characterised by a single parameter: the radioisotope tracer age. The piston flow model is particularly useful for the interpretation of ^{14}C data in confined aquifers with low thickness-to-distance ratio, where for a constant tracer input a possible influence of dispersivity is usually negligible.[42,53,78] Such simple models as the PFM and EM in the case of a constant tracer input give tracer age directly without any calibration. However, the input concentration is seldom well known. Sometimes it can be found by calibration of model(s) describing the tracer behaviour at the entrance to the system, i.e. in the recharge area. The choice of a proper hydrochemical model is sometimes based on the knowledge of the present state of the recharge area and aquifer hydrochemistry. However, very often both the recharge area and its state in the past remain unknown, and the hydrochemical model must be included in the calibration process.

The piston flow model (eqn 4)

For confined, granular, and noncarbonate formations with distant recharge areas the validity of the PFM for dating was confirmed in a number of case studies by comparison of the radiocarbon ages with either conventional flow date (e.g. see Ref. 56), or with 10 000 year isochrome supposed to be represented by the position of the middle of the $\delta^{18}O$ and δD shifts caused by climatic changes at the end of the last glacial period (e.g. see Ref. 12). However, if the isotopic shift is employed to calibrate the transport model by fitting the initial ^{14}C content, the two tracer methods are not independent, and the comparison of parameters cannot be regarded as a way for obtaining the validation.

Note that when comparing the ^{14}C PFM age with the isotope shift, the piston flow model is also assumed for water molecules with ^{18}O and ^2H tracers. However, in the case of ^{14}C a steady state is assumed (a constant tracer input) and the principle of radioactive decay employed, whereas ^{18}O or ^2H are considered to be in a transient state and the principle of the transfer of a variable input employed.

The hydrochemistry of radiocarbon is usually taken into account by models in which the initial activity is corrected to obtain a value expected as a result of all processes except the radioactive decay.[22,51,61,73] Problems related to dissolution and precipitation of carbonates in a typical carbonate aquifer were discussed by Bishop & Lloyd.[11] Unfortunately, as mentioned, the majority of investigators do not take into account the influence of matrix diffusion. According to Małoszewski & Zuber,[44,45] in carbonate rocks, especially if microporosity is high, the radiocarbon method does not work properly due to an additional delay caused by a reversible exchange between dissolved inorganic carbon and solid carbonates. It was shown that if the exchange is dominated by reversible reactions, its influence cannot be taken into account by hydrochemical models applied so far for corrections of initial ^{14}C content. This is because a reversible exchange in a steady state does not influence the concentration of any component while delaying its movement.[45] For instance, Fontes & Garnier[22] observed for a carbonate formation the flow velocity calculated from ^{14}C data to be about 300 times lower than the transit velocity estimated from the hydraulic conductivity. This difference can mainly be attributed both to the matrix diffusion and exchange reactions of carbon species.[44,45]

As the exchange reactions probably play a dominant role in the total retardation of the ^{14}C movement in carbonate rocks, validation can be extremely difficult because the correction factor is large and its accuracy is very low.

The radiocarbon method, like other environmental radioisotope methods is particularly useful in reconnaissance stages of aquifer investigations. However, in such cases the information needed for validation is not available. In consequence, in routine applications, the PFM (eqn 4) is usually employed without any validation, which may lead to serious errors, especially if the PFM is applied in situations which do not satisfy its assumptions, e.g. if flow lines with different flow times meet at the sampling site.[15,35]

Radiocarbon ages exceeding about 10 000 years are not reliably related to the flow parameters because only for the Holocene period can the recharge rate be assumed as approximately constant. Similarly, in intensively exploited aquifers, the environmental tracer age, which is by definition related to the past, will not yield the actual flow parameters observed by conventional methods. Therefore, in such cases, the tracer age is not compatible with the water age defined by eqn (1), and, consequently, both the validation of the tracer model by the flow model and an opposite procedure can be questioned. However, some exceptions are known, especially if a low accuracy is accepted. For instance, studies of the Great Artesian Basin (Australia) and the Milk River Aquifer (Canada) discussed further suggest that the tracer ages for these large systems agree with hydrologic ages up to 1–2 million years within a factor of 2–3.

The exponential model

The exponential model (EM) was derived for unconfined aquifers under the assumption of the exponential distribution of transit times between the recharge area and the discharge site with no mixing of tracer between the flow lines.[13,20,23,42,78] The tracer is mixed only at the discharge site. The exponential distribution of transit times means that the model applies to unconfined aquifers with negligible transit time through the unsaturated zone, at least close to the sampling site. The model is mathematically identical with the model of ideal mixing known in chemical engineering and lake studies, which is a source of misleading remarks common in literature on environmental tracers in groundwater systems (e.g. 'the EM is applicable because the aquifer is well mixed' whereas an ideal mixing cannot exist in an aquifer, or 'the EM is not applicable because the aquifer is not well mixed' whereas the EM is just applicable under the condition of no mixing in the system).

Practical applications of the EM for steady state tracer input are strongly limited due to the addition of man-made radioisotopes to the atmosphere by nuclear bomb tests which for radioisotopes tracers have changed the constant tracer input to a variable one. Additional difficulty for the ^{14}C method may be expected if flow lines of different age, which reach a given sampling site, have different DIC (Dissolved Inorganic Carbon) contents. Similar difficulties can be expected for all non-ideal tracers in cases of flows which cannot be approximated by the PFM.

Some combinations of the piston flow model with the distributed parameter approach

The piston flow model, in both steady and transient states, is also applied to the interpretation of such environmental radioisotopes as ^{32}Si, ^{39}Ar, ^{36}Cl and $^{234}U/^{238}U$. In such cases, the model usually becomes complex because it must be coupled with a hydrochemical model which takes into account the underground production and other losses than those caused by the radioactive decay.[9,24] As mentioned, discussion of hydrochemical models is beyond the scope of the present work, but some case studies are worth considering in a general way as examples of problems encountered in the calibration and validation processes. Some models applied in the case studies discussed within this chapter can be listed under the lumped parameter approach whereas others come under the distributed parameter approach.

The ^{36}Cl dating method was studied in the Great Artesian Basin, Australia.[9,10,69] The piston flow model in its simple form (eqn 4) was corrected for secular in situ production, and the calibration procedure consisted of selection of the most adequate model of $^{36}Cl^-$ and Cl^- hydrochemistry. Comparison of ^{36}Cl ages with hydrologic ages suggests that an indirect validation of both the ^{36}Cl method and the piston flow model was obtained. However, each of the hydrochemical models employed for the interpretation yields different ages, and in some cases (particularly close to the recharge area) the selection of the adequate model without the knowledge of the conventional flow pattern would not be possible. Therefore, depending on the experimenter's choice, the validation can be regarded either as questionable or as achieved. Undoubtedly, the ^{36}Cl method supplied additional information on the origin of salinity and the importance of particular recharge areas. As mentioned, a general agreement between tracer ages and hydrologic ages suggested for that aquifer practically constant recharge conditions during a period of about 1 million years. However, the difficulties encountered in the determination of unique values of tracer ages for that simple and relatively well known hydrochemical groundwater system also suggests that the ^{36}Cl dating method cannot be regarded as generally validated for little known systems. Contrary to the study reported below, constant and little scattered values of $\delta^{18}O$ and δ^2H are observed among the flow lines,[6] which is difficult to explain for a system supposedly containing water recharged without major breaks under different climatic conditions of the Quaternary.

A number of interesting studies were devoted to the Milk River Aquifer, Alberta, Canada, which was initially regarded as a simple hydrodynamic and hydrochemical system because it dips gently from the recharge area and some of its chemical components are either constant or change their concentrations in a monotonic way.[57] Several scientific teams applied different conceptual and mathematical models. The results of their studies supply excellent material for the discussion of problems related to calibration, validation and identifiability processes.

Phillips *et al.*[57] assumed that the ion filtration process, caused by outflows from the Milk River Aquifer through both overlying marine shales of the Pakowki formation (50–300 m thick) and underlying Colorado shales (400 m thick) to the Bow Island sandstone, controls the chloride content and the stable isotope composition of water. Assuming further that the ^{36}Cl/Cl ratio is not influenced by ion filtration, these authors employed the piston flow model, with that ratio corrected for secular in situ production of ^{36}Cl, to calculate the isochrones. The age obtained at the end of the aquifer was about 2×10^6 years. A comparison of the observed Cl-δD relationship with that predicted by ion filtration may be regarded as an attempt to validate indirectly the model.

Hendry & Schwartz[30] came to the conclusion that the origin of hydrochemical and isotopic patterns in the Milk River Aquifer can be explained by diffusion exchange between the aquifer and the aquitards. They employed and adapted the transient state solution to the dispersion equation for a step input function[68] (formally it is a dispersion model but for the dispersivity assumed to be equal to 100 m, the model behaves as the piston flow model at the scale of the Milk River Aquifer). The unidimensional transport equation for the aquifer was coupled with the unidimensional diffusion equation for the aquitard and applied for two chosen flow paths. The time obtained for active inflow of meteoric water was 1–2 million years whereas the time for the inflow water with different isotopic composition (due to supposed changes in climatic conditions) was 0·25–0·5 million years. As Hendry & Schwartz[30] were very critical about the model of Phillips *et al.*,[57] their paper caused a lively discussion on the applicability of 'over-simplistic models'[30,31] and models with 'very large number of adjustable parameters' for which 'the level of effort required is typically much higher than the level of confidence in the degree of realism of the simulations,[58] and which 'infrequently qualify as unique solutions'.[58]

Nolte *et al.*[54] presented a mathematical model based on the conceptual model of Hendry & Schwartz,[30,31] which relates tracer concentrations along flow paths to exchange between the aquifer and aquitard by molecular diffusion, and to the start of active flow sometime in the past (transient state). The unidimensional transport equation (without the dispersion term, i.e. equivalent to the piston flow model) for the aquifer was coupled with the unidimensional diffusion equation for the aquitard. Two versions were considered: with and without in-situ ^{36}Cl production in the aquifer (production in the aquitard was neglected). Similarly to Hendry & Schwartz,[30] the solution was obtained for a semi-infinite system with a constant flow velocity. The model has three fitting parameters: the flow velocity, the distance from the recharge area achieved by the tracer front during the active flow (related by flow velocity to the age of water at that distance, i.e. to the start time of the flow), and the diffusion parameter which couples the molecular diffusion coefficient in the aquitard with both the aquitard porosity and the aquifer thickness. Nolte *et al.*[54] fitted their model to the space distributions (along flow lines) of two tracers, Cl^- and $^{36}Cl^-$, for the parameters shown in Table 1.

Table 1. Parameters of the piston flow model combined with diffusion equation for exchange between the Milk River Aquifer and aquitard

Parameter	Eastern flow path	Western flow path
Fitted to $^{36}Cl^-$ and Cl^- data by Nolte *et al.*[54]		
v (m/a)	0·10	0·07
x_M (km)	140	109
A [$a^{-1/2}$]	$0{\cdot}825\times10^{-4}$	$1{\cdot}65\times10^{-4}$
Calculated by Nolte *et al.*[54] from fitted parameters		
t_o(a)	$1{\cdot}4\times10^{6}$	$1{\cdot}6\times10^{6}$
D_a(m^2/s)	$6{\cdot}3\times10^{-12}$	$6{\cdot}3\times10^{-12}$
Calculated from Nolte's *et al.*[54] model fitted to δ^{18}O and δ^2H data within this work for v and X_M as above		
D_a(m^2/s)	$1{\cdot}0\times10^{-10}$	$1{\cdot}0\times10^{-10}$

$A = n_a(D_a)^{1/2}/h$, where n_a and D_a are aquitard porosity and diffusion coefficient, respectively, and h is aquifer thickness for a given path.

The model of Nolte *et al.*[54] can also be used to calculate the distributions of δ^{18}O and δ^2H along the flow lines. In Figs 1 and 2 these distributions are fitted to the experimental data for the flow velocity and the distance of the front of active flow found by Nolte *et al.*[54] The diffusion parameter, which combines aquifer thickness, aquitard porosity and the coefficient of molecular diffusion in the aquitard,[54] was the only fitted parameter. The δ^{18}O values for the end components were taken as in Ref. 30, and the δ^2H values were taken as those given by the observed δ^{18}O–δ^2H correlation.[30] It should be stressed that the end values of both δ^{18}O and δ^2H correspond in approximation to the values of modern recharge at the recharge area and to the isotopic composition of the Bow Island formation presented in Drimmie *et al.*,[19] and, therefore, they can be regarded as known parameters. Large scatter of experimental points in Figs 1 and 2 can be attributed to changes in climate and atmospheric circulation during

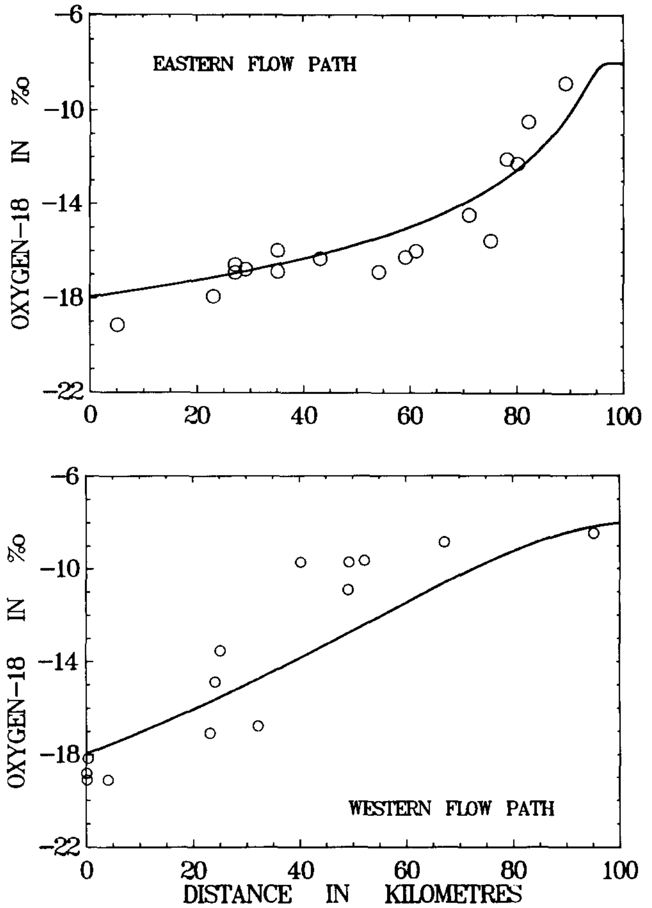

Fig. 1. Oxygen-18 data and 'the best fit' of Nolte's *et al.*[54] model for two flow lines in the Milk River Aquifer (see Table 1 for parameters).

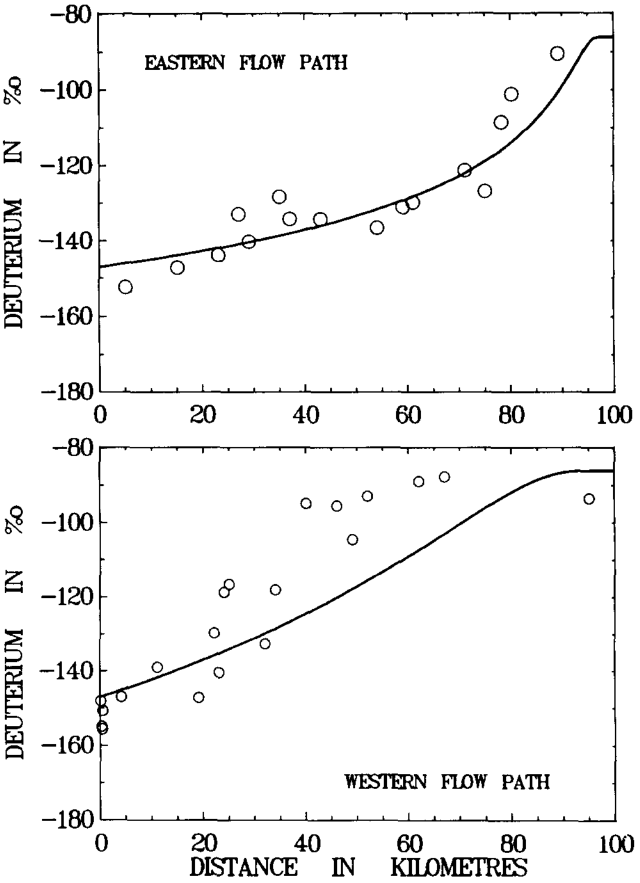

Fig. 2. Deuterium data and the same model as in Fig. 1.

the recharge history. As shown in Table 1, Hendry & Schwartz[30] assumed the same diffusion coefficient for different tracers in the Colorado shale. A similar value for Cl^- was obtained by Nolte *et al.*[54] from their diffusion parameter. The diffusion parameter obtained within this work for $H_2{}^{18}O$ and ^2H_2O yields the coefficient of molecular diffusion of water in the aquitard about 16 times larger than that for chloride, which seems to be reasonable but requires verification as discussed further.

As mentioned, Hendry & Schwartz[30] obtained for Cl^- ages of 1–2 million years and for ^{18}O ages of 0·25–0·5 million years, which was explained by these authors as a result of a climatic change which probably occurred later than the start of active flow. This assumption was strongly opposed by Phillips *et al.*[58] and defended by Hendry & Schwartz.[31] Unfortunately, the latter authors did not try to explain why the isotopic composition of the Quaternary meteoric water entering the aquifer at the start of the active flow was tacitly supposed to be the same as that of very old water stored in the buried aquifer. The model presented by Nolte *et al.*[54] and its calibration extended here are free of such inconsistencies, because the active flow of fresh water starts at the same time as the flow of water with different isotopic composition. Note that the mathematical models of Hendry & Schwartz[30] and Nolte *et al.*[54] are very similar and based on the same conceptual model. Therefore, most probably, discordant conclusions result both from different accuracies of calibration (in Ref. 30 the theoretical curve considerably differs from the experimental $\delta^{18}O$ values for the eastern flow) and from different values of the fitted parameters (diffusion coefficients for H_2O and Cl^- in the aquitard in the present work differ from each other, whereas in Ref. 30 the same values were used).

The solution to the transport equation coupled with the aquitard diffusion equation discussed above are based on the assumption of a constant flow velocity, whereas the discharge through the Pakowki formation decreases the volumetric flow rate along the flow paths. However, as the aquifer thickness and porosity also decrease, the change in the flow velocity is probably low. Nevertheless, Ivanovich *et al.*[37] presented a flow model based on the assumption of linearly decreasing flow velocity, coupled with hydrochemical models, obtaining for $^{36}Cl^-$ and $^{129}I^-$ equally good, or equally poor, fits as those obtained for constant velocity flow models. Therefore, from the comparison of the results of these authors with those of earlier works it seems impossible to say if the flow velocity is constant or decreasing. Similarly, Drimmie *et al.*[19] found from ^{14}C, measured in the initial part of the aquifer, the flow velocity one order of magnitude larger than those estimated from other tracers for the whole length of the aquifer. In this case it is difficult to explain that discrepancy unless a higher filtration through the aquitard is assumed for the initial part of the aquifer.

It should be mentioned that the ages obtained from models fitted to $^{36}Cl^-$, Cl^-, $\delta^{18}O$, δ^2H and $^{129}I^-$ data are generally about 2 times greater than the water ages found from hydrodynamic modelling,[30,32] which may reasonably be explained by possible periods of no recharge during high glacials. However, at the same time this difference exemplifies difficulties in validation of flow and/or tracer models at great time scales. The picture becomes even more complicated when the results of Ivanovich *et al.*[36] are considered. These authors found uranium migration velocity to be in agreement with water velocity determined from the hydrodynamic modelling, which, in this case, leads to an unacceptable conclusion that uranium migrates 2 times faster than all the other tracers, unless the error of age determinations is given by a factor of 2.

It should be mentioned that in addition to the two conceptual models discussed above, i.e. ion filtration and diffusion between the aquifer and aquitard, other possibilities were also suggested. For instance, Fabryka-Martin *et al.*[21] excluded both ion filtration and diffusion from the underlying Colorado shales as the source of salinity and claimed that salinity comes from low-permeability units within the aquifer. If this is true, all the models discussed above, in spite of good fits, perhaps yield correct ages but other parameters remain doubtful.

Two other conceptual models were also proposed to explain the trends observed for $\delta^{18}O$ and δ^2H data. Hendry & Schwartz[30] suggested that the down-stream end of the Milk River Aquifer could have a composition that once was determined by evaporative processes. Drimmie *et al.*[19] claim that the aquifer contains water recharged under warmer climatic conditions than exist today and that mixing with more saline formation water becomes important deeper in the aquifer (the mechanism of mixing was not specified).

Without going into details one may conclude that if mathematical models based on different and even contradictory conceptual models (e.g. diffusion exchange or ion filtration) yield similarly good fits and ages, either the models were not sufficiently well calibrated and validated, or the methods are not sensitive enough to solve any real problem. In the case of the Milk River Aquifer, similar ages yielded by different tracers can be regarded as a successful result of the study aimed at the comparison of tracer dating methods.[26,37] However, can one rely on these methods if in spite of so much experimental and theoretical effort it remains unknown which of the possible processes governs the distribution of the investigated species? A successful use of different methods should be based on a conceptual model which is both supported by mathematical models liable to calibration and validation processes and is consistent with other evidence, not necessarily employed directly in the mathematical modelling. In spite of great experimental effort, the evidence gathered has appeared to be insufficient to obtain fully identified solutions. Therefore, one may conclude that the mathematical models discussed of the tracer behaviour in the Milk River Aquifer, whether well calibrated or not, can perhaps be regarded as partly validated in respect to tracer ages, proving also the applicability of simple models in this respect. However, in spite of good calibration and partial validation of all the mathematical models employed, their identification and consequently, the identification of the conceptual model has not been achieved. The difficulties can be overcome either by efforts directed at obtaining a more complete validation, or by reduction of the number of adjustable parameters. For instance, measurements of the diffusion coefficients of Cl^-, $\delta^{18}O$ and/or δ^2H in core samples taken from the Colorado shales could serve either for the reduction of the number of adjustable parameters (if used in the formulation of the mathematical model) or for a partial validation (if in agreement with the values obtained earlier from the calibration). Similar results can probably be obtained by calibration of a model to tracer distributions in the aquitard, when such distributions are available.

Andrews & Fontes[8] have recently reexamined the underground production of ^{36}Cl in the Great Artesian Aquifer and in the Milk River Aquifer and came to the conclusion that in situ production of that radioisotope makes age determinations impossible in aquifers with variable Cl^- contents and above several mg/litre. In such a case the ^{36}Cl would be useless for age determinations of old systems which usually have high chloride contents. However, for the models employed by Hendry & Schwartz[30] and Nolte *et al.*[54] the initial activity was not so important as were the changes in the activity observed along the flow paths.

LUMPED-PARAMETER MODELS FOR A VARIABLE TRACER INPUT

General

The lumped parameter approach based on eqn (3) is routinely applied to the interpretation short-term (months and years) variations of three ideal tracers of water molecules, i.e. $H_2{}^{18}O$ and ^2H_2O (tritium, $\delta^{18}O$ and δ^2H, respectively) when time records of their concentrations are available. Examples of applications to other tracers such as combined tritiugenic ^3He (usually in combination with ^3H_2O), ^{85}Kr and Freons are also known. Grabczak *et al.*[28] and Zuber[78] compared for two systems the ages obtained from these gaseous tracers with tritium ages and came to rather pessimistic conclusions about their applicability. The limitations of gaseous tracers in small systems were attributed to possible gains and losses by molecular diffusion during percolation through the unsaturated zone. A different conclusion was reached by Weise & Moser[72] who demonstrated for several systems a general agreement between ages determined by different tracers. Further discussion of the gaseous tracers is given in the section devoted to distributed parameter models.

Due to its relatively short half-life time (12·4 years), tritium is found in measurable concentrations only in unconfined aquifers and in some confined aquifers close to the recharge areas. It can be found with the aid of eqn (3) that the seasonal variations of stable isotopes in precipitation, or in surface waters, induce variations at discharge sites of very small groundwater systems having the mean transit time only up to about 2–4 years.

The exponential model (EM), the dispersion model (DM), and the combined exponential-piston flow model (EPM)[42,77] are commonly used, though other similar models are also known. The exponential model was defined earlier, whereas the dispersion model, represented by a solution to the dispersion equation, in addition to the mean transit time of tracer (tracer age), has one other parameter which represents the apparent dispersion of tracer caused by different transit times of flow lines which meet at the sampling site, i.e. at a spring or a well.[42,77] The exponential-piston flow model is supposed to represent an aquifer with an exponential distribution of transit times of flow paths in the unconfined (recharge) area, which changes on its way into a piston flow (e.g. in the confined part). The same concept can be applied to unconfined aquifer if samples are taken from a withdrawal well screened at the depth which excludes the interception of flow lines with short transit times.[42,77]

In the lumped-parameter approach different models (e.g. EM, EPM, or DM) can often be equally well calibrated (fitted) especially for systems with short turnover time in respect to the half-life time of a given radioisotope tracer.[20,42,77] Sometimes, in more complex cases, modelling can be performed by combination of two, or three models[33,47] as for instance, the EPM itself is a combination of two single-parameter models. However, even when a few-year long record of output tritium concentration is available, a unique calibration of a model with more than two parameters seems to be impossible.[29] Therefore, if a combination of models simply leads to the number of fitting parameters above two, the combination of models should be avoided. If some information on the system and adequate data are available, the combination of single- or two-parameter models leads to another category of models which are discussed further.

The lumped-parameter models are usually applied under an assumption of a steady flow. However, natural systems are seldom characterized by a steady flow, and thus a variable flow approach seems to be a must. Unfortunately, the mathematical treatment then becomes complicated because new variables appear instead of some parameters, e.g. $Q(t)$ and $V(t)$, and long records of concentration and flow data are needed.[78] It has appeared that even for highly variable flow, when the variable part of the system is small in comparison with the whole system, the information obtainable from the variable flow approach is similar to that obtainable from the steady flow approximation.[80] In such cases a somewhat better fit (calibration) obtainable from the variable flow approach does not seem to justify the much greater effort needed in comparison with the steady flow approximation.

Calibration for steady and variable flow approaches is performed by fitting the calculated output concentration to the measured time record of tracer. Usually it is difficult to obtain a unique calibration due to a too short record of data. A direct validation by comparison with predictions to greater time scales, or indirect validation by comparison of parameters with those obtained independently, is seldom available.

One of the main difficulties is related to the estimation of the input function. Tritium concentrations are usually averaged on a yearly basis whereas $\delta^{18}O$ and δD are on a monthly basis. Even if the monthly infiltration rates and tracer contents in precipitation are known, the monthly input fluxes of tritium, $\delta^{18}O$ and δD are not well known because the evaporation and transpiration in a given month only partly come from the precipitation of that month. Similarly, the infiltration which originates from melt water in spring contains tracers related to the precipitation in winter. In arid and semi-arid zones, strong fractionation of stable isotopes caused by evaporation prior to the infiltration process and recharge by highly irregular events make the approach discussed within this chapter inapplicable.

The methods applied for the estimation of the tritium input function were discussed in detail by Grabczak *et al.*[29] Whichever of the approximate methods is used, the input function contains explicit or hidden fitting parameter(s), commonly tacitly omitted in modellers' presentations. In some cases, when the infiltration ratio is properly chosen, its influence can be strongly reduced,[29] especially for moderate and humid climates where the mean isotopic composition of the modern recharge is close to the mean isotopic composition of precipitation. The only exception free of difficulties in the estimation of the input function is related to river bank filtration studies, where the input function is directly measurable by sufficiently frequent sampling of river water and the DM applied to model the movement

Table 2. Models and parameters fitted to tritium data of Nowe spring

Number	Model	t_t [a]	Pe^{-1}	η	β	σ [T.U.]
		For 0 T.U. in old component				
1	DM	130	1·0	—	0·70	0·546
2	DM	70	0·5	—	0·78	0·510
3	DM	95	0·5	—	0·58	0·475
		Without old component				
4	DM	190	0·8	—	—	0·622
5	DM	135	0·5	—	—	0·736
6	EM	400	—	—	—	0·906
7	EPM	300	—	1·04	—	0·522

See text for definitions of parameters. The goodness of fit is given by

$$\sigma = \left[\sum_{i}^{n} (c_{mi} - c_{ti})^2\right]^{1/2} / n,$$

where c_{mi} and c_{ti} are measured and theoretical concentrations, respectively, and n is the number of experimental points.

of tracer between a river and pumping wells.[48,66] In such a case a calibrated model gives directly the best solution available for the prediction of the behaviour of a conservative pollutant for the same pumping rates and river level. However, a model derived for a constant flow rate, though properly calibrated, is not necessarily valid for other pumping rates or river levels. For a sorbable pollutant, the validation of the transport model combined with the reaction model will be unavoidable. Unfortunately, it is difficult to give general advice on the validation process for such a type of modelling.

Validation and identification of models

In the case of the DM applied to environmental tracer data in the lumped parameter approach, the dispersion parameter ($D/(vx) = Pe^{-1}$, where Pe is the Peclet number and D is the coefficient of dispersion), should not be used for validation by comparison with values known either from artificial tracer experiments and calibration of pollutant transport models or from theoretical predictions, due to reasons explained earlier. There are two exceptions to the above statement: in river bank infiltration modelling, the dispersivity may, in some cases, be comparable with that obtainable by other field methods (because the 'injection line' is sometimes sufficiently short to be approximated by point injection); and in the use of environmental tracer profiles to study the infiltration rate in the unsaturated zone, where the dispersivity is usually very low, mainly depending on molecular diffusion.

Problems encountered in the processes of calibration and model identification can be presented by a study in which long records of tritium exist. In cases of short records of tritium, the difficulties can even be more serious. Grabczak *et al.*[29] presented a 7-year record of tritium data for two karst springs. For the Chuderski spring two types of models were shown to yield practically the same good fit. In that case it was impossible to perform the calibration without assuming the presence of a tritium-free component, i.e. without an additional adjustable (fitting) parameter, defined as the fraction of old, tritium-free component(β). The dispersion model (DM) was easily calibrated, but its solution was not unique due to the interplay of parameters (in that case three adjustable parameters). For solving the inverse problem, the most reliable model was chosen as that with the lowest number of fitting parameters, i.e. the exponential model (EM, in that case with two adjustable parameters, i.e. tritium age, t_t, and fraction of tritium free water, β). For the Nowe spring, the DM was also easily fitted but due to three adjustable parameters the results were not unique.

Within this work the previous data of these two springs are extended by new tritium observations[81] and reinterpreted in order to demonstrate that, in spite of the considerable effort, the most reliable models were not found in the original work. However, it must be stressed that the improved interpretation given here is little related to the prolonged observation time. The improvement is achieved mainly by selection of another conceptual model (EPM without tritium-free component instead of DM and tritium-free component) in the process of calibration. In Table 2, the models, parameters, and the goodness of fits (σ) are summarised for the Nowe spring, whereas the experimental points and best fit curves are shown in Fig. 3. The first three models are those given in Ref. 29, but fitted to the new set of data. Next, four models were fitted under the assumption of a single flow component. For the DM and EM, the fit is somewhat poorer than in the previous cases (larger σ), but in general the models 4–7 can be regarded as more reliable than 1–3 because the number of adjustable parameters was reduced from three to two (in general, models with lower numbers of fitted parameters are considered to be more reliable[34]). Considering both the goodness of fit and the number of adjustable parameters, the EPM (7) can be regarded as identified. Note that qualitatively all the models give similar results indicating a great tritium age of water discharged by the spring. Quantitatively, the most reliable is the EPM, though its identification was neither easy nor free of doubts.

The Chuderski spring discharges just above the Nowe spring and the Wrobel spring, the latter discharging water with the same tritium content as the Nowe spring. As the presence of tritium-free component in the Nowe spring has been rejected in the present interpretation, one cannot assume that such a component exists in the Chuderski spring. Therefore, the data of that spring were also reinterpreted, but assuming that the old water component has identical tritium content as the water in the springs Nowe and Wrobel. For the sake of easy calculations the average tritium concentration in the old component was taken, which according to Fig. 3 was equal to 10·7 T.U. In Table 3 the models, parameters

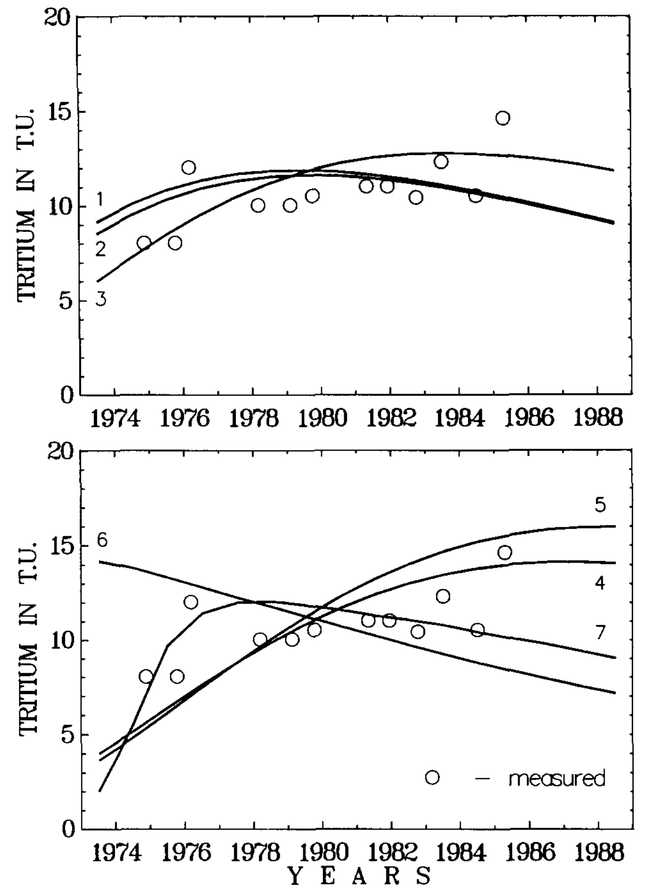

Fig. 3. Different models fitted to the tritium data of the Nowe spring (curve numbers correspond to model numbers in Table 2).

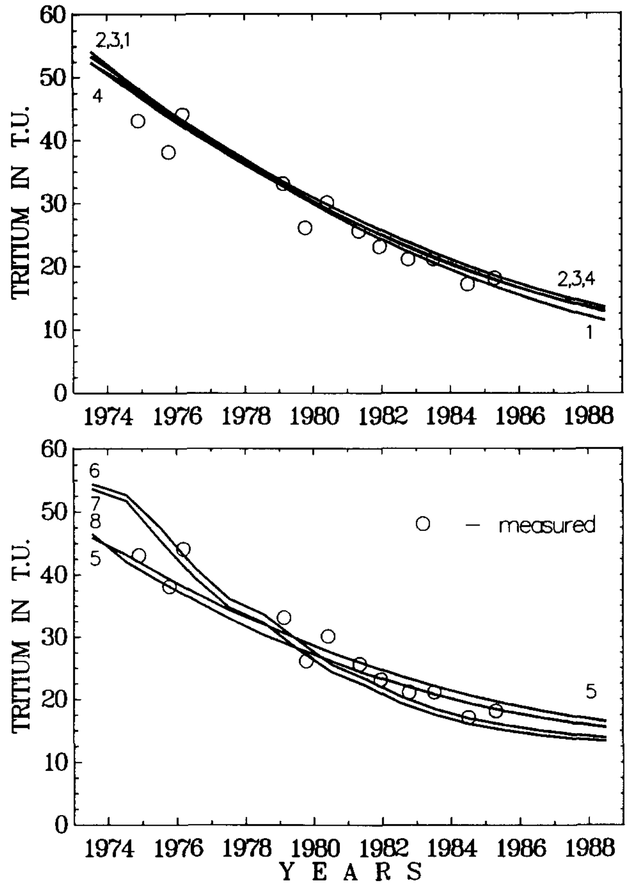

Fig. 4. Different models fitted to the tritium data of the Chuderski spring (curve numbers correspond to model numbers in Table 3).

and goodness of fits are summarized for the Chuderski spring, whereas in Fig. 4 the experimental points and best fit curves are shown. Similarly to the previous case, the new conceptual model based on the assumption of no tritium-free component in the Nowe spring, and the old component in the Chuderski spring to be represented by the water of the Nowe spring, did not yield an essential improvement of fits. The values of parameters obtained do not differ considerably in comparison with the values obtained originally (5 and 8 versus 1–4 in Table 3). Models 6 and 7 have even larger values of σ. Due to a low number of parameters and a reasonably good fit, model 8 can be claimed to be identified and adequate.

Table 3. Models and parameters fitted to tritium data of Chuderski spring

Number	Model	t_t [a]	Pe^{-1}	β	σ [T.U.]
	For 0 T.U. in old component				
1	DM	15	0·25	0·82	0·815
2	DM	20	0·25	0·78	0·766
3	DM	30	1·0	0·73	0·922
4	EM	15	—	0·76	0·809
	For 10·7 T.U. in old component				
5	DM	12	0·8	0·85	0·837
6	DM	3	0·9	0·75	1·059
7	EM	2·5	—	0·75	1·067
8	EM	11	—	0·85	0·757

See text for definitions of parameters and Table 2 for σ.

It can be mentioned that the tritium data of both springs were also interpreted by other investigators (Fig. 5c in Ref. 25) who fitted the EM and obtained different results from those presented here. The validation of the models presented within this work has recently been obtained by comparison of hydraulic parameters calculated from the tracer ages with those known from conventional methods.[81]

DISTRIBUTED-PARAMETER MODELS WITH LUMPING FOR TIME RECORDS OF TRACERS

The principles of the multi-cell models (MCM) for the interpretation of environmental tracer data in hydrology were described by Simpson & Duckstein.[63] In general, by modelling the cell sizes and flow routes it is possible to account for some variations of the parameters in the system. Because of that it is called by some modellers distributed-parameter modelling.[74] However, the parameters are lumped within each compartment. Thus, this category of models should be called distributed models with lumping. Its popularity results for an easy conceptual and mathematical formulation. On the other hand, an easy formulation tempts the modeller to introduce too large a number of fitting parameters, which may lead to an unnoticed ambiguous calibration. The use of this approach for solving the inverse problem from time records of concentration at a given site[59] seems to be little justified because one- and two-parameter models give equally good fits[42] and a lower number of fitting parameters are more reliable.[34]

The multi-cell models are also applicable to tracer data in variable flow. They seem to have a distinct advantage over the lumped-parameter models because they are able to model both the concentration and flow variation.[75,76]

DISTRIBUTED PARAMETER MODELS WITH LUMPING FOR SPACE TRACER DATA

The multi-compartment models (MCM) are particularly suitable for modelling the tracer distributions in space and for space distribution of recharge components. It is the only method available at the operational level for the interpretation of scarce data in large systems, which can neither be approximated by the PFM nor by distributed parameter models discussed further. As stated by Simpson & Duckstein,[63] the design of a given compartment network is determined by a prior knowledge of the flow system, or by calibration procedure, or by both. Unfortunately, in a number of case studies with the MCMs a clear distinction between known, assumed to be known, and fitted parameters is not given. As a result many interesting examples of the application of the MCMs are not free of doubts related to their calibration and validation, because with large numbers of fitting parameters,resulting from large numbers of compartments (cells), the calibration often seems to be ambiguous as discussed below.

1. Time records of tritium data obtained at seven localities in the Edwards Aquifer, Texas, were used to calibrate a MCM of 34 cells.[15] These cells were arranged in a two-dimensional network, and the turnover times, recharge rates, effective porosities, and storages could have been varied for each cell. The model was claimed to be validated by yielding the recharge rates in agreement with independent estimates. However, as the model was constructed on the basis of these estimates and large numbers of fitting parameters were large, both calibration and validation seem to be dubious.

2. On the basis of a prior geological knowledge and 13 radiocarbon determinations, a three-dimensional model consisting of 26 cells (17 cells in the upper and 9 in the lower layer) was constructed for a deep granular aquifer in Arizona.[16] The calibration yielded the flow rates through aquifer boundaries, the flows between the cells, the long-term mean annual recharge, and the mean transit times to the cells. However, the ^{14}C determinations were available only for the upper layer of cells. In addition seven determinations indicated a modern age, within the accuracy of the ^{14}C method, with the ages of the remaining six cells varying from about 1900 to 4300 years. One may doubt if reliable values of residence times and flows in 26 cells can be obtained by calibration with several ^{14}C determinations. In addition, the problem of the total dissolved carbon was not taken into account, i.e. it was tacitly assumed that in all flow components the concentrations of the dissolved carbonates were the same. In conclusion, most probably, the calibration was not unique.

3. A multi-compartment model was also used to model ^{14}C data in a vertical profile of the Madrid Basin.[41] The ^{14}C ages calculated along flow lines with the aid of the PFM agreed in approximation with the isochrones obtained from the finite difference flow model (Fig. 2 of the paper cited). The ^{14}C data were also used in a model based on the opposite principle to the PFM, i.e. in the MCM consisting of 62 cells, which was designed on the information available from the flow net model. The ^{14}C concentrations were calculated for 57 cells, under different assumptions related to the initial concentration and diffusion into five 'dead' cells, and compared with nine experimental ^{14}C determinations (in two cases two determinations corresponded to one cell, and in one case a single determination corresponded to two cells). It was concluded that ^{14}C data probably will not permit a better calibration of any model, but the MCM coupled with a flow net model could provide a simplified method to analyse solute transfer in groundwater.

One may doubt how models based on controversial principles, i.e. the PFM and MCM, can yield satisfactory results for the same data. However, it is well known that for a constant input in a steady state all the models give approximately similar ages, if these ages do not significantly exceed the half-life time of a given radioisotope.[20,42,77]

4. A unidimensional MCM was also used to interpret the tritium distribution along the flow direction in a large shallow aquifer in South-Australia.[7] The number of fitting parameters was kept low, so the calibration was undoubtedly unambiguous. The model seemed to be validated as the parameters obtained were in agreement with independent estimates. A more sophisticated, distributed-parameter model,[18] was also fitted, and yielded nearly the same recharge rates.

The agreement of the recharge rates obtained from the models with those found by conventional methods can be regarded as a partial validation. However, some doubts may be expressed with respect to the tracer transfer through the unsaturated zone. In both models the tritium was assumed to reach the water table immediately, whereas for the obtained recharge rate of about 0·03 m/a and the thickness of the unsaturated zone of 2–4 m the transport to the saturated zone should take several years or more, even if moisture content was low. Therefore, as the assumption of a fast transfer through the unsaturated zone was far from reality, it is difficult to say why both models yielded recharge rates in agreement with independent determinations.

5. The power and some pitfalls of the MCMs can be appreciated from a very interesting study in which the spatial distribution of a conservative tracer (deuterium) was used to calibrate the flow model of a regional carbonate-alluvial groundwater system in Nevada.[38] Thirty-four deuterium values were used for recharge and 40 to represent mean values in cells. Cell volumes were assumed on the basis of geological evidence. Due to the lack of constraints three scenarios were considered with somewhat different cell arrangements, recharge distributions and flow routes. Recharge rates for alluvial cells were based on experimental evidence whereas those for carbonate cells were speculative, but within the total recharge rate known for the whole system. Invariant recharge rates and deuterium concentrations were assumed. The model consisted of 17–20 cells arranged in two tiers. Depending on the scenario, 14 or 15 deuterium values were known for the cells. Calibration of the model yielded the values of volumetric flow rates between the cells. Once the model is calibrated it yields the mean groundwater ages and age distributions. The mean ages exceeded 10 000 years for several cells and in some cells ages up to 100 000 years were calculated. It is evident that for such age values the assumptions of invariant recharge and deuterium concentrations are highly questionable. There is no doubt that the differences in deuterium values which in the model were attributed to differences in latitude and elevation, also resulted from the climatic changes in the past.

It should be mentioned that for a conservative tracer in steady state (as assumed) the influence of matrix diffusion in fissured rocks cannot be discovered. For the carbonate part of the system, an effective porosity of 3% was assumed.[38] If this values is close to the mobile water porosity (fractures, solution channels, conducting fault zones), the calculated ages correspond to the water ages as defined within this paper. However, if this value is close to the matrix porosity the calculated ages correspond to the tracer age. In the latter case, the mobile water volumes in the carbonate cells are much smaller than those originally estimated.

MULTI-TRACER MULTI-CELL MODELS (MTMCM)

A novel approach to the multi-cell modelling of environmental tracer data was presented in a series of papers by Adar & Neuman,[1,2] Adar & Sorek,[3] and Adar *et al.*[4,5] The principle of this approach is summarized as follows:[4] 'The aquifer is divided into cells within which the isotopes and dissolved constituents are assumed to undergo complete mixing. For each mixing cell mass-balance equations expressing the conservation of water, isotopes and dissolved chemicals are written. These equations are solved simultaneously for unknown rates of recharge into the various cells by quadratic programming. The degree to which individual dissolved constituents may be considered conservative is tested a priori by means of a chemical equilibrium model such as WATEQF. Constituents which do not pass this test are either disregarded or suitable assigned a small weight in the quadratic program'. The idea is to solve the inverse problem for systems without hydrologic information where the hydrochemical data are available from a sufficient number of wells. The number of equations must exceed the number of unknown flows. For the aquifer parameter estimation from additional incorporation of periodic variations of the water table the wells are also used to measure the hydraulic heads.[3] The method is used in a constrained way, which means that the number of cells cannot exceed the number of sampling sites. Similarly to the MCM approach, the dispersion in the aquifer is modelled by the number of cells and their arrangement. The general validity of the multi-tracer multi-cell modelling (MTMCM) was proved on synthetic data.[4] Similarly to many other tracer methods and models, the MTMCM approach is particularly applicable to systems where conventional information is unavailable or inadequate. Therefore, it would be unrealistic to expect a possibility for its validation in each case. It seems that the validity of a given MTMCM approach, whether tested or not by the process of validation, will mainly depend on the presence of a sufficient number of conservative constituents, on the accuracy of assumptions related to the conservative behaviour of nonconservative constituents, and on the validity of assumptions on invariant flow and concentration inputs. In addition, even such conservative tracers as ^{18}O, ^{2}H, Cl^- and Br^- may change their concentrations due to either ion filtration through clay membranes or diffusion exchange with aquitards. The MTMCM approach in its present form does not account for such effects, which in some cases may lead to false results in spite of a unique calibration.

DISTRIBUTED PARAMETER APPROACH

Usually no sufficient data are available to attempt the distributed parameter approach. However, the approach is well applicable to small systems in which multiple sampling facilities exist. It is also applicable to large systems with a large number of tracer data and/or with known flow patterns.

Robertson & Cherry[60] investigated a small granular aquifer situated at a flow divide between two watersheds. A dense line of borings along a cross-section perpendicular to the flow divide, and the installation of bundle-type piezometers, each consisting of nine individual piezometers with short slotted and screened tips permitted detailed observations of the hydraulic heads and the performance of hydraulic tests and tritium sampling at desired depths. A numerical flow model was constructed for the observed cross-section as a prerequisite for the modelling of the tritium transport. A known analytical unidimensional solution to the dispersion equation was used and calibrated by selecting the flow velocities and dispersivities to obtain fits with the spatial distribution of tritium data along flow lines at different sites. The dispersion model can be regarded as validated because it yielded flow velocities comparable with those known from the hydrologic observations. The best fit was obtained for a dispersivity of 0·02 m. Such dispersivity is expected from the molecular diffusion in a porous medium in the cases of low flow velocities (< 1 m/a), and, thus, the agreement of the dispersivity observed with that expected can be regarded as part of the validation process. Though in that part of the study the transport velocities and dispersivities for given flow lines were treated in a lumped way, the general approach was of the distributed-parameter type.

The next part of the study was exclusively of the distributed-parameter type, because the Galerkin finite element numerical solution[67] to the two-dimensional dispersion equation was employed with calibration by fitting both the spatial and time distributions of tritium. Again the dispersivities were equal to those resulting from the known coefficient of molecular diffusion in a porous medium. That study also showed how the dispersivity may depend on the approach chosen and sampling method. Obviously, sampling along the whole profile of any observation well would yield quite different dispersivities.

Smethie *et al.*[64] observed ^{85}Kr concentrations along chosen flow lines in the Bordon aquifer by point sampling. The tracer ages calculated from the PFM were in agreement with the hydrologic ages known from the flow model. A two-dimensional model for the cross-section parallel to flow direction was also used. Due to the monotonic input function of ^{85}Kr the longitudinal dispersivity was negligible, and the sensitivity to changes in transverse dispersivity very weak. A similar piston flow model approach was used by Busenberg & Plummer[14] for environmental Freons used as hydrologic tracers.

An interesting application of the ^{14}C method in a modified version of the PFM (changes in flow rate were taken into account as the ^{14}C concentrations were calculated from the equation of advective flow) was reported by Wei *et al.*[71] who claimed a partial validation of the flow model of the Paris Basin (the cited authors also introduced the term 'partial validation' with a meaning similar to that defined in Ref. 46). The validation was obtained by comparison of the ^{14}C ages observed with those calculated from the flow rate for adjusted effective porosity which was not defined. This porosity and the validation process can be explained in terms of the present paper as follows. According to eqn 7 the total open (effective) porosity is equal to the sum of matrix and fracture porosities, and in approximation to matrix porosity. The adjusted value of porosity was equal to 15% which for a limestone aquifer with a hydraulic conductivity of 1.5×10^{-5} m/s means that the transport of tracer took place in the whole accessible volume, whereas the flow of water was in the factures. Therefore, the ^{14}C age must differ from the water age due to matrix diffusion and possibly due to exchange in the matrix. Wei *et al.*[71] adjusted the effective porosity to obtain a good fit of the ^{14}C ages with the flow data. The obtained value of 15% is of a reasonable order of magnitude for the total porosity of a carbonate rock. According to the modellers' judgment this value can be regarded either as a known quantity or as a fitted one. In the former case the claim of validation is acceptable whereas in the latter case such a claim remains unjustified.

Solomon & Sudicky[65] considered theoretically advantages of the ^{3}H/^{3}He method in the distributed parameter approach over the tritium method. In their opinion the ability to obtain reliable estimates of spatial variations in recharge rates combined with accurate tracer ages (in that case equal to groundwater ages) in shallow unconfined aquifers will undoubtedly provide valuable constraints when calibrating models of groundwater flow and solute transport.

Simpkins & Bradbury[62] applied analytical solutions to the transport equation for modelling the downward movement of ^{18}O in a thick, fine-grained till unit. The radiocarbon ages calculated from the PFM approximation yielded water velocities in agreement with those found by calibration of δ^{18}O in the transport equation and with those found from Darcy's Law, which can be regarded as the validation of both tracer methods employed.

To the distributed-parameter models one may also add those based on simple flow models; for instance, in the case of the exponential flow model, if the tracer concentration is measured as a function of depth. The simplest solutions are known for homogeneous aquifers and a constant input of tracer.[13,23,70] Calibration is simply obtained by fitting the theoretical depth profile of concentration to that observed.

For an aquifer which could be approximated by unidimensional flow with variable tracer and flow inputs along the aquifer length, Colville[18] solved numerically the equation of flow conservation combined with the equation of tritium conservation. As mentioned, the model was validated, though the assumption related to a fast tritium transfer through the unsaturated zone can be questioned. The numerical form of the model makes its routine applications difficult.

CONCLUSIONS

Tracer methods are usually used either as a complementary tool, to obtain information unavailable from other methods, or as a reconnaissance tool in early stages of investigations. In any case, a conceptual model and the corresponding mathematical model must be based on known physical, chemical, and/or biological principles. Usually, a model can easily be calibrated but its validation remains unsolved because independent data are not available. In such cases there is little confidence in the results obtained but they may, at least, serve as starting points for further studies.

Calibration of a model with too great a number of fitting parameters, leads to ambiguous solutions which are not liable to validation. Unfortunately, very often the calibration obtained is not tested whether the solution is unique. For a fully successful use of the tracer method the phenomena governing the tracer transport must be accounted for (e.g. matrix or aquitard diffusion, or enrichment due to ion filtration when applicable) and the definitions of the calibration and validation fully understood and implemented.

In the case of mathematical models applied to the interpretation of environmental isotope data the general definitions of calibration and validation should, of course, be the same as those commonly accepted in hydrology. However, it is very difficult to satisfy the requirement for validation before a practical application of a model. By definition the validation process is a qualitative one based on the modeller's judgment. If validation has not been obtained for all the properties of a model (variables, parameters and initial and boundary conditions), but only for some of them (partial validation), care should be exercised to avoid far-reaching conclusions. Usually, the validation is not obtainable and a model is applied by analogy to other systems investigated earlier.

In the case of lumped-parameter models applied to time records of data, the most reliable models are those with the lowest number of fitting parameters. Sometimes the validation can be obtained by comparison of parameters derived from the mean age with those obtainable independently. Other parameters, if any, can be compared qualitatively with independent geological information(e.g. whether the dispersion parameter in the dispersion model, or the volume ratio in the combined exponential and piston flow model is consistent with the known structure of the system).

For spatially distributed data, the multi-cell model (MCM) approach due to its relative simplicity and versatility is the best. However, care should be taken to avoid the introduction of too great a number of cells, which is not justified by the number of available sampling sites. Even if the arrangement of cells is based on a prior geological knowledge of the system, too great a number of fitting parameters (explicit and/or hidden) makes the calibration doubtful. The problem of a unique calibration and validation for such models has not been solved so far.

The multi-tracer multi-cell model (MTMCM) approach is very promising and theoretically sound as far as the calibration process is concerned. However, assumptions related to the conservative behaviour of some chemical components of water are seldom well satisfied and thus the problem of validation must be solved. Further studies are needed on the validation methods for both the MCM and the MTMCM.

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