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Environmental isotopes in the hydrological cycle

Principles and applications

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Volume VI

Modelling

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Principles and Applications

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Volume I	**Introduction: Theory, Methods, Review**
Volume II	**Atmospheric Water**
Volume III	**Surface Water**
Volume IV	**Groundwater: Saturated and Unsaturated Zone**
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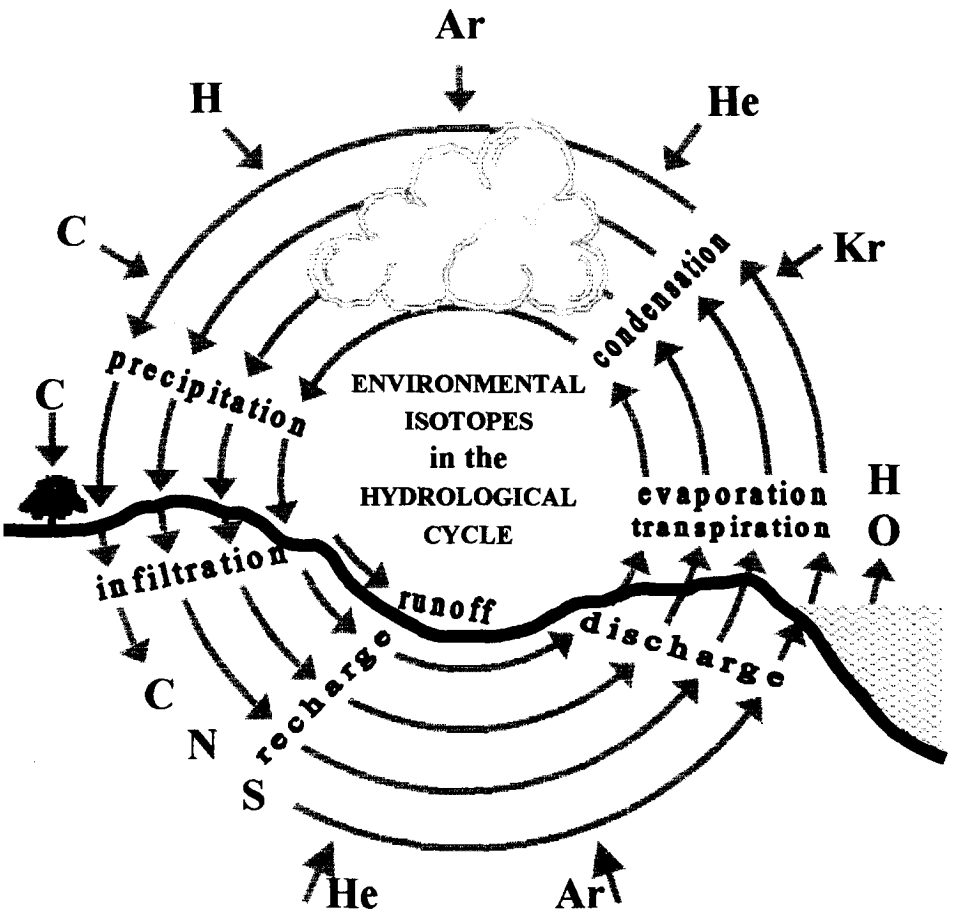

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PREFACE

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

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

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

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

In view of the fact that the IHP's objectives include also a multi-disciplinary approach to the assessment and rational management of water resources and taking note of the advances made

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

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

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

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

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

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

Paris / Vienna, March 2000

PREFACE TO VOLUME VI

This last volume in the series of textbooks on environmental isotopes in the hydrological cycle provides an overview of the basic principles of existing conceptual formulations of modelling approaches. While some of the concepts provided in Chapter 2 and Chapter 3 are of general validity for quantitative interpretation of isotope data; the modelling methodologies commonly employed for incorporating isotope data into evaluations specifically related to groundwater systems are given in this volume together with some illustrative examples.

Development of conceptual models for quantitative interpretations of isotope data in hydrogeology and the assessment of their limitations and field verification has been given priority in the research and development efforts of the IAEA during the last decade. Several Co-ordinated Research Projects on this specific topic were implemented and results published by the IAEA. Based on these efforts and contributions made by a number of scientists involved in this specific field, the IAEA has published two Technical Documents entitled "Mathematical models and their applications to isotope studies in groundwater studies - IAEA TECDOC-777, 1994" and "Manual on Mathematical models in isotope hydrogeology - IAEA TECDOC-910, 1996". Results of a recently completed Co-ordinated Research Project by the IAEA entitled "Use of isotopes for analysis of flow and transport dynamics in groundwater systems" will also soon be published by the IAEA. This is the reason why the IAEA was involved in the co-ordination required for preparation of this volume; the material presented is a condensed overview prepared by some of the scientists that were involved in the above cited IAEA activities.

This volume VI providing such an overview was included into the series to make this series self-sufficient in its coverage of the field of Isotope Hydrology. A special chapter on the methodologies and concepts related to geochemical modelling in groundwater systems would have been most desirable to include. The reader is referred to IAEA-TECDOC-910 and other relevant publications for guidance in this specific field.

Valuable contributions in the preparation of this volume were accomplished by A.Zuber (Poland), P.Maloszewski (Germany), M.E.Campana (USA), G.A.Harrington (Australia), L.Tezcan (Turkey), and L.F.Konikow (USA), as acknowledged with each chapter.

Vienna, March 2000

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CONTENTS

1 MODELLING INTRODUCTION

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During the last four decades the use of isotopes, either naturally occurring (*environmental isotopes*) or intentionally injected (*artificial isotopes*) have proved their value in studies related to water resources assessment, development and management. The applications in a large variety of hydrological problems are based on a general concept of *tracing*. The term *Isotope Hydrology* is now realised as a scientific discipline comprising proven methodologies applied to a wide spectrum of hydrological problems as an integral part of the investigations in water resources and related environmental studies.

The potential role and contributions of isotope methods in the water resources sector can be grouped into the following general categories:

1) **Determination of physical parameters** related to flow, the dynamics of transport and the structure of the hydrological system,
2) **Process tracing** - delineation of processes involved in circulation of water and mass transport of dissolved constituents,
3) **Identification of the origin (genesis)** of water,
4) **Component tracing** - determination of pathways and mixing ratios of component flows,
5) **Determining the time scale** involved in hydrological events.

Due to the natural labelling of water in the hydrological cycle, the environmental isotopes have the distinct advantage of facilitating the study of water movement and hydrological processes on much larger temporal/spatial scales than intentionally injected, artificial tracers which are often used for site-specific, local scale hydro-engineering problems.

The type of information that can be obtained from isotope techniques in hydrological systems is:

1) **Qualitative information,** pertaining to system boundaries, hydraulic discontinuities and stratifications, hydraulic interconnections, origin of water, presence and process of replenishment, sources of pollution (including water salinization), and cause-effect relationships of different processes involved during flow and circulation of water in hydrological systems;

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2) **Quantitative information** concerning water fluxes (i.e. rate of direct replenishment of groundwater, fluxes into the system from boundaries), mixing proportions of component flows originating from different sources, travel times involved in hydrological systems and characteristic dynamic parameters related to mass-transport processes.

Quantitative evaluations to be made from environmental isotopes require conceptual mathematical models, so as to describe both the tracer distribution within the system or isotope input/output relationships under given flow and transport conditions. Since temporal/spatial variations of the environmental isotopes can not be controlled by the investigator; quantitative information to be derived from observed isotope concentrations in any given hydrological system will have to rely on specific input pattern of different isotopic species.

The most commonly used modelling formulations in this regard can be classified into three broad categories as follows:

1) **lumped-parameter models, based on linear systems approach (transfer-function type of modelling) for a tracer case**

2) **compartmental simulation models, which can be considered as a quasi-physical distributed-parameter modelling approach**

3) **models involving mathematical formulations of advective transport with dispersion and their analytical and/or approximate numerical solutions.**

In most cases, tracer input and the observed output (isotope data collected on spatial and/or temporal variations) are available, and quantitative interpretation, in mathematical terms, is an *inverse problem*. While the formulations to be discussed in later sections are of general validity for any tracer case, their use, particularly with the most commonly employed environmental isotopes are emphasized in this Volume VI.

It is evident that the first requirement in the application of natural isotopes for this purpose is determination of the *tracer input* into the system under investigation, which is the isotopic composition of the inflow(s). For most commonly used environmental isotopes, natural processes governing their occurrence result in time- and space-dependent variations. The time-variant input(s) for a given system and the known decay rate (in the case of radioactive isotopes) enable quantitative estimates, based on the observed isotope variations within the system or on observed concentrations at the outflow of the system, through the use of the mathematical modelling approaches cited above. The case of a constant input concentration, which may need to be adopted for some systems, is a sub-set of this general approach.

Basic data concerning the natural isotope content of precipitation, as an input to the hydrological systems, has been collected by the IAEA from a Global Network of Isotopes in Precipitation (GNIP) since 1960. The measurements made on ^{18}O, ^{2}H and ^{3}H content of monthly composite precipitation samples regularly being collected from this global network, provide the basic data needed in this regard. Furthermore, data from national networks being operated in some countries

supplement this global network; the overall data are published regularly by the IAEA and are also available at http://www.iaea.org/programs/ri/gnip/gnipmain.htm".

This volume provides an overview of the basic concepts and formulations of modelling approaches cited above with some illustrative examples of their applications. The reader is referred to the references given in each chapter for in-depth coverage of the above cited modelling approaches, as applied for quantitative evaluation of isotope data in hydrology.

2 LUMPED PARAMETER MODELS

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2.1 INTRODUCTION

A comprehensive description of the lumped-parameter models applicable to the interpretation of environmental tracers in groundwater systems is given. It will be shown that the lumped-parameter models are particularly useful for interpreting the tracer data which were obtained at separate sampling sites, when it is neither possible, nor justified, to use distributed-parameter models, as the latter require more detailed knowledge of the investigated system, which is often unavailable. A more detailed description of the approach and a number of examples can be found in Małoszewski and Zuber (1996) and in other references given further. A user-friendly programme (FLOWPC) for the interpretation of environmental tracer data by several most commonly used models is available from the IAEA.

For a better understanding of the tracer method and the interpretation of the tracer data, several definitions are recalled. Some of these definitions are more or less generally accepted and frequently used (e.g., Gardner and Ely 1967, Levenspiel 1972, Lohman et al. 1972, NEA 1990); whereas remaining are unfortunately used only occasionally. As a consequence of infrequent use of adequate definitions, a lot of misunderstandings occur in literature, especially when radioisotope ages versus water ages are considered, or when mathematical models equivalent to the behaviour of a well-mixed reservoir are used for groundwater systems in which good mixing never occurs. As explained further, some misunderstandings also result from a common identification of tracer ages with water ages in fractured rocks whereas in fact these two physical quantities differ considerably.

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, which has been added (injected) to the system. Environmental tracers are added by natural processes whereas their production is either natural or results from the global activity of man.

An *ideal tracer* is a substance behaving in the system exactly as the traced material, at least as far as the sought parameters are concerned, and which has one property that distinguishes it from the traced material. For an ideal tracer, there should be neither sources nor sinks in the system other than those related to the sought parameters. In practice a substance which has other sources or sinks can also be regarded as suitable tracer, if they can be properly accounted for, or if their influence is negligible within the required accuracy.

A *conservative tracer* is an ideal tracer without sinks (there is no decay, sorption or precipitation).

A *conceptual model* is a qualitative description of a system and its representation (e.g. description of geometry, parameters, initial and boundary conditions) relevant to the intended use of the model.

A *mathematical model* is a mathematical representation of a conceptual model for a physical, chemical, and/or biological system by expressions designed to aid in understanding and/or predicting the behaviour of the system under specified conditions.

In a *lumped-parameter model* (*black-box model*) spatial variations of parameters are ignored and the system is described by adjustable (fitted) parameters.

Verification of a mathematical model, or its computer code, is obtained when it is shown that the model behaves as intended, i.e., that it is a proper mathematical representation of the conceptual model and that the equations are correctly encoded and solved.

Model calibration is a process in which the mathematical model assumptions (e.g., type of the model) and parameters are varied to fit the model to observations. Usually, calibration is carried out by a trial-and-error procedure, and it can be quantitatively described by the goodness of fit. Model calibration is a process in which the *inverse problem* (*ill-posed problem*) is solved, i.e., from known input-output relations the values of parameters are determined by fitting the model results to experimental data. *Sought* (*fitted, matched*) *parameters* are found in the process of calibration. The *direct problem* is solved if for known or assumed parameters the output results are calculated (model prediction). In the FLOWPC programme an option is included (when no observations exist) which serves for direct calculations. Testing of hypotheses is performed by comparison of model predictions with experimental data.

Validation is a process of obtaining assurance that a model is a correct representation of the process or system for which it is intended. Ideally, validation is obtained if the predictions derived from a calibrated model agree with new observations, preferably for other conditions than those used for calibration (e.g., larger distances and longer times). Contrary to calibration, the validation process is qualitative and based on the modeller's judgement. In the case of the tracer method the validation is often performed by comparison of the values of found parameters with the values obtainable independently from other methods. In such a case it is perhaps more adequate to state that the model *is confirmed*, or *partially confirmed*.

In spite of contradictions expressed by some authors (e.g., Konikow and Bredehoeft 1993), the difference between validation and confirmation is rather verbal, and mainly depends on the definitions used and their understanding (e.g., some authors by the working definition of validation understand the process of calibration).

Partial validation can be defined as validation performed with respect to some properties of a model. For instance, in the modelling of artificial tracer tests or pollutant transport, the dispersion equation usually yields proper solute velocities (i.e., can be validated in that respect), but seldom adequately describes the dispersion process in predictions at much larger distances.

The *turnover time* (t_w; other terms: *age of water leaving a system, mean exit age, mean residence time of water, mean transit time, hydraulic age, kinematic age*) is usually defined as the ratio of the mobile water volume (V_m) to the volumetric flow rate (Q) through the system:

$$t_w = V_m/Q \qquad \textbf{(2.1)}$$

For vertical flow in the recharge area, especially in the unsaturated zone, Q in Eq.2.1 can be expressed by recharge rate (I):

$$t_w = V_m/I \qquad \textbf{(2.1a)}$$

If a system can be approximated by unidimensional flow pattern, this definition yields $t_w = x/v_w$, where x is the length for which t_w is determined, and v_w is the mean water velocity, defined below. *Darcy's velocity* (v_f) is defined as the ratio of Q/S, S being the cross-section area perpendicular to flow lines. The *effective porosity* is understood as that in which the water movement takes place (Lohman et al. 1972). Consequently, the *mean water velocity* (v_w) is defined as the ratio of Darcy's velocity to the effective porosity, $v_w = v_f/n_e$ (other equivalent terms: *pore velocity, interstitial velocity, travel velocity, transit velocity*). Other definitions of the effective porosity are also common. For instance, it is common to define the effective porosity as that which is effective to a given physical process, e.g., diffusion. Of course, in such cases, the effective porosity differs from that which is directly related to Darcy's law.

The *mean tracer age* (t_t; other terms: *mean transit time of tracer, mean travel time of tracer*) can be defined as:

$$t_t = \frac{\int_0^\infty t'(C_I)(t')\,dt'}{\int_0^\infty C_I(t')\,dt'} \qquad \textbf{(2.2)}$$

where C_I is the tracer concentration observed at the measuring site (the outlet of a system) as the result of an instantaneous injection at the entrance.

The mean tracer age is equal to the mean water age only if there are no stagnant zones in the system, and the tracer is injected and measured in flux. Flux injection and measurement mean that at both the entrance and outlet the amounts of tracer in particular flow lines are proportional to their volumetric flow rates. That condition is automatically satisfied in natural systems for tracers entering the system with infiltrating water and measured in outflows. However, if sampling is performed at a certain depth of a borehole, that condition may perhaps be satisfied for the sampled flow line, but surely not for the whole system. Radiocarbon most probably does not satisfy in some cases the flux injection because it enters groundwater systems mainly due to the production of CO_2 by plant roots. Therefore, its natural injection is not necessarily proportional to the volumetric flow rates. The problem of a proper injection and measurement is more acute in artificial tracing, however, one should be aware that even an ideal environmental tracer may in some cases yield an age which differs from the water age. The problem of stagnant zones, which is of particular importance for fissured rocks, will be discussed further.

Immobile systems are beyond the scope of this work, but for the consistency of age definitions they should mentioned. The *water age of an immobile system* is usually understood as the time span for which the system has been separated form the atmosphere. In such cases, the radioisotope age of an airborne radioisotope, which has no other sources and sinks than the radioactive decay, can be identified with the age of water. The *radioisotope age* (t_a) is defined by the radioactive decay:

$$C(t_a)/C(0) = \exp(-\lambda t_a) \qquad \textbf{(2.3)}$$

where $C(t_a)$ and $C(0)$ are the actual and initial radioisotope concentrations, respectively, and λ is the radioactive decay constant.

Unfortunately, few radioisotope tracers are available for dating both mobile and immobile old groundwater systems. Therefore, for such systems, the accumulation of some decay products is rather used (e.g., ^4He and ^{41}Ar). Similarly, the dependence of δ^2H and $\delta^{18}O$ in meteoric waters on the climatic conditions which existed when the recharge took place may supply information on the age of both mobile and immobile systems in terms of geological periods of known climates. Obviously, the ages of immobile systems, or systems which were immobile for some time, should not be interpreted directly in terms of hydraulic parameters.

2.2 BASIC PRINCIPLES OF THE LUMPED-PARAMETER APPROACH FOR CONSTANT FLOW SYSTEMS

In the *lumped-parameter approach* the groundwater system is treated as a whole and the flow pattern is assumed to be constant. Usually the flow rate through the system is also assumed to be constant because variations in the flow rate through the system and changes in its volume were shown to be negligible when distinctly shorter than the mean age (Zuber et al. 1986).

Detailed description of the lumped-parameter approach can be found in a number of papers (Amin and Campana 1996, Małoszewski and Zuber 1982, 1996, Zuber 1986). For the most commonly applied models, the schematic presentation of underground water systems is given in Fig.2.1, and the relation between the variable input (C_{in}) and output (C) concentrations is:

$$C(t) = \int_{-\infty}^{t} C_{in}(t')\,g(t-t')\exp[-\lambda(t-t')]dt' \qquad (2.4)$$

An equivalent form is:

$$C(t) = \int_{0}^{\infty} C_{in}(t-t')\,g(t')\exp(-\lambda t')\,dt' \qquad (2.5)$$

where t' is time of entry, t-t' is the transit time, and the g(t–t') function is called the *response function*, which describes the output distribution of a conservative substance (tracer) injected instantaneously at the inlet, and the integration from or to infinity means that the whole input curve (C_{in}) has to be included to get a correct output concentration (C_{out} in Fig.2.1). Other common terms for the g(t) function are: *transit time distribution*, *residence time distribution (RTD) of tracer*, *tracer age distribution*, and *weighting function*. As discussed further the RTD of tracer is not necessarily equivalent to the RTD of the investigated fluid.

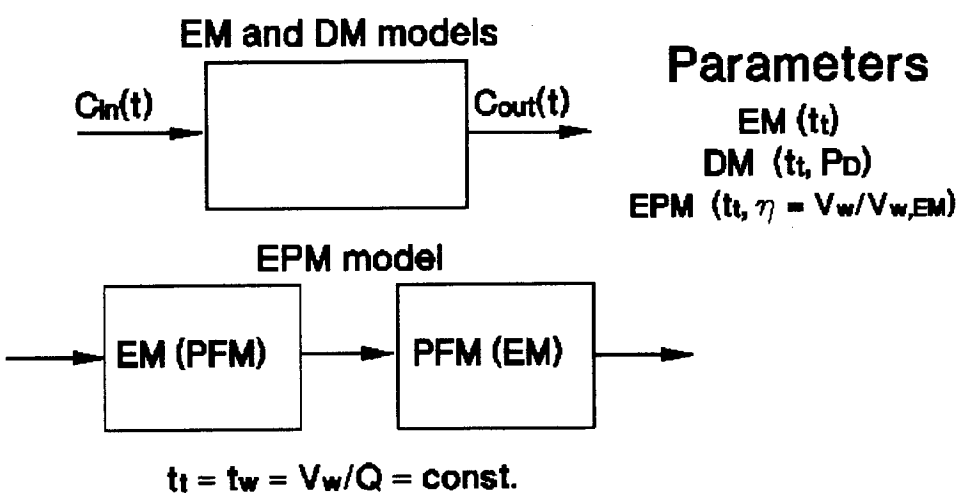

Fig.2.1 Schematic presentations of groundwater systems in the lumped-parameter approach.

Sometimes it is convenient to express Eq.2.4 or 2.5, as a sum of two convolution integrals, or two input functions. The most common case is that one component is either free of tracer, or the tracer concentration can be regarded as being constant. As shown further in some cases such approach is justified by independent information, which defines the fraction of tracer

free (or constant) component. In other cases, the fraction of tracer free component is used as an additional fitting parameter. In the FLOWPC programme an option is included for an older fraction of water (β) which either contains a constant tracer concentration, or is free of tracer.

The response function represents the normalised output concentration, i.e., the concentration divided by the injected mass, which results from an instantaneous injection of a conservative tracer at the inlet. It is impossible to determine the response functions of groundwater systems experimentally. Therefore, functions known from other fields of science are used. The response function, which is either chosen by the modeller, or found by calibration, defines the type of the model whereas the parameters of the model are found by calibration. Calibration means finding a good fit of concentrations calculated by Eq.2.4 or 2.5, to the experimental data, for a known or estimated input function (time record of C_{in}). Usually, when referring to a model of good fitting, the type of the model and the values of its parameters are reported.

In chemical engineering, the response function is often identified with the E(t) function which describes the exit time distribution (or the residence time distribution, RTD) of the investigated fluid. By definition, the mean value of the E-function is equal the volume of the system divided by the volumetric flow rate, and is equal to the mean exit age of the fluid (i.e., to the mean residence time of the fluid). In the case of groundwater systems, the response function, which describes the exit distribution of the tracer, can be identified with the exit time distribution of water flow only under favourable conditions, which exist when there are no stagnant zones in the investigated system. When stagnant zones are present, even an ideal tracer may be delayed in respect to the water flow due to diffusion exchange between mobile and immobile zones. That problem will be discussed further in more detail.

2.3 MODELS

2.3.1 THE PISTON FLOW MODEL

In the *piston flow model* (PFM) approximation the flow lines are assumed to have the same transit time, and the hydrodynamic dispersion and diffusion are negligible. Therefore, the tracer moves from the recharge area as if it was in a can. The response function is given by the well-known Dirac delta function, $g(t') = \delta(t' - t_t)$, which inserted into Eq.2.4 yields:

$$C(t) = C_{in}(t - t_t)\exp(-\lambda t_t) \qquad \textbf{(2.6)}$$

Eq.2.6 means that for the PFM the output concentration at a given time is equal to the input concentration at the time t_t earlier, and changed only by the radioactive decay during the time span t_t. The transit time of the tracer (t_t) is the only parameter of the model, and the shape of the input concentration function is followed by the output concentration. It will be shown further that the PFM is applicable only to systems with constant tracer input. The most commonly used are the three models considered in the following sections.

2.3.2 THE EXPONENTIAL MODEL

In the *exponential model* (EM) approximation, the flow lines are assumed to have the exponential distribution of transit times, i.e., the shortest line has the theoretical transit time equal to zero, and the longest line has the transit time equal to infinity. It is assumed that there is no exchange of tracer between the flow lines, and then the following response function is obtained:

$$g(t') = t_t^{-1}\exp(-t'/t_t) \qquad (2.7)$$

This relationship is mathematically equivalent to the response function of a well-mixed reservoir, known in chemical engineering. Some investigators reject the EM because in principle no good mixing may occur in aquifers whereas others claim the applicability of the EM to be indicative of good mixing conditions in a groundwater system. Both opinions are wrong because, as mentioned, the model is based on an assumption of no exchange (mixing) of tracer between particular flow lines (Eriksson 1958, Małoszewski and Zuber 1982, 1996, Zuber 1986). If tracer exchanges between the flow lines with an exponential distribution of travel times, its distribution will tend to be described by the dispersion model discussed further. Expected effects are similar to the effects shown for tracer distributions in a laminar flow in a capillary (Małoszewski and Zuber 1996, Fig.A.1). Understanding of all effects which may lead to differences between the tracer response function and the distribution of flow lines is very useful for a proper interpretation of tracer data.

For the exponential model approximation, mixing occurs only at the sampling site (spring, abstraction well, stream or river). In general, groundwater systems are never well mixed, and they may contain mixed waters only if two, or more, water flows meet, or in transition zones where the hydrodynamic dispersion and diffusion play an important role.

Similarly to the PFM, the mean transit time (age) of tracer is the only parameter of the EM, which unambiguously defines the whole transit time distribution (Fig.2.2). Therefore, when reporting the tracer age, the model used, or the response function should also be given. The response function of the EM shows the model to be inapplicable to systems in which infinitesimally short flow lines do not exist. In other words, the EM is not applicable when samples are taken well below ground surface, e.g., from boreholes screened at large depths, mines, and artesian outflows. Experience shows that very often, due to a too short record of the tracer data, the exponential model yields a good fit though its use is not justified. In such cases, it should be remembered that the obtained result is a rough approximation, and the real situation can be described more adequately by one of the models discussed in the next sections. Evidently in such cases no unique solution is available.

The EM and other models with a broad distribution of ages describe situations in which only the shortest flow lines supply to the sampling site a decaying tracer (e.g., tritium or ^{3}H), or a non-decaying tracer with the input function starting from zero (e.g., freons). Therefore, in the

case of a large value of the mean tracer age, no information is in fact available on the part of the system with flow lines without tracer. In consequence, the knowledge on the whole system is derived from the information available for its fraction with low ages (short transit times). In other words, the remaining part of the system, which does not supply tracer to the sampling site, may have a quite different distribution of flow lines than that assumed in the model.

2.3.3 THE COMBINED EXPONENTIAL-PISTON FLOW MODEL

In the *exponential-piston flow model* (EPM) approximation, the aquifer is assumed to consist of two parts in line, one with the exponential distribution of transit times, and another with the distribution approximated by the piston flow. The response function of the EPM is:

$$g(t') = (\eta/tt)\exp(-\eta t'/tt + \eta - 1) \quad \text{for} \quad t' \geq tt(1 - \eta^{-1}) \qquad \textbf{(2.8)}$$

$$= 0 \quad \text{for} \quad t' < tt(1 - \eta^{-1})$$

where η is the ratio of the total volume to the volume with the exponential distribution of transit times, i.e., $\eta = 1$ means the exponential flow model. The response function is independent of the sequence in which EM and EPM are combined. The EPM has two fitting (sought) parameters, i.e., t_t and η. Examples of the response functions are shown in Fig.2.3. For low values of η that model is close to the EM whereas for large values of η it is somewhat similar to the dispersion model with a low value of the apparent dispersion parameter. That model is somewhat more realistic than the exponential model because it allows for the existence of a delay of the shortest flow lines.

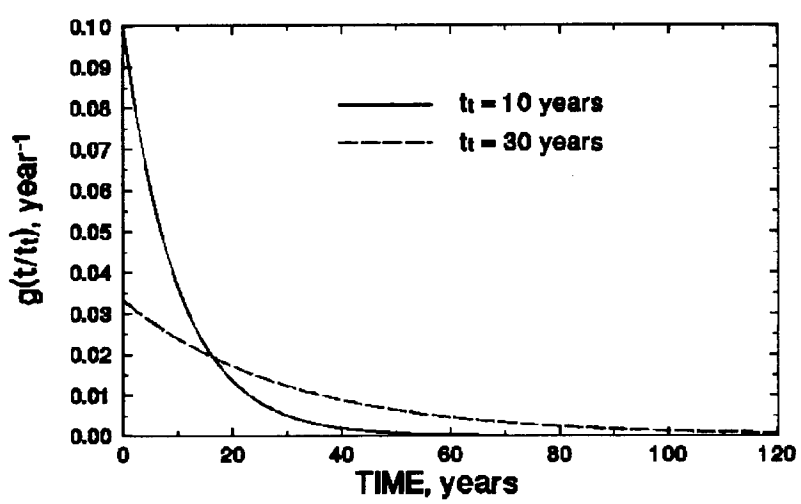

Fig.2.2 Examples of response functions of the exponential model (EM).

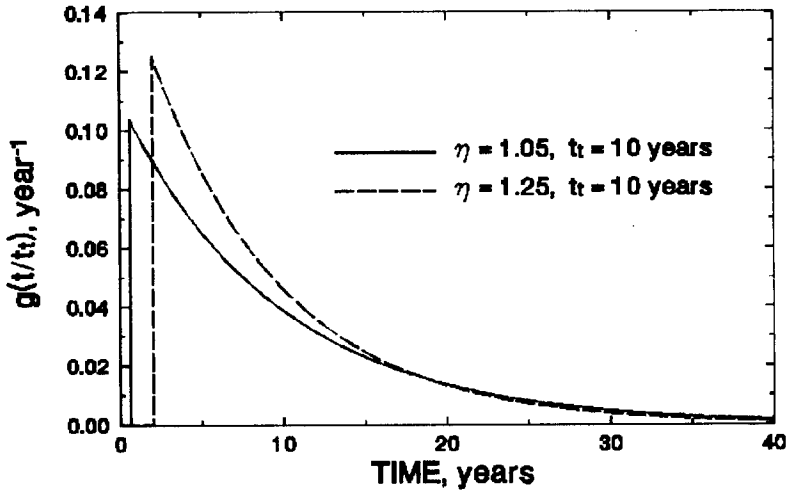

Fig.2.3 Examples of response functions of the exponential-piston flow model (EPM).

2.3.4 THE DISPERSION MODEL

In the *dispersion mod*el (DM), the following uni-dimensional solution to the dispersion equation for a semi-infinite medium is used as the response function (Kreft and Zuber 1978):

$$g(t') = (4\pi P_D t'/t_t)^{-1/2} t'^{-1} \exp[-(1-t'/t_t)^2/(4P_D t'/t_t)] \qquad (2.9)$$

where P_D is the apparent dispersion parameter (reciprocal of the Peclet number), which is unrelated to the common dispersivity of groundwater systems, and mainly depends on the distribution of travel times. The higher the value of the dispersion parameter, the wider and the more asymmetrical the distribution of the travel times. Examples of the response functions are shown in Fig.2.4, for the P_D values of 0.05 and 0.5, which bracket the most common situations. However, in some published case studies, the interpretation of ^3H records yielded the values of the dispersion parameter as high as 2.5 (Małoszewski and Zuber 1982, Zuber 1986, Zuber et al. 2000) whereas lower values than 0.05 are rather unexpected. Some authors, instead of Eq.2.9, apply the solution to the dispersion equation for an infinite medium, which is inadequate, especially in cases of high values of the dispersion parameter (Kreft and Zuber 1978, Małoszewski and Zuber 1982, Zuber 1986).

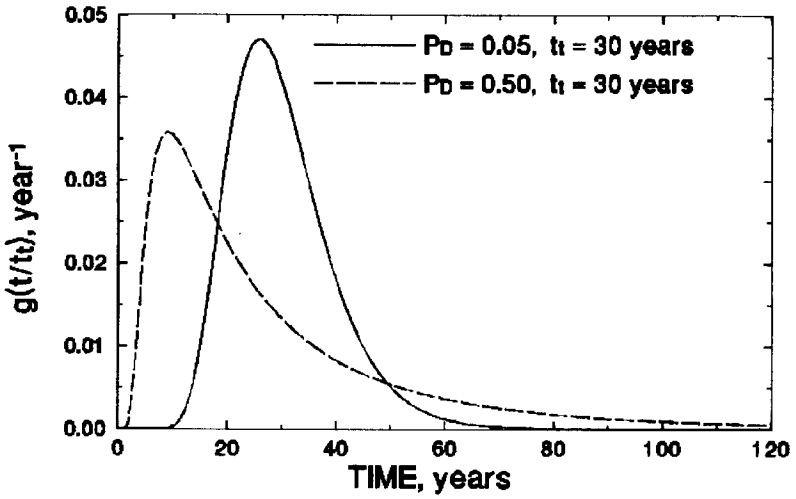

Fig.2.4 Examples of response functions of the dispersion model (DM) for typical values of the dispersion parameter.

2.4 CASES OF CONSTANT TRACER INPUT

The lumped-parameter approach is applicable for any tracer with variable input. It is also applicable for radioisotopes with a constant input concentration. However, in the latter case, a unique interpretation is possible only for models with a single sought parameter, because two unknown values cannot be found from a single equation. The most typical solutions to Eq.2.4 for a constant input (C_o) are:

$$C = C_o \exp(-\lambda t_t) \qquad \text{for PFM} \qquad \textbf{(2.10)}$$

$$C = C_o/(1 + \lambda t_t) \qquad \text{for EM} \qquad \textbf{(2.11)}$$

$$C = C_o \exp\{(2P_D)^{-1} \times [1 - (1 + 4\lambda P_D t_t)^{1/2}]\} \qquad \text{for DM} \qquad \textbf{(2.12)}$$

The investigators who apply Eq.2.10 for dating and understand its limitations often use the term *apparent tracer age* for the PFM tracer age (e.g., Solomon and Cook 1996). Eqs.10-12 demonstrate that the radioisotope age found from Eq.2.3 is a correct representation of the mean tracer age (t_t) only for the PFM, which, as mentioned, is equal to the mean water age (t_w) under favourable conditions. In spite of a number of works, in which differences between the ages resulting from particular models and the radioisotope age were shown, it is a quite common mistake to identify the radioisotope age, given by Eq.2.3 with the mean tracer age. It is especially common in the case of ^{14}C measurements of samples taken from systems with either an unknown flow pattern, or with a flow pattern described by evidently another model than the PFM. For a graphical presentation of C/C_o values yielded by different models see Fig.2.2 in Małoszewski and Zuber (1982), Fig.4 in Małoszewski and Zuber (1986), or Fig.27 in Zuber (1986). As it is impossible to get a unique solution if two or more sought parameters

are used, the age cannot be found from C/C_o. Therefore, if no other information is available, at least bracket age values yielded by the PFM and EM should be given.

In general, when the flow pattern is unknown, the interpretation should be performed for different models, and the ages obtained can be regarded as brackets of the real values. That problem is serious only for large relative ages. As mentioned above, it can easily be shown that if the tracer age is lower than the half-life of the radioisotope ($t_a < T_{1/2} = 0.693/\lambda$), all the models yield close values of ages independently of the assumed flow pattern (Małoszewski and Zuber 1982, 1996, Zuber 1986).

In the case of constant tracer input, the age can be found from a single measurement. The only way to validate, or confirm, a model is to compare its results with other independent data, if available. However, the environmental tracers are particularly useful in investigations of little known systems, where no other data are available for comparisons. Therefore, the general validity of particular models is judged on the basis of vast literature of the subject.

2.5 CASES OF VARIABLE TRACER INPUT

2.5.1 THE TRITIUM METHOD

Tritium (^3H; $T_{1/2}$ = 12.43 years) concentrations in atmospheric waters were constant and very low (5-10 TU) before the hydrogen bomb tests, which started in 1952. The highest concentrations, up to about 6000 TU during summer months in the northern hemisphere, were observed in 1962-63. Since then, the atmospheric concentrations exponentially decrease reaching 10-20 TU in late 90-ties, with characteristic maximum contents in spring and summer months and minimum contents in autumn and winter months. High ^3H concentrations in the precipitation of early sixties offer a unique opportunity for dating young groundwater systems in a relatively wide range of ages. In the case of piston flow, or systems with very low dispersivity, the ^3H method yields ages of waters recharged after 1952 because for older waters the present concentrations are close to zero. However, for systems approximated by the exponential model, even the ages of the order of 1000 years can be determined. For typical dispersive systems, the ages of 100-200 years are often observed. Therefore, the environmental ^3H is still the most useful tracer for dating young waters, especially in the northern hemisphere. Unfortunately, in the tropics the atmospheric ^3H peak was much lower, and in the southern hemisphere its was even more damped and delayed (Gat 1980), which makes the dating more difficult or even impossible.

Seasonal variations of the ^3H concentration in precipitation as well as variations in the precipitation and infiltration rates cause difficulties in the estimation of the input function, i.e., $C_{in}(t)$. For each calendar year the value of the input can be expressed as:

$$C_{in} = \sum_{i=1}^{12} C_i I_i / \sum_{i=1}^{12} I_i = \sum_{i=1}^{12} C_i \alpha_i P_i / \sum_{i=1}^{12} \alpha_i P_i \qquad (2.13)$$

where C_i, P_i and I_i are the ^3H concentration in precipitation, precipitation rate, and infiltration rate for the i-th month, respectively. The infiltration coefficient ($\alpha_i = I_i/P_i$) represents the fraction of precipitation which enters the groundwater system in the i-th month. The record of C_{in} values, calculated for each year prior to the latest sampling date, represents the input function. For the interpretation of old ^3H data, the record of C_{in} should include constant C_{in} values observed prior to the beginning of the rise in 1954 caused by hydrogen bomb test in the atmosphere, in other cases the calculations of the input function can be started since 1954.

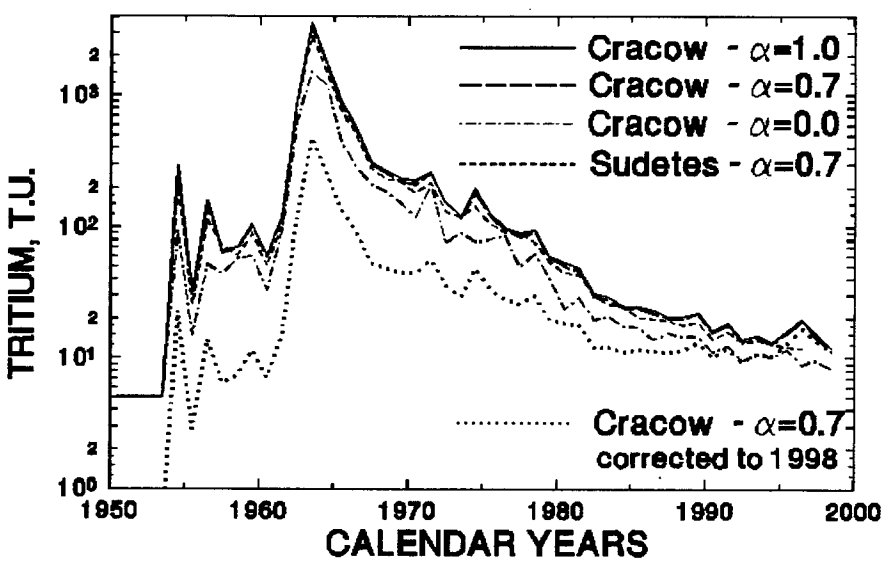

Fig.2.5 ^3H concentration (logarithmic scale) in precipitation ($\alpha = 1.0$) and input functions for $\alpha =$ 0.7 and 0.0 calculated for Cracow (Poland) station. Shown for comparison is the input function for Świeradów station (Sudetes Mts., Poland), and one of the input functions corrected for the radioactive decay to 1998.

Some authors tried to estimate the infiltration coefficients for particular months (Andersen and Sevel 1974, Przewłocki 1975). In general, these coefficients usually remain unknown, and approximations have to be applied. If it is assumed that the infiltration coefficient in the summer months (α_s) of each year is the same fraction of the infiltration coefficient in the winter month (α_w), i.e., $\alpha = \alpha_s/\alpha_w$, Eq.2.13 simplifies into Eq.2.14 (Grabczak et al. 1984).

$$C_{in} = [(\alpha \sum_{i=4}^{9} C_i P_i)_s + (\sum_{i=10}^{3} C_i P_i)_w] / [(\alpha \sum_{i=4}^{9} P_i)_s + (\sum_{i=10}^{3} P_i)_w] \qquad (2.14)$$

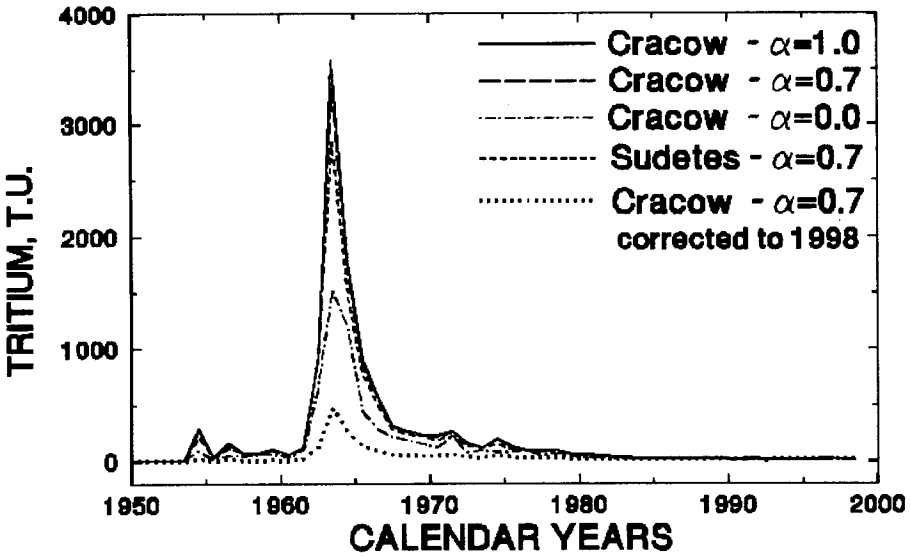

Fig.2.6 The same as in Fig.2.5, but the ^3H concentration is in linear scale.

In the northern hemisphere the summer months are from April to September (from the fourth to the ninth month), and the winter months are from October to March (from the tenths to the third month of the next calendar year). Monthly precipitation amounts should be taken from the nearest meteorological station, and the ^3H data should be taken from the nearest station of the IAEA network. As complete records are usually unavailable, the record of a given station has to be completed by extrapolating correlation with another station for which a complete record exists, either in original or correlated form (Davis et al. 1967). Experience shows that in a rough approximation, the input functions from distant stations, with climatic conditions similar to those of the investigated area, can be used, especially for ages larger than about 20 years. ^3H concentrations in precipitation and examples of the input functions are given in Figs.2.5 and 2.6. The logarithmic scale of Fig.2.5 gives a better idea about the concentrations which have been observed since 1954, and the long tail of the ^3H pulse whereas the linear scale of Fig.2.6 serves for a better understanding the pulse character of the ^3H input. That pulse character and low values of the tail gave reasons to opinions that the ^3H method would be of little use in near future. However, it seems that the ^3H method will remain the best method for dating young waters for two decades at least. It is also evident that for large values of α no drastic changes in the input function are observed.

It is well known that under moderate climatic conditions the recharge takes place mainly in winter months. Therefore, in some early publications the α coefficient was assumed to be equal to zero or 0.05. However, the isotopic composition of shallow groundwaters is usually equal, or close, to the yearly mean weighted isotopic composition of precipitation, even in areas of prevailing potential evapotranspiration over precipitation in summer months. It means that in the summer months the evapotranspiration partly removes water stored in the unsaturated zone both in the summer and winter months. In consequence, the remaining

water, which reaches the groundwater table, represents the winter and summer precipitation. When local precipitation and isotope data exists, or if they are available from a nearby station, the value of the α coefficient can be estimated from Eq.2.15.

$$\alpha = [(\sum_{i-10}^{3} P_i\delta_i)_w - \delta(\sum_{i=10}^{3} P_i)_w]/[\delta(\sum_{i=4}^{9} P_i)_s - (\sum_{i=4}^{9} P_i\delta_i)_s] \qquad \textbf{(2.15)}$$

In that equation δ_{is}, δ_{iw} are the stable isotope compositions of the precipitation in the summer months and winter months, respectively; and δ is the mean isotopic composition of local groundwater ($\delta^{18}O$ or $\delta^{2}H$) (Grabczak et al. 1984). Eq.2.15 is useful if sufficiently long (a few years) records of the isotopic composition and precipitation rates are available. However, for moderate and humid tropical climates, the α coefficient is commonly within the range of 0.4-0.8, and experience shows that within this range the accuracy of modelling only slightly depends on the assumed α value, if the ages are greater than 10-20 years. In general, if the input function is not found independently, the α coefficient is either arbitrarily chosen by the modeller, or tacitly used as a hidden fitting (sought) parameter. As mentioned, the larger the number of sought parameters, the lower the reliability of modelling. Therefore, the number of sought parameters should be kept as low as possible. In any case, the method used for the calculation of the input function should also be reported. It is a common mistake to assume α = 0 on the basis of conventional hydrological observations, which indicate the lack of net recharge in some areas during summer months, because it does not mean the lack of the summer ^{3}H in recharging water, as mentioned above.

2.5.2 THE ^{3}H-^{3}He METHOD

^{3}H concentrations in the atmosphere are now much lower than during the bomb test peak and they still decrease, which cause the ^{3}H method to be less useful in near future than in the last four decades. In consequence, other tracer methods are considered as potential tools, which may either replace the ^{3}H method or prolong its applicability (e.g., Plummer et al. 1993). As ^{3}H decays to ^{3}He, the measurements of the tritiugenic ^{3}He accumulated in groundwater systems potentially prolong the dating range resulting from the ^{3}H peak (Małoszewski and Zuber 1983). In the ^{3}H-^{3}He method the ^{3}He to ^{3}H ratio is usually considered, which for the PFM yields a well-known formula in which the tracer age is independent of the input (Torgersen et al. 1979):

$$t_t = \lambda_T^{-1} \ln[1+{}^{3}He_T/{}^{3}H] \qquad \textbf{(2.16)}$$

where λ_T is the radioactive decay constant for ^{3}H ($1/\lambda_T = T_{1/2}/\ln 2 = 17.9$ a), ^{3}H is the ^{3}H content, and $^{3}He_T$ is the tritiugenic ^{3}He content expressed in ^{3}H units (for ^{3}He expressed in ml STP of gas per gram of water, the factor is 4.01×10^{14} to obtain the ^{3}He content in TU).

Unfortunately, Eq.2.16 is not applicable to other flow models. If Eq.2.5 is used for the calculation of the theoretical ^3H output function, the following equation should be used or the daughter ^3He theoretical output (Małoszewski and Zuber 1983):

$$C_{He} = \int_0^\infty C_{Tin}(t-t')g(t')[1-\exp(-\lambda_T t')]dt \qquad \textbf{(2.17)}$$

where C_{Tin} is the ^3H input function, and C_{He} is the helium concentration expressed in the same units as in Eq.2.16.

Several recent studies showed the applicability of Eq.2.16 for vertical transport through the unsaturated or saturated zone, where samples are taken at different depths of a chosen profile, and the dispersivity is negligible. Then, the ^3H-^3He method in the PFM approximation is advantageous to the ^3H method because only several samples taken at different depths close to the surface supply the same information as the ^3H peak and allow to determine recharge rate (Eq.2.1a) as shown by Cook and Solomon (1997). That is especially important as in most cases the ^3H peak, which corresponds to the atmospheric peak in 1963, has disappeared, or is preserved in vertical profiles only under exceptionally favourable conditions, and at large depths. The method can also be used in horizontal flow in the saturated zone, if the particular flow lines are observed with the aid of multi-lever samplers. In the latter case the ^3H-^3He method has been shown to be particularly useful to calibrate flow and transport models in shallow aquifers. As mentioned, another advantage of the method is its potentially longer applicability in near future in comparison with the ^3H method.

Specific limitations of the ^3He method result from the need to separate the *tritiogenic helium* from helium originating from other sources (atmospheric solubility, excess air and *radiogenic* production) as discussed in detail by Torgersen et al. (1979), Weise and Moser (1987), and Schlosser et al. (1989). For the PFM approximation, age uncertainties caused by these sources, and by fast diffusion of ^3He in comparison with the diffusion of $^3H^1HO$, were shortly reviewed by Solomon et al. (1998).

Other difficulties are common to all gaseous tracers and they are mainly related to possible escapes or gains by enhanced diffusion when water is in contact with air in the unsaturated zone or in karstic channels. For instance, Grabczak et al. (1982) determined the models and ^3H ages for withdrawal wells exploiting an unconfined aquifer with thick loess and sandy covers, and for several karstic springs. In all the cases the concentrations of ^{85}Kr, ^3He and freon-11 (CCl_3F) were in disagreement with the values expected on the basis of the ^3H models. These disagreements were explained as diffusion losses or gains caused by sharp differences in concentration between water and air either in the unsaturated zone of the recharge areas or in channels partly filled with water near the outflows from a karstic aquifer. In the case of ^3H, the age is counted from the moment of recharge at the surface whereas for gas tracers it starts rather at the water table (Solomon et al. 1993, 1998), which makes

additional difficulty in other applications than the observations of vertical profiles for recharge studies.

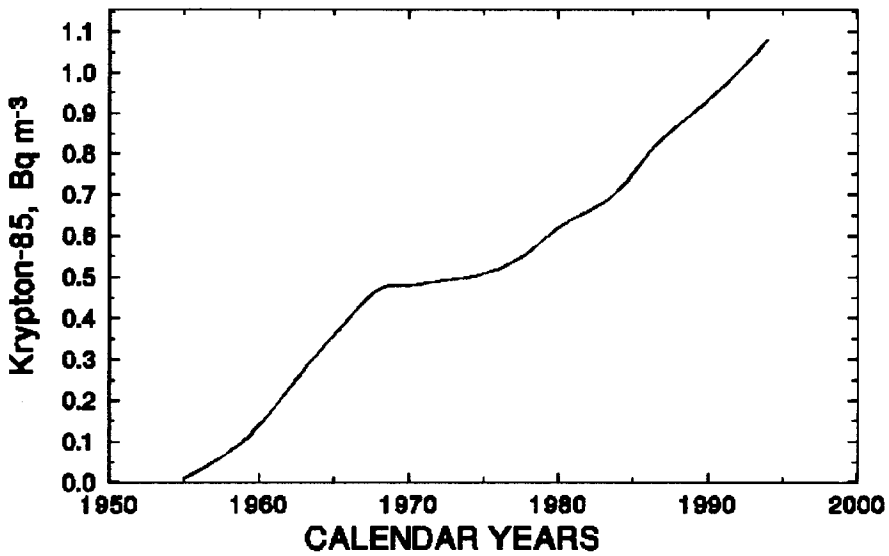

Fig.2.7 Specific activity of ^{85}Kr in the air of the northern hemisphere (Cook and Solomon 1997, Sartorius 1998, and CGGC 1999), directly applicable as the input function.

2.5.3 THE KRYPTON-85 METHOD

The presence of radioactive ^{85}Kr ($T_{1/2}$ = 10.76 years) in the atmosphere results from emissions from nuclear power stations and plutonium production for military purposes. In spite of large spatial and temporal variations, the input function based on yearly averages is quite smooth as shown in Fig.2.7 for the northern hemisphere. For the southern hemisphere, the specific activity is about 0.2 Bq/m^3 lower (Sartorius 1993). The ^{85}Kr concentration is expressed in units of the specific activity, and, therefore, it is independent of the krypton solubility in water, and of the possible excess of air in water, which is related to a common effect of incorporation of air bubbles in the recharge area. The ^{85}Kr method was initially hoped to replace the ^3H method in near future. However, serious limitations result from large samples required due to low solubility of Kr and low concentrations of ^{85}Kr), and possible excess or deficit of ^{85}Kr caused by exchange with the atmosphere, especially in karstic channels and thick unsaturated zones, similarly to the discussed earlier ^3He tracer. In spite of these limitations the krypton-85 method is probably the most promising replacement of the ^3H method in future. Other potential gaseous tracers are discussed further.

Depth profiles for vertical flow or multi-level samplers make the method useful for studies of recharge rates (Cook and Solomon 1997). However, for the typical applications of the lumped parameter models (interpretation of data obtained in abstraction well and springs), the solutions of the direct problem, i.e., the calculations of the output concentrations show a need

of prolonged records of sampling (Małoszewski and Zuber 1983). For short tracer ages, say, up to about 5 to 10 years, the differences between particular models are slight, similarly to the constant tracer inputs. For larger ages, the differences are not negligible.

2.5.4 THE CARBON-14 METHOD

Usually the ^{14}C content is not measured in young waters in which ^{3}H is present unless mixing of components having distinctly different ages is investigated. However, in principle, due to a distinct bomb peak of ^{14}C concentration, the lumped-parameter approach for variable input can be applied. A high cost of ^{14}C analyses and a low accuracy related to the problem of the so-called initial carbon content make that approach impractical. However, it is suggested that when the ^{14}C data are available, the lumped-parameter approach can be used to check if they are consistent with the results obtained from the ^{3}H modelling.

2.5.5 THE OXYGEN-18 AND DEUTERIUM METHOD

Seasonal variations of $\delta^{18}O$ and $\delta^{2}H$ in precipitation are under favourable conditions observed in outlets of small catchments with the mean ages up to about 4 years (a common definition of a small catchment is that with the surface area up to 100 km^2 (Buttle, 1998). Due to a strong damping of the seasonal input variations in outflows, a frequent sampling over several years is usually required both at the input and the outlet. The input data should be taken from a local precipitation collector and the outlet data form a chosen drainage site, i.e., a spring or stream draining the investigated retention basin (Bergman et al. 1986, Małoszewski et al. 1992).

$$\delta_{in}(t) = \bar{\delta} + [\alpha_i P_i(\delta_i - \bar{\delta})]/(\sum_{i=1}^{n} \alpha_i P_i / n) \qquad (2.18)$$

where $\bar{\delta}$ is the mean input which must be equal to the mean output of $\delta^{18}O$ or $\delta^{2}H$ values and n is the number of months (or weeks, or two-weeks periods, because in that method a shorter time unit is preferable) for which the observations are available. When the information on α_i is not available, it can be replaced by α, similarly to the ^{3}H method. Then α is either calculated from Eq.2.15, or assumed, and appears as a coefficient for the precipitation of the summer months whereas $\alpha = 1$ is put for the winter months.

The stable isotope method is also useful for determining the fraction of river, or lake, water flowing to pumping wells near rivers (lakes), and the travel time of that water from the river (lake) to the well, if the isotopic composition of the river (lake) water sufficiently varies seasonally. The isotopic composition in the pumping well is the mixture of the river and groundwater (Stichler et al. 1986, Hötzl et al. 1989, Małoszewski et al. 1990):

$$\delta_w(t) = p\delta_r(t) + (1-p)\delta_g(t) \qquad (2.19)$$

where p is the fraction of the river water and subscripts w, r and g stay for the pumped, river and local groundwater, respectively. The value of p can be found by rearranging Eq.2.19 and using the mean isotopic compositions of particular components:

$$p = (\bar{\delta}_w - \bar{\delta}_g)/(\bar{\delta}_r - \bar{\delta}_g) \qquad \textbf{(2.20)}$$

The isotopic composition of local groundwater (δ_g) is either constant or only slightly varies in comparison with the isotopic composition of river water (δ_r). In consequence, the travel time from river to the withdrawal well is found by fitting Eq.2.21 whereas the fraction of the river water is obtained from Eq.2.20 (Stichler et al. 1986, Hötzl et al. 1989, Małoszewski et al. 1990).

$$\delta_w(t) = p\int_0^\infty \delta_r(t-t')\,g(t')\,dt' + (1-p)\bar{\delta}_g \qquad \textbf{(2.21)}$$

The stable isotope method used for small retention basins or bank filtration usually requires a frequent sampling, which makes it costly. Therefore, in the case of small retention basins its applicability is limited to research purposes. In the case of bank filtration, the method is undoubtedly cheaper than a number of drilled wells needed to obtain data for construction of a numerical flow and transport model.

2.5.6 OTHER POTENTIAL METHODS

Among other environmental tracers with variable input the most promising for age determinations of young waters are freons (chlorofluorocarbons), particularly freon-12 (CCl_2F_2), and sulphur hexafluoride (SF_6) which has been shown to be a good atmospheric tracer. Their input functions monotonically increase due to the global contamination of the atmosphere by industry (Fig.2.8). In the southern-hemisphere their concentrations are somewhat lower. Freons enter groundwater systems similarly to other gases with infiltrating water in which they are dissolved in low concentrations. As mentioned, exchange with the air in the unsaturated zone makes the input function less accurately defined than for the ^3H. Under extremely favourable conditions (low filtration rate and high diffusion coefficient in the unsaturated zone), the response function should probably start at the water table. The use of freons is also limited due to sorption effects, which are still little known. Another difficulty results from the dependence of the input function on their solubility, i.e., on the pressure and temperature at the recharge area, which is especially serious when the altitude of the recharge area remains unknown. However, the most serious difficulties are related to possible local contamination of shallow groundwaters by industry, and legal and illegal disposal sites (e.g., disposal of refrigerators into sinkholes in karstic areas). Therefore, chlorofluorocarbons are more commonly used to observe the contaminant transport in groundwater systems, and to calibrate numerical transport models, than to determine the age of water. Due to stripping effects, all gaseous tracers are not applicable in investigations of waters rich in CO_2 and CH_4.

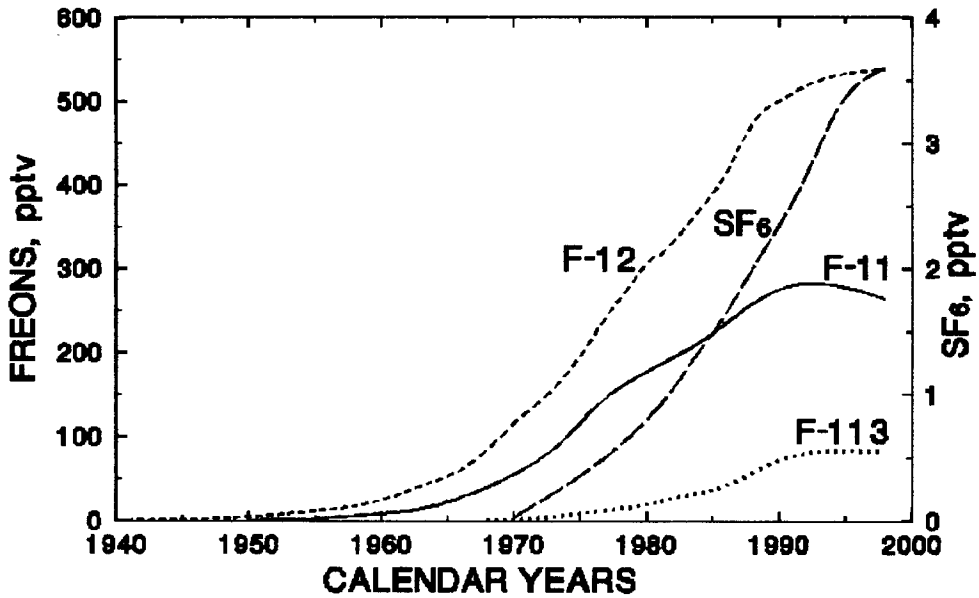

Fig.2.8 Atmospheric concentrations of freons and SF_6 in pptv (10^{-12} parts per volume). F-11 and F-12 after ORNL (1993), Cook and Solomon (1997) and CGGC (1999); F-113 after Cook and Solomon (1997) and CGGC (1999), and SF_6 after Mais and Levin (1994), Mais et al. (1996) and CGGC (1999). The input functions are obtainable by applying appropriate gas solubility for the recharge temperature and pressure.

Increased ^3H concentrations in groundwaters is a temporary phenomenon due to a short half-life of that radioisotope and a short duration of the atmospheric peak. Theoretically, the atmospheric peak of bomb produced ^{36}Cl, with half-life of about 3.01×10^5 years, should be an ideal tracer for relatively young groundwaters. However, the spatial differences in peak concentrations make this tracer difficult to apply in a similar way to ^3H. An exception was for early recharge rate studies where the position of the peak in vertical profiles was measured and interpreted by the PFM approximation (see Bentley et al. 1986 for a review).

2.6 EXAMPLES OF ^3H AGE DETERMINATIONS

Examples of ^3H age determinations for relatively long records of ^3H data can be found in references given earlier whereas in Figs.2.9 and 2.10 two other examples are given after Zuber and Ciężkowski (in press) who gave a number of examples with short records of data. In the first case a large number of models can be fitted whereas in the second case an infinite number of models can be fitted, considering the accuracy range of the experimental data. However, the models shown are not inconsistent because if a given model yields a lower age of the ^3H component, a larger fraction (β) of the ^3H-free water is obtained. The total mean ages are given by models with $\beta = 0$. There is no doubt that for the spring in Szczawina the

total mean age is of the order of 150 years and for the spring in Łomnica Nowa this age is of the order of 1 ka. In both cases the final selection of the model was performed on the basis of the geology of the area and isotopic altitude effect as discussed in next section.

2.7 DETERMINATION OF HYDROGEOLOGIC PARAMETERS FROM TRACER AGES

Principles of the interpretation of ^3H data, especially in combinations with other environmental tracer data, can be found in a number of text books, manuals, and reports. However, the hydrologic meaning of the tracer age in double porosity rocks (fractured rocks), or triple porosity rocks (karstic rocks) differs from that in granular rocks where it is related directly to the flow rate. The difference in the meaning of the tracer age between single porosity and double porosity rocks is schematically shown in Fig.2.11. For fractured rocks, due to diffusion exchange between the mobile water in fractures and stagnant or quasi stagnant water in the micropores of matrix, the tracer transport at large scales can be regarded as if it were flowing through the total open porosity (Neretnieks 1980, Małoszewski and Zuber 1985). Unfortunately, that problem is tacitly omitted in a number of research papers and text books. Therefore, basic formulas relating the mean tracer ages obtained from lumped-parameter models with hydrologic parameters are recalled below. However, it should be remembered that these simple relations for the fractured rocks are of approximate character, and they are valid only at large scales and for dense fracture networks.

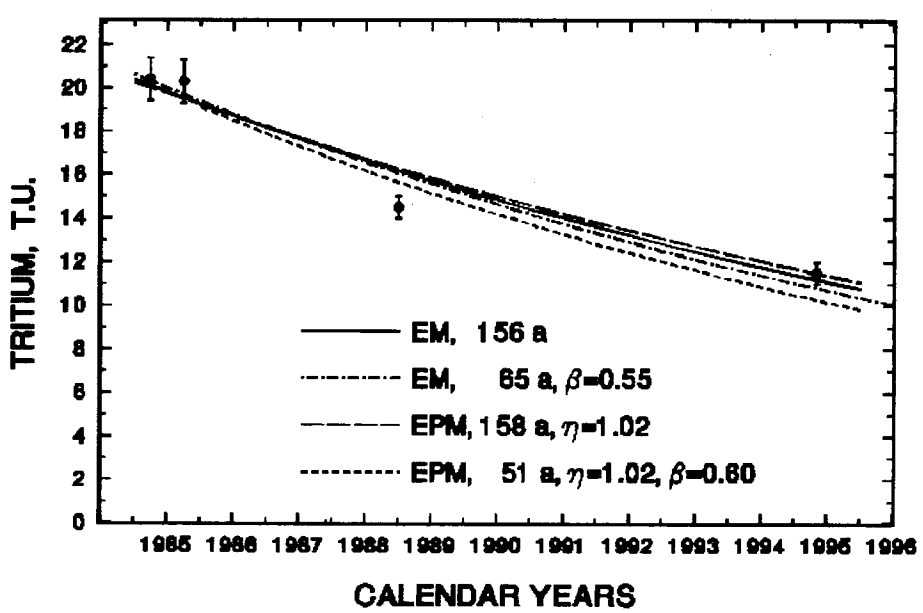

Fig.2.9 ^3H data and fitted models, a spring in Szczawina, Sudetes Mts., Poland.

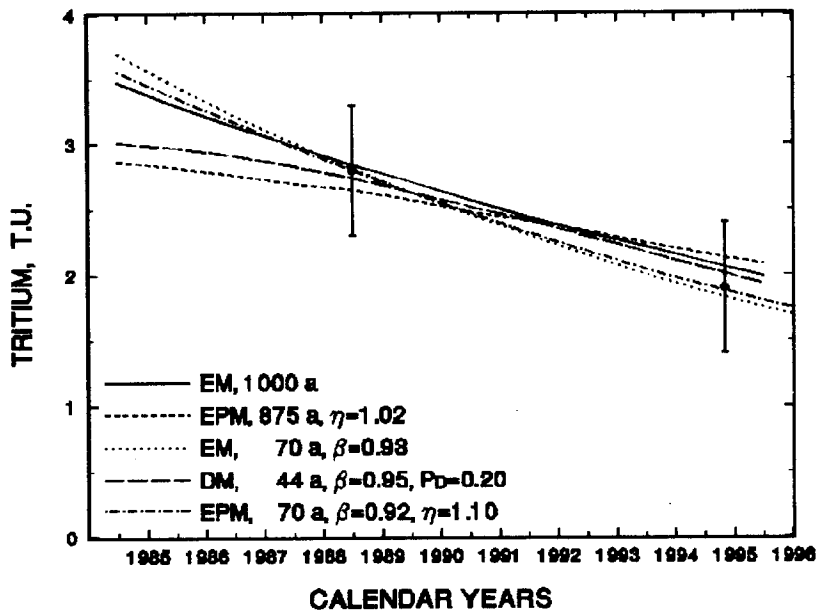

Fig.2.10 ^3H data and fitted models, a spring in Łomnica Nowa, Sudetes Mts., Poland.

The volume of water (V_w) in the part of a given system discharged by a spring is given as:

$$V_w = Q \times t_t \qquad \textbf{(2.22)}$$

where Q is the outflow rate. That volume of water in granular systems is practically equal to the volume of mobile water because fraction of water in the micropores of grains is negligibly low). For fractured rocks, that volume is equal to the total volume (mobile water in fractures and stagnant or quasi stagnant water in matrix (Fig.2.11). Consequently, for a single porosity rock, the rock volume (V_r) occupied by V_w is given as:

$$V_r = V_w/n_e \qquad \textbf{(2.23)}$$

where n_e is the effective porosity, which is close to the open porosity and total porosity (n). For fractured rocks, the following equation applies:

$$V_r = V_w/(n_f + n_p) \cong V_w/n_p \qquad \textbf{(2.23a)}$$

where n_f and n_p are the fracture and matrix porosities, respectively. The approximate form of Eq.2.23a is the result of the fracture porosity being usually negligibly low in comparison with the matrix porosity ($n_f << n_p$). A similar equation applies for triple porosity rocks (karstic-fractured-porous), where the karstic porosity is usually low in comparison with the fracture porosity (Zuber and Motyka 1998). The approximate form of Eq.2.23a and the following similar approximations are of great practical importance because the fracture porosity (plus karstic porosity in triple porosity rocks) usually remains unknown whereas n_p is easily

measurable on rock samples (taken from unweathered rock at the outcrops, or from drill cores). Matrix porosity based on literature data can be used when no samples are available. If the dimensions of the investigated system are known from the geological map and cross-sections, the rock volume is also known, and it can serve for the verification of the age by comparison with the volume found from Eq.2.23a.

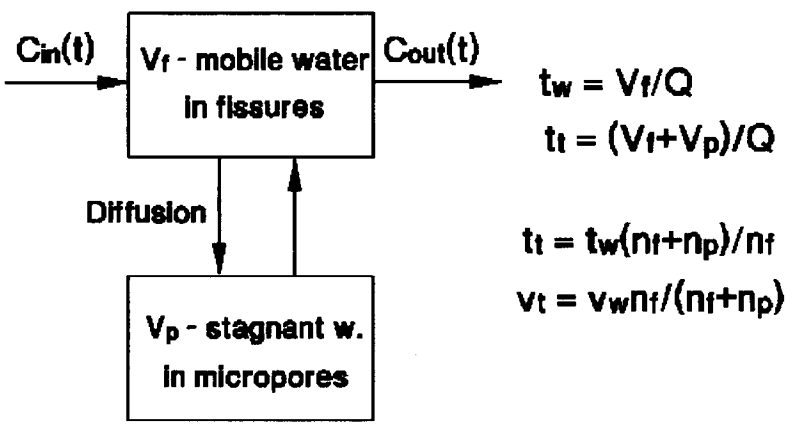

Fig.2.11 Schematic presentation of the tracer transport in fractured rocks at large scales when the tracer is able to penetrate fully into the stagnant water in the matrix.

When the mean distance (x) from recharge area to the sampling site is known, the following relation applies for single porosity rocks:

$$t_t = t_w = x/v_w = x/v_t \qquad \textbf{(2.25)}$$

which means that the tracer age (travel time) and velocity are equal to those of water.

For fractured rocks (double porosity), instead of Eq.2.25 the following relations are applicable (Fig.2.11):

$$t_t = x/v_t = t_w(n_f + n_p)/n_f = (x/v_w)(n_f + n_p)/n_f \qquad \textbf{(2.25a)}$$

In consequence, the tracer travel time is $1 + n_p/n_f$ times longer than the travel time of water (i.e., tracer velocity is $1 + n_p/n_f$ times slower than water velocity). The fracture porosity is difficult to estimate, and, therefore, if the tracer velocity is known, the water velocity remains unknown, and vice versa, if the water velocity is known, the tracer velocity remains unknown.

For single porosity rocks, Darcy's velocity (v_f) is related to water and tracer velocity by effective porosity:

$$v_f = n_e v_w = n_e v_t \qquad \textbf{(2.26)}$$

For fractured rocks, Darcy's velocity is related in a good approximation to water velocity by fracture porosity, because that porosity is usually close to the effective porosity:

$$v_f = n_e v_w \cong n_f v_w = n_f v_t (n_f + n_p)/n_f = v_t (n_f + n_p) \cong v_t n_p = (x/t_t) n_p \qquad \textbf{(2.26a)}$$

The approximate form of Eq.2.26a means that from tracer velocity (or age) it is easy to calculate Darcy's velocity without any knowledge on the fracture system. The hydraulic conductivity (K) is defined by Darcy's law, i.e., $v_f = (\Delta H/\Delta x) \times K$, where $(\Delta H/\Delta x)$ is the hydraulic gradient. In consequence, Darcy's law yields the following relations:

$$K = n_e x/[(\Delta H/\Delta x) t_t] \qquad \textbf{(2.27)}$$

for a single porosity rock, and

$$K \cong (n_p + n_f) x/[(\Delta H/\Delta x) t_t] \cong n_p x/[(\Delta H/\Delta x) t_t] \qquad \textbf{(2.27a)}$$

for a fractured rock.

In both Eq.2.27 and 2.27a, the hydraulic gradient represents the mean value along the flow distance. The simplified form of Eq.2.27a is of great practical importance because it allows estimation of the regional hydraulic conductivity from the tracer age without any knowledge on the fracture network (Zuber and Motyka 1994). A number of examples of different applications of the lumped parameter approach can be found in references given above as well as in other works. Two selected examples related to fractured rocks are given below.

The ^3H ages shown in Figs.2.9 and 2.10 are related to two springs discharging at the foot of the same morphological unit of a gneiss formation (Zuber and Ciężkowski in press). The matrix porosity was assumed to be 0.007, i.e., similar to the values measured on rock samples taken from another gneiss formation of the same geological age in the Sudetes. The mean ^3H ages estimated from the simplest models are about 160 and 1000 years for Szczawina and Łomnica, respectively. However, according to the stable isotope data, the recharge takes place mainly on a plateau at the top of the unit. Therefore, the models should be selected in accordance with that information. It seems that most adequate are the exponential models (EM) for the local component recharged directly above the springs on the slope of the unit, with a dominance of the ^3H-free component recharged at the plateau. The following equation holds for a two-component mixing:

$$t_{t,\,mean} = (1 - \beta) \times t_{t,\,young} + \beta \times t_{t,\,old} \qquad \textbf{(2.28)}$$

where β is the fraction of the ^{3}H-free component, and subscripts young and old correspond to the ^{3}H and ^{3}H-free components, respectively. From Eq.2.28 the age of the ^{3}H-free (old) component can be estimated, if the mean and ^{3}H (young) component ages have been correctly determined.

The parameters of the two flow systems are summarised in Table 2.1. For these calculations, the flow distances were estimated from the morphology map. For the ^{3}H components, they were taken as the half slope distance, and for the ^{3}H-free component they were taken as the distance from the adequate part of the plateau (for details see Zuber and Ciężkowski, in press). The mean hydraulic gradients were assumed to follow the morphology.

Considering approximate character of the age, distance and hydraulic gradient estimations, the accuracy of the parameters given in Table 2.1 is probably not better than about 50%. In any case a comparison with other crystalline rock systems suggests their correctness. They are also internally consistent because the slope above the Łomnica spring is distinctly shorter than that above the Szczawina spring, which results in a lower fraction of the ^{3}H component in the former. It is difficult to say if the difference between the hydraulic conductivity of both ^{3}H systems is significant. However, a distinctly lower value of the hydraulic conductivity of the ^{3}H-free system in Łomnica than in Szczawina most probably results from a larger part of the plateau covered by less permeable Cretaceous sediments.

Table 2.1 Parameters of the Szczawina and Łomnica systems (Zuber and Ciężkowski in press).

Site	Age [a]	Q [m^3/hour]	V_w 10^6 m^3	V_r 10^8 m^3	K [10^{-8} m/s]
Szczawina	158	0.72	1.0	1.4	0.9
Szczawnina					
Young fraction	65	0.32	0.2	0.3	1.0
Old fraction	230	0.40	0.8	1.1	0.8
Łomnica					
Young fraction	70	a)			0.5
Old fraction	1000				0.1

Remark: a) unmeasurable due to a partial discharge of the spring in a stream.

In the urbanised area of Lublin city, eastern Poland, groundwater is exploited from Cretaceous marls which are fractured to the depth of about 100-200 m. In spite of dense urbanisation, the water is of a good quality. A number of wells and springs were sampled twice for ^3H determinations at the beginning of 1995 and end of 1997. All the concentrations were below 10 TU with slow declines. Models fitted to the data were similar to those shown in Fig.2.10, and the greatest mean ^3H ages were in the range of 250-500 years. The regional hydraulic conductivity in the range of 4-15 m/d was obtained from Eq.2.27a for the matrix porosity of 0.40 and estimated distances of flow yielded. Hydrodynamic modelling and pumping tests yielded the hydraulic conductivity of 2.5-10 m/d in most of the watershed, and 50-300 m/d at the tectonic zones of the valley axes. Therefore, in spite of a low accuracy of age determinations resulting from a low number of ^3H determinations, the hydraulic conductivity obtained is in a general agreement with that derived from the conventional methods. Large values of regional ^3H ages, which result from the matrix diffusion (Eq.2.25a), explain the good quality of water in that densely urbanised area. However, when some non-decaying pollutants appear in the groundwater, their removal will also take a very long time.

2.8 THE LUMPED-PARAMETER APPROACH VERSUS OTHER APPROACHES

The multi-cell approach has been introduced to the tracer method in hydrology by Simpson and Duckstein (1976), and Przewłocki and Yurtsever (1974). When uni-dimensional arrangement of cells is applied the method can be regarded as a less versatile version of the lumped-parameter approach. For a single cell, it is equivalent to the EM, and for a very large number of cells, it approaches the PFM. However, when more complicated arrangements are applied (e.g., different volumes of cells, two- and three-dimensional cell arrangements) the number of sought (fitted) parameters increases and unique solutions are not available. Therefore, the multi-cell models can be regarded as a distributed parameter approach with lumping. When interrelated tracer data distributed in time and space are available, the multi-cell modelling is definitely advantageous over the lumped parameter approach. Unfortunately, quite frequently publications appear in which a single ^3H determination, or a mean value of several samples taken in a short period of time, is interpreted either with the aid of the EM or the multi-cell approach. Such publications should be regarded as examples of incorrect interpretation.

As mentioned, the lumped parameter models are particularly useful when no sufficient data exist to justify the use of multi-cell models, multi-tracer multi-cell models (Adar 1996), or numerical solutions to the transport equation. They are also very useful in early investigations of little known systems. For a separate sampling site (e.g., a spring, or a withdrawal well), only the use of the lumped parameter models is sufficiently justified. Some investigators express opinions that in the era of numerical models, the use of a lumped-parameter approach is out of date. However, it is like trying to kill a fly with a cannon, which is neither effective

nor economic. Experience shows that a number of representative hydrologic parameters can be obtained from the lumped-parameter approach to the interpretation of environmental tracer data in a cheap and effective way.

2.9 CONCLUDING REMARKS

The lumped parameter approach is particularly useful for the interpretation of ^{3}H data in groundwater systems with separate sampling sites as, for instance, in investigations of the dynamics of small catchments (Kendall and McDonell 1998). ^{18}O has also been shown to be applicable in investigations of small retention basins and bank filtration from rivers and lakes. As mentioned, the ^{3}H-^{3}He method is advantageous over the ^{3}H method for recharge rate measurements. The use of ^{85}Kr is still troublesome and costly, and its advantages have not been proved so far. Measurements of freons have become routinely used in some countries (especially in the USA), though, most probably, due to a lower accuracy inherent to their character, they cannot so far compete with the ^{3}H method.

As mentioned a user-friendly computer-programme for the interpretation of environmental tracer data by the lumped-parameter approach is available free from the IAEA (FLOWPC). In that programme the PFM, EM, EPM, LM (linear model), LPM (combined linear-piston flow model), and DM are included, and it contains options for the applications of stable isotopes and other tracers (excluding ^{3}He), as well as for using any α value, and any β value with a chosen constant tracer concentration. In addition, ASCII files of the response, input and output functions are yielded. Curves shown in Figs.2.2 to 2.6, 2.9 and 2.10 were calculated with the aid of the FLOWPC.

When solving the inverse problem it should be remembered that in general the lower the number of fitted (sought) parameters, the more reliable the results of modelling (Himmelblau and Bischoff 1968). A better fit obtained with a larger number of parameters does not necessarily mean that a more adequate model was found. The modelling procedure should always start with the simplest models. More sophisticated models with additional parameters should be introduced only if it is not possible to obtain a good fit with a simple model, or if other information excludes a simpler model. However, it should be remembered that if a single parameter model yields a good fit, an infinite number of two parameter models also yield equally good fits. Therefore, in such situations other available information should be used for the final selection of the most adequate model. As the inverse solutions belong to the category of ill-posed problems, and the record of the experimental data is usually very short, exact and unique solutions are in general not available. However, even non-unique and/or non-exact solutions are better than a lack of any quantitative, or semi-quantitative, information.

An additional difficulty results from heterogeneity of groundwater systems. As shown by Varni and Carrera (1998), and Małoszewski and Seiler (1999), in highly heterogeneous systems, the mean tracer age may considerably differ from the mean water age. In some cases

the tracer age practically represents the upper, more active part of the system, whereas in strongly stratified systems, dispersive losses of tracer to deeper layers may result in an apparent value of the β coefficient. Similarly other parameters do not necessarily represent properly the system investigated. However, in spite of all the limitations, experience shows the lumped-parameter approach to the interpretation of environmental tracer data is of practical importance and usually yields representative results. Experience also shows that even such heterogeneous systems as karstic rocks can effectively be interpreted by that approach (e.g., Małoszewski et al. 1992, Rank et al. 1992).

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3 COMPARTMENTAL MODEL APPROACHES TO GROUNDWATER FLOW SIMULATION

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3.1 INTRODUCTION

Compartmental or mixing-cell models have been applied to groundwater flow systems by a number of investigators. Note that the expressions "compartment", "cell" and "mixing cell" are synonymous and used interchangeably in this paper. The compartmental model represents the groundwater system as a network of interconnected cells or compartments through which water and one or more dissolved constituents (tracers) are transported. Within a given cell, perfect or complete mixing of the tracer occurs, although some models relax this constraint. Flow rates of water and tracer between cells can be calculated by:

1) use of a flow model that solves the partial differential equations of groundwater flow

2) calibration with observed tracer data

3) a flow algorithm based on linear or non-linear reservoir theory, or

4) some combination of the preceding.

Each cell in the model depicts a region of the hydrogeological system; regions are differentiated based upon their hydrogeological uniformity, the availability of data, the degree of resolution desired, and constraints imposed by numerical solutions.

Compartmental models have been used to solve the inverse problem (estimating aquifer properties and recharge boundary conditions) (Adar and Neuman 1986; 1988; Adar et al. 1988; Adar and Sorek 1989; 1990). Other applications have sought to determine groundwater ages and residence times (Campana 1975; 1987; Campana and Simpson 1984; Campana and

Mahin 1985; Kirk and Campana 1990), or analyze tracer data and delineate groundwater dynamics (Yurtsever and Payne 1978; 1985; 1986). Other investigators have used them as transport models (Van Ommen 1985; Rao and Hathaway 1989). A recent pioneering approach uses a compartmental model to constrain a finite-difference regional groundwater flow model (Harrington et al. 1999).

The three compartmental models described herein represent different approaches and levels of sophistication. The first, a relatively simple model by Campana, is calibrated with the spatial distribution of the environmental isotope deuterium. Calibration with deuterium yields estimates of groundwater flow rates and residence times within a regional aquifer system. The second approach by Harrington uses a compartmental model, calibrated with ^{14}C, to constrain a finite-difference regional groundwater flow model of the Otway Basin in South Australia. To our knowledge this represents a first. The final application, by Levent Tezcan, describes a distributed mixing-cell model that can simulate groundwater flow and transport; he applies it to a karst aquifer on the Mediterranean coast of Turkey. Tezcan's model also functions like a watershed model in that it simulates the surface hydrology in addition to subsurface flow.

3.2 A SIMPLE COMPARTMENTAL MODEL: THEORY AND APPLICATION TO A REGIONAL GROUNDWATER FLOW SYSTEM

3.2.1 THEORY

We use a numerical compartmental or mixing-cell model (Campana 1975; Simpson and Duckstein 1976) to simulate flow in a subsurface flow system. The code has been applied to a variety of subsurface flow systems (Campana 1975; 1987; Campana and Simpson 1984; Campana and Mahin 1985; Kirk and Campana 1990; Campana and Byer 1996). The compartmental model represents the groundwater system as a network of interconnected cells or compartments through which water and a dissolved constituent (tracer) are transported. Each cell in the model depicts a region of the hydrogeological system; regions are differentiated based upon their hydrogeological uniformity, the availability of data, and the degree of resolution desired. Cells can be of any desired size and can be arranged in a one-, two-or three-dimensional configuration. The model can be used as a "stand-alone" model or coupled to a flow model.

Our compartmental model permits the user to specify the flow paths between cells and the discharge from the system. Discharge can also be calculated using linear reservoir theory. To do so requires an initial estimate of the flow system, such that an initial set of specifications can be established. During the calibration process, these parameters are adjusted by the modeller to obtain agreement between the simulated and observed tracer concentrations. We use environmental isotopes as tracers.

The following sections describe the equations governing the flow of water and tracer in a network of cells or compartments.

3.2.1.1 TRACER MASS BALANCE

The basic equation, applied to each cell, or compartment, is (Simpson and Duckstein 1976):

$$S(N) = S(N-1)+[BRV(N)\times BRC(N)] - [BDV(N)\times BDC(N)] \quad \textbf{(3.1)}$$

where: S(N) = cell state at iteration N, the mass of tracer within the cell; BRV(N) = boundary recharge volume, the input volume of water at iteration N; BRC(N) = boundary recharge concentration, the input tracer concentration; BDV(N) = boundary discharge volume, the output volume of water leaving the compartment or cell; and BDC(N) = boundary discharge concentration, the output tracer concentration.

Tracer concentrations and water volumes crossing model boundaries and entering/leaving a cell on the boundary of the model are given the prefix "system" or "S". Thus, recharge entering a cell from outside the model boundaries has a characteristic tracer concentration SBRC (system boundary recharge concentration) and volume SBRV (system boundary recharge volume). The similar case holds for discharge from the system (SBDC and SBDV).

The mass balance equation, Eq.3.1, is applied successively to each cell during a given iteration; discharge (BDV and BDC) from an "upstream" cell becomes recharge (BRV and BRC) to a "downstream" cell. The BDC(N) term on the right-hand side of Eq.3.1 is the only unknown and can be determined from one of two mixing rules, the simple mixing cell (SMC), which simulates perfect mixing, or the modified mixing cell (MMC), which simulates some regime between perfect mixing and piston flow. For the SMC:

$$BDC(N) = [S(N-1) + BRV(N)*BRC(N)]/[VOL + BRV(N)] \quad \textbf{(3.2)}$$

For the MMC:

$$BDC(N) = S(N-1)/VOL \quad \textbf{(3.3)}$$

where: VOL = volume of water in the cell, equal to the cell's total volume times its volumetric moisture content (for unsaturated flow) or its effective porosity (for saturated flow). Note that the MMC simulates pure piston flow as BRV $\rightarrow$ VOL and perfect mixing as BRV $\rightarrow$ zero. Although pure piston flow within a cell is possible, pure piston flow for the entire array of cells is not implied because some degree of mixing occurs between cells (Campana and Simpson 1984). The same mixing rule must be used for each cell during a given model run. We used the MMC rule in the model described herein.

3.2.1.2 TRANSIENT FLOW

The above equations cannot account for changes in storage within the groundwater system. Previous compartment models have treated transience (Yurtsever and Payne 1986). Following previous workers (Campana 1975; Yurtsever and Payne 1986) we simulate transient flow by

assuming that the outflow from a groundwater reservoir is proportional to the storage in the reservoir (Dooge 1960; 1973):

$$S = KQ \tag{3.4}$$

where: S = storage above a threshold, below which the outflow is zero; K = storage delay time of the compartment; and Q = volume rate of outflow from the element. Eq.3.4 describes a conceptual element known as a linear reservoir.

In the context of the compartment model, Eq.3.4 for a single compartment is:

$$VOL(N) = K*BDV(N) \tag{3.5}$$

Eq.3.5 does not account for the presence of a threshold in the compartment, but can be adapted for such a case by rewriting Eq.3.5:

$$VOL(N) - PHI = K*BDV(N) \tag{3.6}$$

where PHI = threshold volume of the compartment, below which the discharge from the compartment is defined as zero. If VOL(N) is less than or equal to PHI, then BDV(N) is defined as zero.

If K is held constant for all N, then the system described by either of the above equations is a linear, time-invariant system; if K is a function of time or iteration number, i.e., K = K(N), then the system is a linear, time-variant system (Mandeville and O'Donnell 1973).

If Eq.3.5 is rewritten for iteration N+1 and substituted into Eq.3.7, a volume conservation equation for a given compartment or cell:

$$VOL(N+1) = VOL(N) + BRV(N+1) - BDV(N+1) \tag{3.7}$$

the result is

$$VOL(N+1) = VOL(N) + BRV(N+1) - [VOL(N+1)/K] \tag{3.8}$$

which simplifies to

$$VOL(N+1) = [K/K+1]\,[VOL(N) + BRV(N+1)] \tag{3.9}$$

At iteration N+1, all quantities on the right-hand side of Eq.3.9 are known, so VOL(N+1) can be calculated. Once this has been accomplished, BDV(N+1) can be calculated from Eq.3.5.

3.2.1.3 AGE CALCULATIONS

When the recharge to the compartmental model does not vary with time, calculation of the mean age or mean residence time of the water in a compartment or cell is relatively straightforward (Campana 1975; 1987).

For the SMC:

$$AGE = \left[\frac{VOL + BRV}{BRV} * DELT\right] + \sum_{i=1}^{k} \left[FBRV_i * AGEFBRV_i\right] \tag{3.10}$$

where AGE = mean age of the water in the cell; DELT = real time between iterations; FBRVi = fraction of all incoming water to the cell (BRV) which is from cell i; AGEFBRVi = mean age of FBRVi; and k = number of upgradient cells which contribute water directly to the cell.

For the MMC:

$$AGE = \left[\frac{VOL}{BRV} * DELT\right] + \sum_{i=1}^{k}\left[FBRV_i * AGEFBRV_i\right] \qquad (3.11)$$

The age distribution and cumulative age distribution of each cell can be simulated by an impulse -response method (Campana 1987). The mean age of the water in each cell can be calculated by an instantaneous injection of tracer through the SBRV inputs to each cell, i.e., the recharge water of age zero. The mean age is then found by:

$$\bar{A} = \frac{\sum_{i=1}^{N} iC(N)_i}{\sum_{i=1}^{N} C(N)_i} * DELT \qquad (3.12)$$

where: C = tracer concentration in cell; and $\bar{A}$ = mean age of the water in the cell, equal to AGE (equations 10 or 11) except for truncation error associated with C. The age distribution of $\bar{A}$ can be obtained from C(N) because the concentration of the tracer in each cell at iterations (N) after the injection is a measure of the fractional amount of water age (N*DELT) in that cell. The cumulative age distribution can be easily determined from the age distribution (Campana 1987).

There are times when the compartment model may be operated under steady state conditions (for a given cell VOL = constant) but the recharge to the model may vary, perhaps to simulate changes in the hydrologic regime induced by climate change. Under such conditions, the equations given above cannot be used to calculate mean ages. More complicated relationships must be used; for the sake of brevity these will not be given here but can be found in (Campana, in press).

A copy of the code and user's manual are available from the author (aquadoc@unm.edu).

3.2.2 APPLICATION TO THE NEVADA TEST SITE FLOW SYSTEM

The compartmental model essentially performs a mass balance on the flow system to determine flow rates, groundwater ages and residence times; it needs a tracer to do this. An ideal tracer is one that moves with the velocity of the water, is easy to sample for and detect, does not react chemically once in the saturated zone, and displays spatial variability. The stable isotopes ^{2}H (deuterium) and ^{18}O, both of which occur as part of the water molecule, come about as close to ideal tracers as there are. We present a compartmental model of the Nevada Test Site groundwater flow system, which underlies a portion of the south-western USA, calibrated with the spatial distribution of deuterium.

3.2.2.1 INTRODUCTION

Four decades of nuclear testing have served as an impetus for numerous studies of the groundwater flow system beneath the Nevada Test Site (NTS) and vicinity, south-western USA. A more recent impetus is the possible location of a high-level nuclear waste disposal site at Yucca Mountain, adjacent to the western boundary of the NTS. Possible radionuclide migration to the accessible environment is a concern; therefore, knowledge of the nature and extent of the NTS groundwater flow system, hereafter referred to as the NTSFS, is of paramount importance. We use the environmental stable isotope ratio $^{2}H/^{1}H$ (deuterium/hydrogenium) to calibrate a simple compartmental model of the ground-water system beneath the NTS and vicinity. ^{2}H has the advantage of being stable and essentially conservative once in the saturated zone. Our model is based upon previous ones (Feeney et al. 1987; Sadler 1990), but encompasses a larger area, provides better information on groundwater residence times, and, more importantly, attempts a transient simulation by treating each compartment as a linear reservoir.

3.2.2.2 HYDROGEOLOGY

The study area lies between 36 and 38 degrees north latitude and 115 and 117 degrees west longitude and covers 19 000 km^2 (Fig.3.1). The area is in the southern Great Basin section of the Basin and Range physiographic province, with a topography of north-trending, block-faulted mountain ranges separated by alluvial basins. Elevations in the study area range from about 3500 meters (m) above mean sea level in the Spring Mountains to below sea level in Death Valley.

Precipitation, temperature, and plant communities in the area are generally a function of elevation. The average annual precipitation increases as a function of elevation, from less than 8 cm in Death Valley and the Amargosa Desert to greater than 70 cm in the upper reaches of the Spring Mountains. Annual pan evaporation rates range from 58 to over 71 cm. Therefore, the climate can be arid on the valley floors while sub-humid at higher elevations. Most of the precipitation occurs during winter as a result of Pacific Ocean fronts, but some occurs during summer as high intensity thunderstorms. Winters are short and mild, while summers are long and hot except at the higher altitudes. Because of the primarily arid conditions, no major perennial streams exist in the study area except local drainage from major springs.

Groundwater is recharged by precipitation in the higher elevations in the north, east, and south-east and by stream-channel infiltration during the infrequent flow events. It also enters the system as subsurface inflow from the north and east. Generally, groundwater flows to the south toward areas of discharge in Oasis Valley, Ash Meadows, Death Valley and Franklin Lake playa (southern Amargosa Desert).

The geology of the region is complex and has been well-described (Winograd and Thordarson 1975). Eleven hydrogeologic units in the region have been identified, ranging in age from

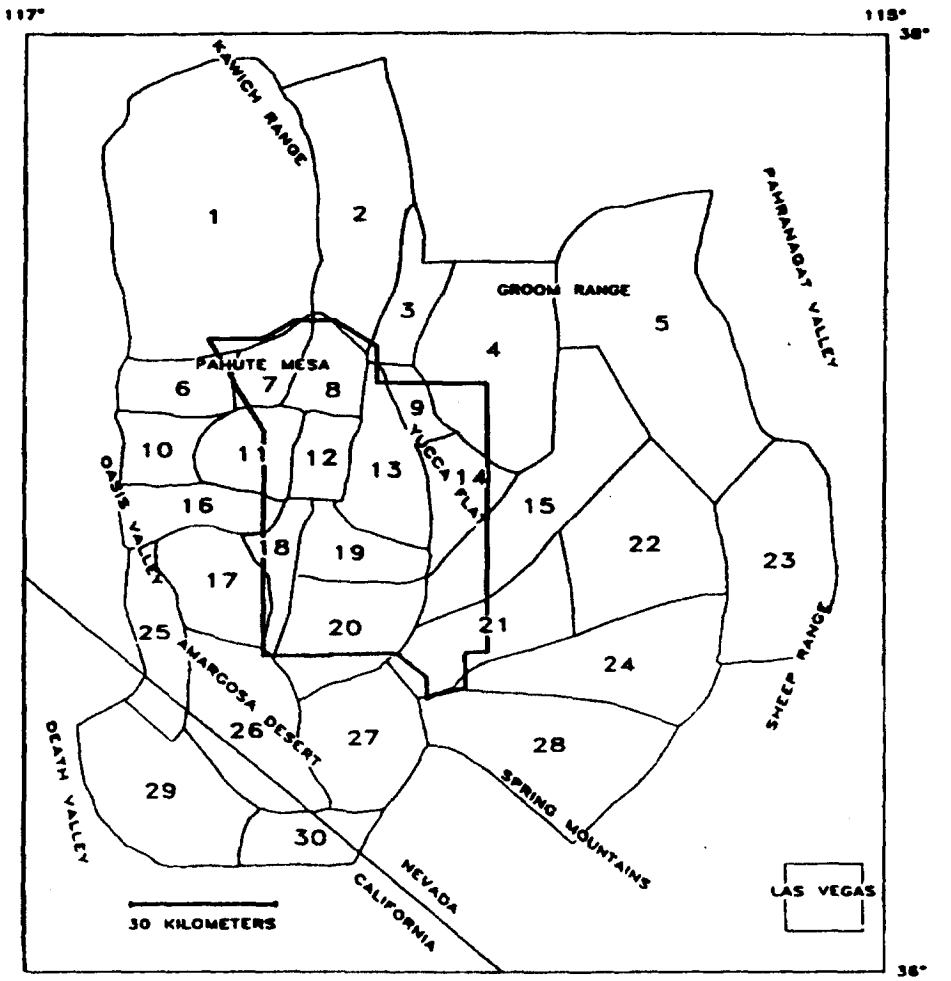

Fig.3.1 The study area and model network, with the Nevada Test Site indicated by heavy line.

Precambrian to Quaternary; five of these are aquitards, six are aquifers. Of these units, two of the most important are the lower clastic aquitard, comprised of Precambrian to Cambrian quartzites and shales, and the lower carbonate aquifer, comprised of Cambrian through Devonian limestones and dolomites. The great thickness of the former, an aggregate of about 3000 m, and areal extent make it a major element in controlling regional groundwater flow; the latter (aggregate thickness of about 4500 m) underlies much of the study area and is the major conduit for regional groundwater flow in the area. The upper clastic aquitard and upper carbonate aquifer are similar to the lower clastic aquitard and lower carbonate aquifer, respectively, but are less important because of their lower thicknesses and more limited areal extents. Other hydrogeologic units worth noting are the basin-fill aquifer, important in the Amargosa Desert, and the various volcanic-rock aquifers and aquitards (Tertiary tuffs and associated lithologies), which are up to 4000 m thick in the western portion of the study area.

The area's structural geology has played a major role in shaping the hydrogeology of the region. Mesozoic and Tertiary folding and thrust faulting significantly deformed the

Precambrian and Palaeozoic rocks; Tertiary normal block faulting produced classic basin and range topography. These same forces were responsible for fracturing the aforementioned carbonate rocks, producing a very transmissive regional aquifer. The intermontane basins filled with sediments derived from the surrounding mountain ranges, in many cases producing a two-tiered flow system characteristic of the region: a shallow system developed in the basin fill overlying a deeper regional system in carbonate and other rocks. In some cases, perched flow systems occur in the basin fill. Downward flow occurs from the basin-fill aquifers and tuff aquitards to the carbonate rocks and interbasin groundwater flow occurs (Winograd and Thordarson 1975).

The NTS flow system is not an isolated regional system but one of a number of such systems in the carbonate-rock province of Nevada, Utah and adjacent states (Mifflin and Hess 1979; Burbey and Prudic 1991; Plume 1996).

3.2.2.3 MODEL DEVELOPMENT AND CALIBRATION

Two sets of δ^2H values (versus the VSMOW standard; see for definitions Volume I) were used: "local" values from high-altitude springs and shallow wells with signatures of -90 to –102‰, representing recharge water; and "regional" values from large, low-altitude springs and deep wells with signatures of -98 to –117‰, representing the flow system groundwater. The latter were used in model calibration and, along with the hydrogeology (e.g., hydrostratigraphy, structure), used to subdivide the flow system into 30 compartments or cells (Fig.3.1). The difference between the regional and local δD values can be explained by relatively depleted subsurface inflow from higher latitudes and possibly past climatic regimes entering the study area and becoming gradually enriched along flow paths by water recharged within the study area. The overall trend of regional δ^2H values is gradual enrichment from north to south with the north-west area being the most depleted and the south-west being the most enriched. Some recharge δ^2H values were estimated from the δ^2H values in precipitation. Complete data can be found in (Sadler 1990).

Initial estimates of the SBRV (both as recharge and subsurface inflow) were based on previous data (Rush 1970; Walker and Eakin 1963; Malmberg and Eakin 1962). The initial recharge estimates were used as starting points and references during calibration.

Flow routing inputs to the model are expressed as the percentage of total discharge from each cell to each of its receiving cells or out of the model boundaries. Initial flow routing values were based on the aforementioned publications on the hydrogeology of the area. Total discharge from a cell was calculated by Eq.3.5.

The parameter VOL equals the volume of active water in a cell. Cell areas were measured with a planimeter from a 1:250 000 scale map. An effective porosity of 2%was used for the carbonate aquifer, which is the mean value of 25 samples presented in (Winograd and Thordarson 1975). The 5% effective porosity measured for the welded tuff aquifer was

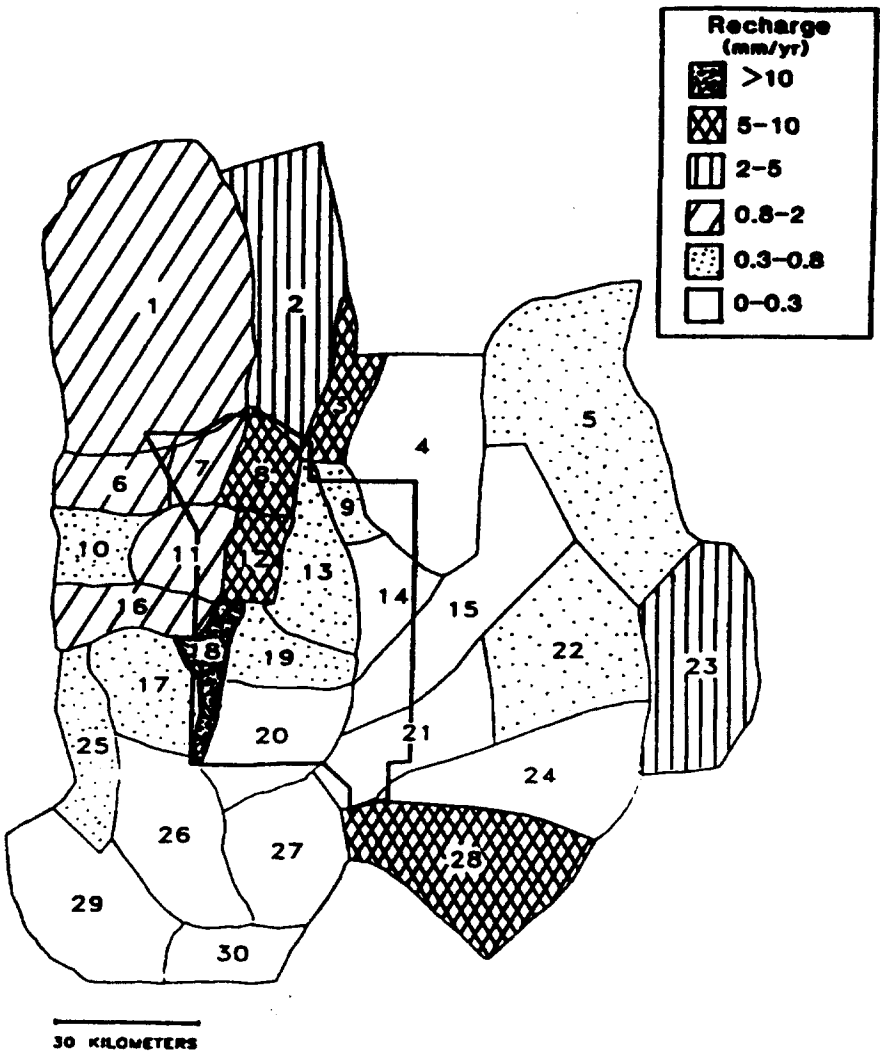

Fig.3.2 Recharge rates in mm/year.

chosen for the volcanic strata based on the observation that most of the flow is transmitted through the welded tuffs; the higher porosities of the non-welded tuffs were not used. The upper clastic aquitard (cells 13 and 19) was assigned an effective porosity of 4%, the mean values of 22 samples presented in. The basin-fill aquifer was characterised as being generally poorly sorted and was assigned an effective porosity of 15%.

The model utilised a 100-year iteration interval and the MMC (modified mixing cell) option. To simulate climate change we increased recharge to the model by 50% and decreased its δ^2H by 5‰ during the period 23 000 to 10 000 years before present (White and Chuma 1987).

Model calibration was accomplished by adjusting SBRV and intercellular flow routing values until the difference between the observed and simulated δ^2H values was within ±1‰, the analytical error for ^2H.

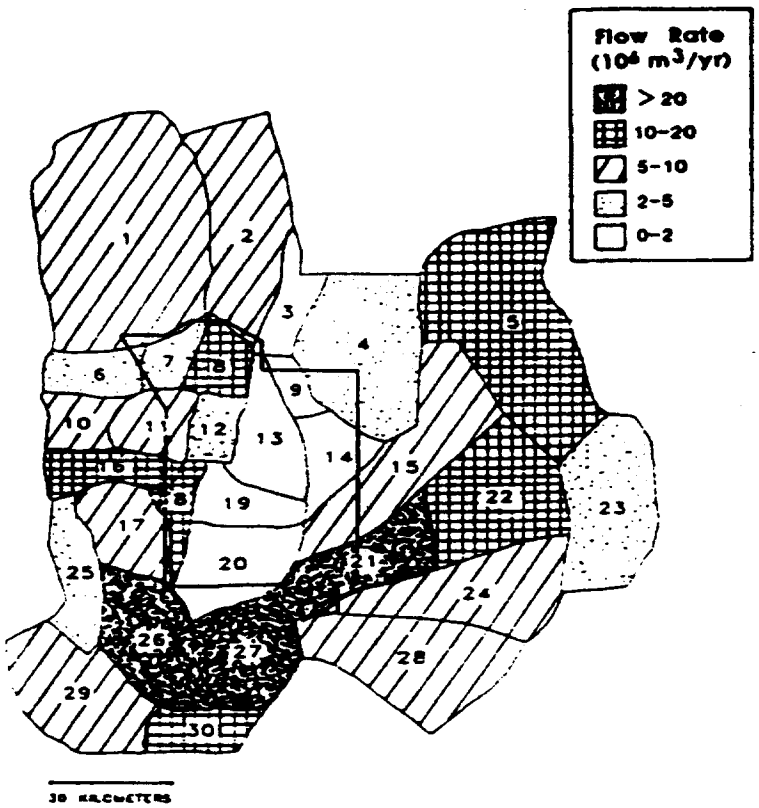

Fig.3.3 Volumetric flow rates in 10^6 m^3 per year.

3.2.2.4 RESULTS AND DISCUSSION

The areal distribution of average annual recharge is shown in Fig.3.2. In general, higher recharge rates are present in the northern region of the model with lower rates in the southern; however, quasi-isolated areas which do not follow this trend have the highest recharge rates within the model area. The high recharge areas in Fig.3.2 correspond to areas of relatively enriched δ^2H values: eastern Pahute Mesa (cell 8); Stockade Wash (cell 12); Fortymile Canyon/Wash (cell 18); the Spring Mountains (cell 28); and the Sheep Range (cell 23).

The total flow rate through the system averages 58.9 x 106 m^{3}a^{-1}. Broad divisions of average flow rates are shown in Fig.3.3. The lowest flow rates correspond to cells that are dominated by the presence of an aquitard (cells 13 and 19), cells immediately downgradient from an aquitard (cells 9, 14, 20, and 25), and a cell which is a moderate recharge area (cell 3). Cells 3, 13, 19, and 20 are thought to divide the Alkali Flat-Furnace Creek and Ash Meadows subbasins. The highest flow rates correspond to a major potentiometric trough in the carbonate aquifer immediately upgradient (cell 21) from the Ash Meadows area (Winograd and Pearson 1976), the terminus of the Ash Meadows subbasin (cell 27), and the constriction and termination of the Alkali Flat-Furnace Creek subbasin (cells 26 and 30).

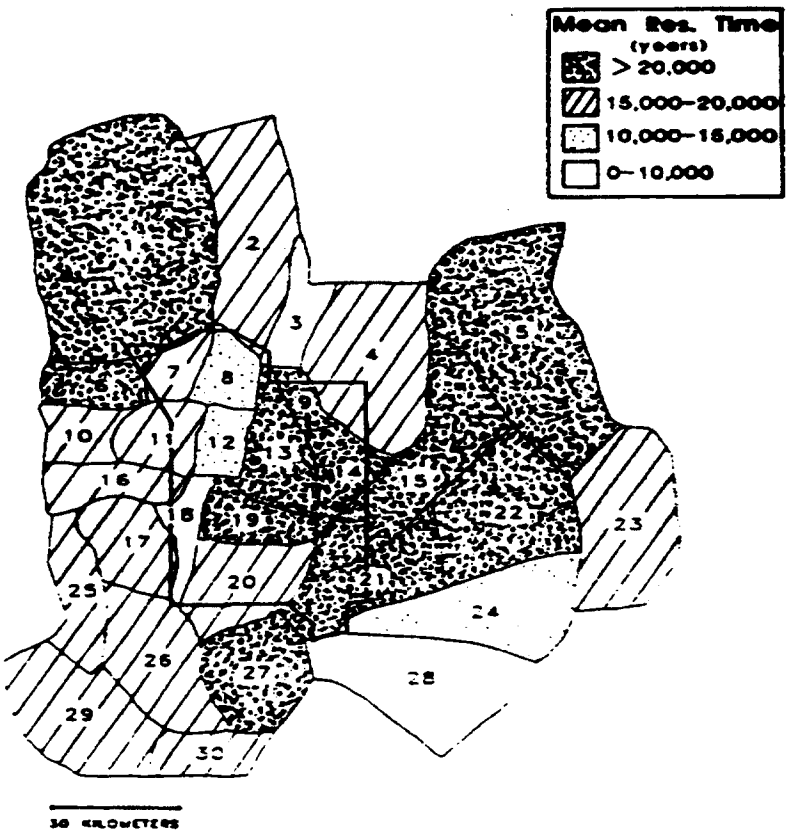

Fig 3.4 Mean groundwater residence times in years.

Other regional models of the area (Rice 1984; Waddell 1982) suggested the possibility of, but did not simulate, subsurface inflow from northern and north-western areas. Therefore, all flow through these previous models is comprised of locally-recharged water and not a combination of locally-recharged and underflow water as in the present model. Our model indicates that a substantial amount (40%, or 23.6 x 106 m^3a^{-1}) of the average total system throughflow is derived from subsurface inflow.

Mean residence times are shown in Fig.3.4. The youngest values are found in the cells with high recharge versus subsurface flow from upgradient cells (cell 3, 18, and 28). Cells 8 and 12 have relatively young waters due to their high recharge rates, while cell 24 receives its relatively young water from cells 28 and 23. The oldest mean residence times are found in the upper clastic aquitard cells (cells 13 and 19), downgradient from aquitards (cells 9, 14, and 15) and in areas where most of the flow originates directly or indirectly as underflow (cells 5, 15, 21, 22, 27, 1, and 6). A decrease in mean residence times along flow paths occurs in many areas and is caused by relatively large amounts of recharge in the direction of flow. The means represent all of the water in a given cell and may include a mixture of very young water recharged locally and very old water received from upgradient cells.

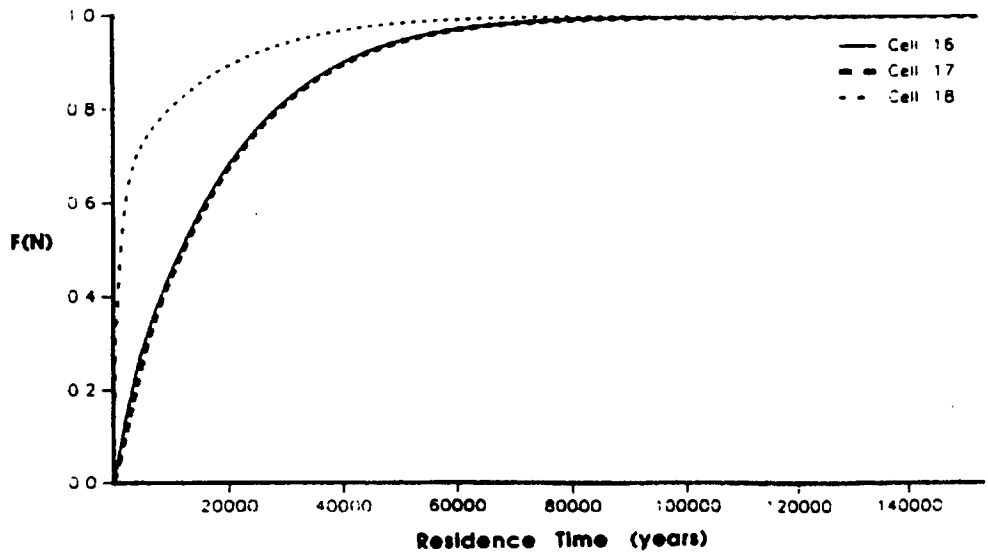

Fig.3.5 Cumulative groundwater residence time distribution F(N) for cells 16 (Oasis Valley/Beatty Wash), 17 (Crater Flat), and 18 (Fortymile Canyon/Wash).

Residence time distributions (RTDs) provide more information on the cells' waters than simply mean or median values (Campana 1987). Cumulative RTDs for six regions are shown in Figs.3.5 and 3.6. Fig.3.5 shows the RTDs [F(N)] for cells 16 (Oasis Valley/Beatty Wash), 17 (Crater Flat) and 18 (Fortymile Canyon/Wash); Fig.3.6 shows F(N) for cells 28 (north-western Spring Mountains), 29 (Furnace Creek Ranch region of Death Valley) and 30 (Franklin Lake playa and vicinity).

Fortymile Canyon/Wash has the highest areally-distributed recharge rate (29.4 mm/year) and a volumetric flow rate second only to the Spring Mountains. Most of the groundwater beneath this region is very young -- 60% of the water is fewer than a few thousand years old. Contrast this fact with the other two regions on Fig.3.6 – Oasis Valley and Crater Flat – where 60% of the waters are at least 15 000 years old. Both of these areas are minor recharge areas; indeed, Oasis Valley is more important as a discharge area.

Fig.3.6 contains the cumulative RTDs of the area's major recharge area (Spring Mountains – cell 28) and two major discharge areas (Furnace Creek Ranch – cell 29; and Franklin Lake playa – cell 30). These latter two cells are major discharge regions and have much older ground waters. Note that even though cell 30 is farther downgradient than cell 17 (Crater Flat) its F(N) is shifted slightly to the left relative to Crater Flat's, indicating slightly younger waters. This apparent discrepancy is easily explained by noting that Franklin Lake playa receives relatively young water (via other cells) from the Spring Mountains and Fortymile Canyon/Wash.

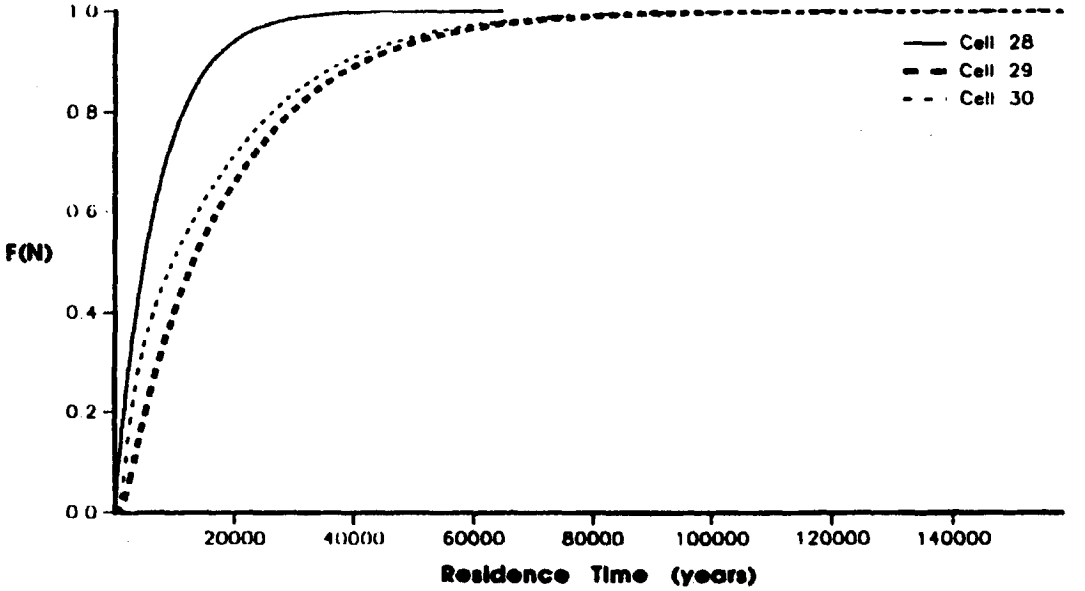

Fig.3.6 Cumulative groundwater residence time distribution F(N) for cells 28 (north western Spring Mountains), 29 (Furnace Creek Ranch area), and 30 (Franklin Lake playa).

3.2.2.5 CONCLUDING REMARKS

We used a deuterium-calibrated mixing-cell model to simulate regional groundwater flow beneath an area of approximately 19 000 km^2 in southern Nevada-California, USA. This model consists of a network of 30 compartments delineated through the integrated interpretation of general hydrogeologic characteristics of the area and deuterium data from approximately 300 sites.

The model shows the significant contribution of subsurface inflow –40% of the average total system throughflow– to the NTS regional groundwater system. This flow enters from the north and east. The eastern subsurface inflow is undoubtedly from the White River regional groundwater flow system. Previous workers (Winograd and Friedman 1972) estimated that about 7.4×106 m^3a^{-1} flowed from Pahranagat Valley (part of the White River flow system and just east of cell 5) to the NTS system; an earlier compartmental model (Kirk and Campana 1990) showed as much as 5.4×106 m^3a^{-1} discharged as underflow from Pahranagat Valley. We estimate the underflow to be between 11.1×106 m^3a^{-1} and 16.8×106 m^3a^{-1}.

High recharge areas within the flow system boundaries are the Fortymile Canyon/Wash-Stockade Wash area, the Spring Mountains, the Sheep Range, and Pahute Mesa. Recharge accounts for 60% of the average system throughflow.

The model provides detailed information on groundwater residence times. The position of a region in the flow path does not necessarily correlate with mean residence time as recharge can mask the effects of old subsurface inflow to a region.

3.3 CONSTRAINING REGIONAL GROUNDWATER FLOW MODELS WITH ENVIRONMENTAL ISOTOPES AND A COMPARTMENTAL MIXING-CELL APPROACH

3.3.1 INTRODUCTION

Numerical groundwater flow models such as MODFLOW (McDonald and Harbauch 1988) are often used to interpret hydraulic head data and physical properties (e. g., porosity, conductivity) of regional aquifer systems. Once calibrated, these models can provide important quantitative information about groundwater recharge, lateral flow and leakage between aquifers. However, proper calibration of regional groundwater models usually requires a greater degree of spatial parameterisation than is available from field data. Hence, many of the input parameters for these models have to be estimated, thus reducing confidence in the final calibrated model.

The benefits of incorporating environmental tracer techniques into hydrogeological investigations are well known. For example, the stable isotope composition ($^{2}H/^{1}H$ and $^{18}O/^{16}O$) of water molecules is often used to identify palaeo-recharge water in aquifers by comparing groundwater compositions with those of present-day rainfall (Edmunds and Wright 1979; Clark et al. 1987; Fontes et al. 1991). Radioactive isotopes such as ^{14}C and ^{36}Cl are commonly employed to infer mean groundwater residence times in regional aquifers (Mazor et al. 1974; Love et al. 1994; Bentley et al. 1986). Nevertheless, environmental tracer data are generally only used in a qualitative or semi-quantitative manner. Hence, there is a need to develop and apply techniques for interpreting tracer data simultaneously with hydrogeologic data to provide more quantitative information about groundwater processes such as lateral flow and leakage.

The compartmental or mixing-cell (CMC) approach is one of the most straightforward ways in which environmental tracer, hydraulic and hydrogeologic data can be analysed simultaneously. Used by numerous authors over the past three decades (Campana and Simpson 1984; Yurtsever and Payne 1978; 1985; 1986; Harrington et al. 1999; Simpson and Duckstein 1976; Allison and Hughes 1975; Przewlocki and Yurtsever 1974; Yurstever and Buapeng 1991; Yurtsever et al. 1986), the CMC approach uses linear mass-balance equations to simulate the transport of conservative or radioactive tracers through an aquifer system. Quantitative estimates of physical processes such as lateral flow and leakage between aquifers are determined by altering fluxes between model cells until simulated tracer concentrations match those observed in the field.

In the following text, we present a new approach for quantitatively interpreting environmental tracer data and constraining regional groundwater flow models. Whereas previous CMC models required the fluxes between model cells to be altered manually, the approach adopted herein is to use the U.S.Geological Survey's groundwater flow model MODFLOW (McDonald and Harbauch 1988) to obtain inter-cellular fluxes and aquifer heads. Further details of the model development and application are presented in (Harrington et al. 1999).

3.3.2 GOVERNING EQUATIONS

The CMC approach is based on the assumption that each compartment or mixing cell in a model aquifer undergoes complete mixing with inputs of water and tracer mass (e.g., via recharge or lateral inflow) over a designated time step. This assumption can be justified providing the size of individual mixing cells and time steps are chosen sensibly. If one also assumes that volumetric inflows over a time step are negligible compared to the volume of the mixing cell, and changes in fluxes of tracer into each cell are linear across time steps, then the following equation may be used to determine the concentration of tracer in a cell after a certain time, t (Harrington et al. 1999):

$$c = c^0 + c^1 t + c^2 t^2 \qquad \textbf{(3.13)}$$

where:

c is the concentration of tracer in the "mixed" cell, [ML^{-3}]

c^0 is the initial concentration of the cell at t=0, [ML^{-3}]

$$c^1 = \frac{\sum_{i=1}^{n} Q_i^0 (c_i^0 - c^0) - \lambda V^0 c^0}{V^0}, \quad [ML^{-3}T^{-1}]$$

n is the number of inputs to the cell

c_i^0 are the input concentrations to the cell at t=0, [ML^{-3}]

Q_i^0 are the input fluxes to the cell at t=0, [L^3T^{-1}]

λ is the decay constant of the tracer, [T^{-1}]

V^0 is the volume of the cell at t=0, [L^3]

$$c^2 = \frac{\sum_{i=1}^{n} Q_i^0 (c_i^1 - c^1) + \sum_{i=1}^{n} Q_i^1 (c_i^0 - c^0) - \lambda (V^1 c^0 + V^0 c^1) - V^1 c^1}{V^0} \quad [ML^{-3}T^{-2}]$$

c_i^1 are the changes in input concentrations per time, [$ML^{-3}T^{-1}$]

Q_i^1 are the changes in input fluxes per time, [L^3T^{-2}]

V^1 is the change in cell volume per time, $[L^3T^{-1}]$

Eq.3.13 allows the concentration of each interconnected mixing cell in a model domain to be determined under transient flow conditions and/or varying tracer input concentrations. This is particularly useful for modelling regional aquifer systems in which the hydraulic head gradient has changed over a long period of time (e.g., 103 - 105 years).

3.3.3 MODEL DESIGN, INPUT DATA AND CALIBRATION PROCEDURE

The CMC model described by Eq.3.13 has been directly linked to MODFLOW, a finite-difference groundwater flow model developed by the U.S.Geological Survey (McDonald and Harbauch 1988). The model domain and cell configuration of the MODFLOW and CMC components of a particular application must be the same to facilitate the linkage between the two models. Initially, hydrogeologic data such as field and estimated values of aquifer porosity and hydraulic conductivity are specified in MODFLOW, along with recharge rates, boundary conditions and time step information. MODFLOW is then executed to provide both hydraulic heads and inter-cellular fluxes (horizontal and vertical) of water for each model cell in the aquifer.

The initial concentration of a tracer (chemical or isotopic) in each cell, and the tracer concentration in recharge water entering each cell (at each time step), are specified in an input file for the CMC model. The CMC model is then executed to obtain a distribution of tracer concentrations through the aquifer system using the fluxes and head data obtained from MODFLOW.

The combined model is calibrated using an iterative procedure, whereby the estimated hydrogeologic input parameters for MODFLOW are altered until the simulated aquifer heads and the simulated tracer concentrations match the observed distributions. The end result is a calibrated regional groundwater flow model from which quantitative estimates of processes such as lateral flow and vertical leakage of groundwater can be obtained with greater confidence than if the environmental tracer data had been excluded.

3.3.4 APPLICATION TO THE OTWAY BASIN, SOUTH AUSTRALIA

The combined hydraulic/environmental tracer approach outlined above has successfully been applied to the Otway Basin of South Australia (Fig.3.7) to quantify mixing between two regional Tertiary aquifers: the Gambier unconfined limestone aquifer and the Dilwyn confined sand aquifer Harrington et al. 1999). Rates of leakage from the Gambier aquifer into the underlying Dilwyn aquifer are required to determine sustainable rates of extraction for the relatively fresh (< 1000 mg/L) Dilwyn groundwater resource.

Both the Gambier unconfined and Dilwyn confined aquifers are connected to the sea in the south-west. Hence, the flow regime of the groundwater in each aquifer has varied over the

last 30 000 years (and beyond) due to eustatic sea level variations (Love et al. 1994). Potential leakage between the two aquifers occurs where relative head gradients favour upward or downward movement. To the east of the zero head difference (ZHD, Fig.3.7), the water table in the unconfined aquifer is higher than the potentiometric head in the confined aquifer. Hence there is potential for downward leakage (confined aquifer recharge) to occur in this area. Conversely, to the west of the ZHD there is potential for upward leakage (confined aquifer discharge). Because eustatic sea level variations have altered the hydraulic head distributions within both aquifer systems in the past, the position of the ZHD, and hence size and position of the potential recharge and discharge zones, has also varied.

The model domain selected for application of the hydraulic/tracer approach was a two-dimensional vertical slice along a transect (A-A', Fig.3.7) that runs perpendicular to potentiometric contours for both the unconfined and confined aquifers. The slice was divided into 30 columns, each of length and width 8660 m (Fig.3.8). Radiocarbon (^{14}C) was chosen as the tracer because it has a half life (~ 5730 years) that enables hydrologic processes to be traced over time scales commensurate with the simulation period for the model (27 000 years). Over the simulation period, the elevation and horizontal position of the western boundary condition was varied to account for eustatic sea level changes. The ^{14}C concentration of recharge water was also varied over the simulation period.

MODFLOW simulations were preformed initially until modelled aquifer heads matched the observed distribution (Fig.3.9a). Intercellular fluxes and heads from the calibrated MODFLOW model were then used as input data for the CMC model to simulate the observed distribution of radiocarbon concentrations in the Dilwyn confined aquifer. From the plot shown in Fig.3.9b, it was obvious that the calibrated MODFLOW model was not accounting for enough leakage of relatively high-^{14}C water from the unconfined aquifer into the confined aquifer. Hence the MODFLOW model had to be re-calibrated using the iterative procedure outlined above. This was achieved by increasing the vertical hydraulic conductivity of the regional confining aquitard that separates the two aquifers, and altering the horizontal hydraulic conductivity of both aquifers. Fluxes and heads from the final calibrated MODFLOW model (Fig.3.9c) provided a much better match between the observed ^{14}C distribution and that obtained from the CMC model (Fig.3.9d).

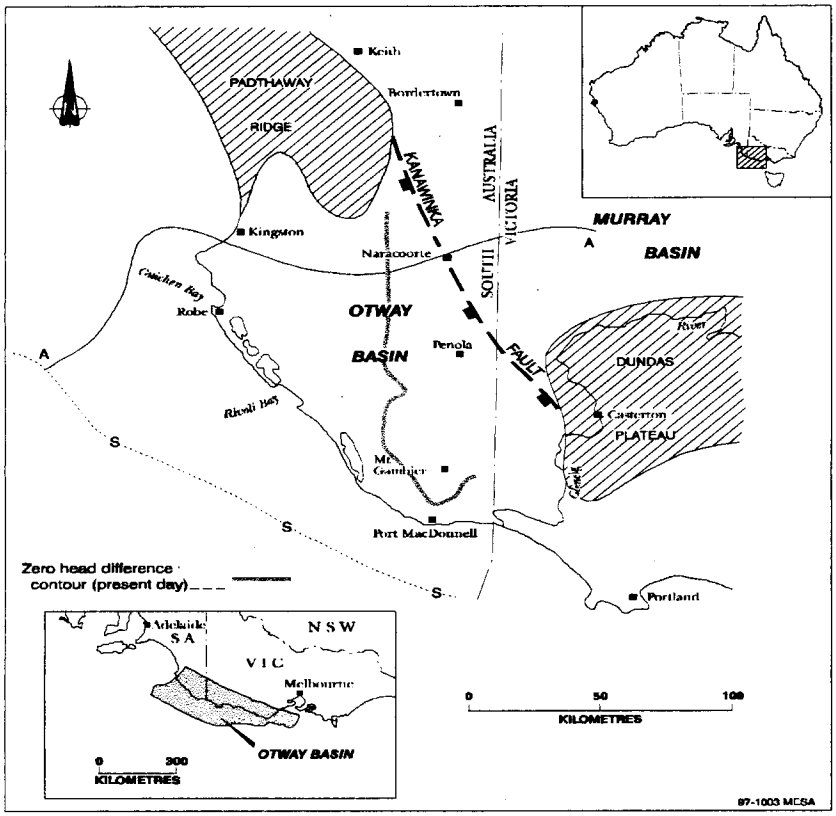

Fig.3.7 Location of transect A-A', Otway Basin, South Australia.

Although the peak ^{14}C concentration was not modelled exactly, we considered it more important to model the shape of the observed ^{14}C distribution rather than the absolute values. The reason for this is that observed concentrations are from the uppermost portion of the confined aquifer and hence do not represent the "average" concentration of the entire aquifer thickness, as calculated in the CMC model. From the comparison the only area where the model was unable to ideally match the trend in observed radiocarbon data is in those cells beyond the present day ZHD (116 kilometres from A) towards the coast. One explanation for this is that our model has used values of hydraulic conductivity for the Dilwyn confined aquifer system that are higher than those in reality. This would result in modelled flow rates being higher and hence modelled radiocarbon concentrations decreasing less rapidly. A previous investigation (Love 1992) has suggested that the confined system may be receiving upward leakage of relatively "older" water from an underlying Cretaceous aquifer near the coast. This would result in the measured ^{14}C activities being lower than the modelled output, as observed.

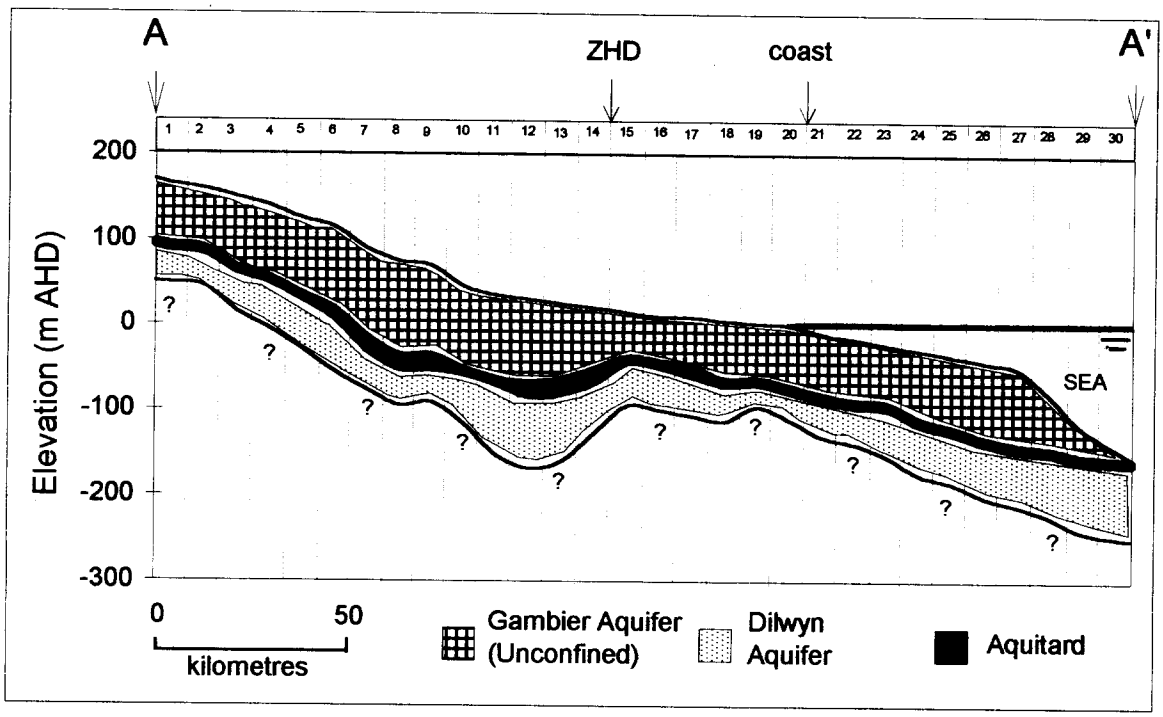

Fig.3.8 Hydrogeological cross-section along transect A-A', Otway Basin. The transect was divided into 30 cells of length and width 8660 m for both the MODFLOW and CMC model applications.

Using the combined hydraulic/environmental tracer approach in the Otway Basin has resulted in quite different estimates of hydraulic conductivity being used in the initial and final MODFLOW calibrations, particularly for vertical conductivity between the aquifers (Fig.3.10). The rates of groundwater flow and inter-aquifer mixing obtained from the final model are therefore more realistic than those calculated from the initial model. For example, leakage from the Gambier unconfined aquifer into the Dilwyn confined aquifer was determined to be less than 1 mm/a along transect A-A' using the initial model, whereas a range in leakage rates of between 2 and 9 mm/a was obtained from the final model. The latter estimates of leakage rates compare well with previous estimates of around 1 mm/a for sites near the ZHD where the head difference, and hence potential for leakage, between the aquifers would be lower (Love et al. 1996).

One of the greatest difficulties encountered when the CMC model was applied in transient mode for 27 000 years was the lack of information about tracer input functions. ^{14}C was considered to be the most robust tracer for regional-scale field applications because variations in the ^{14}C concentration of the atmosphere were probably more global than most other environmental tracers.

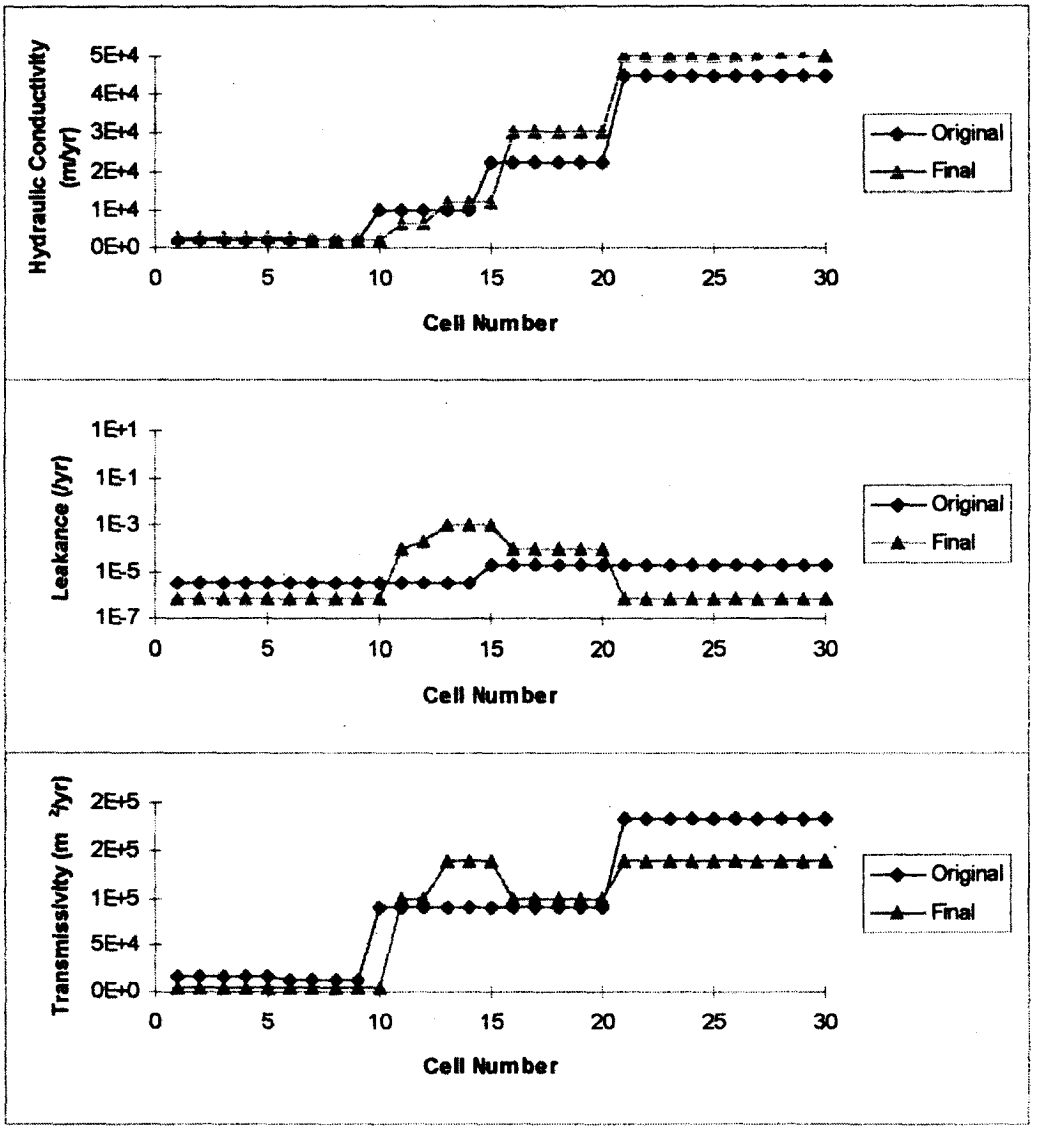

Fig.3.9 Original and final input parameters used to model the observed aquifer head distributions in the Otway Basin. Hydraulic conductivity values relate to the Gambier unconfined aquifer; Leakance (Kv/thickness) values relate to the regional confining aquitard; and transmissivity values relate to the Dilwyn confined aquifer.

3.4 MIXING-CELL MODEL FOR THE SIMULATION OF ENVIRONMENTAL ISOTOPE TRANSPORT

3.4.1 INTRODUCTION

The mixing-cell method is the simplest solution to the advective transport equation. The method is based on the discretisation of the flow domain into a finite number of cells

(compartments) (Fig.3.11) in which perfect mixing for the tracer takes place over discrete time

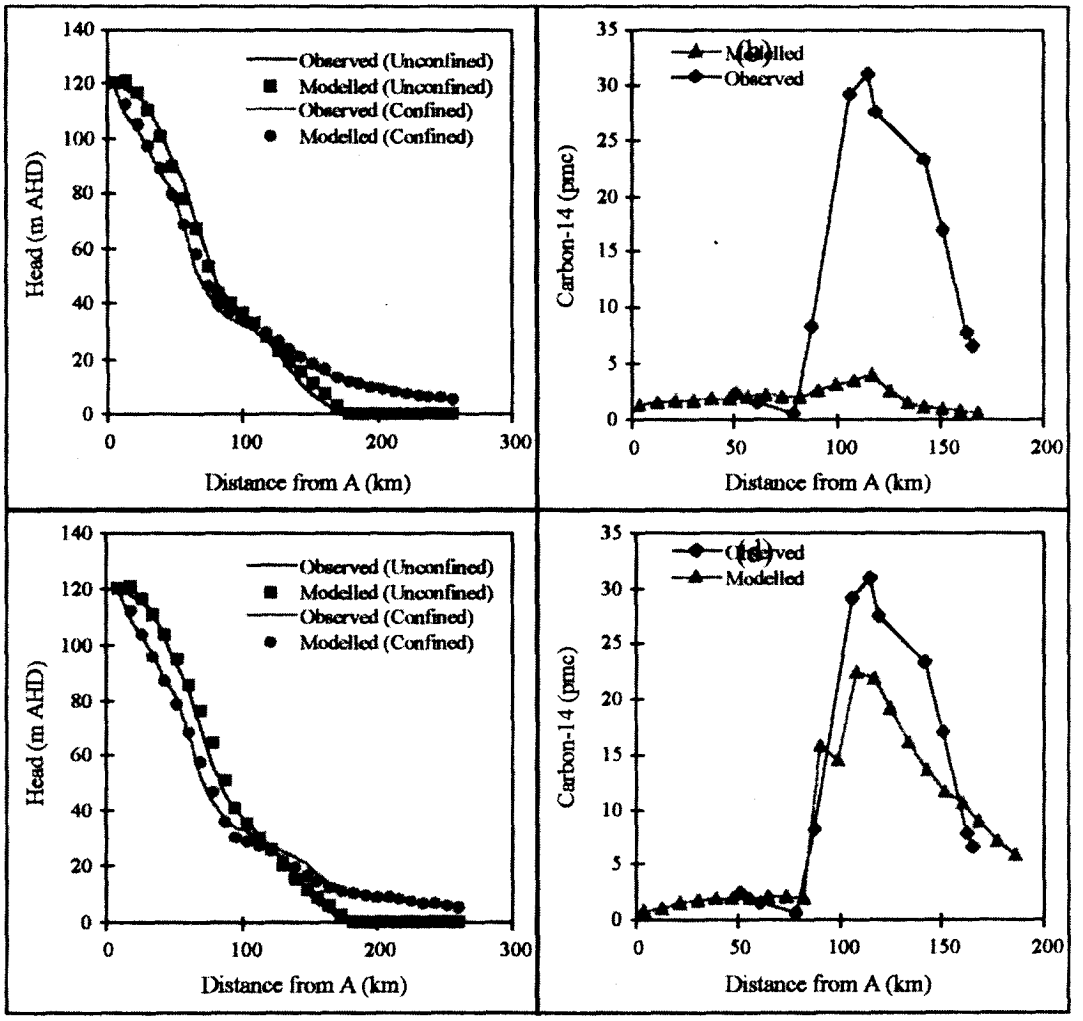

Fig.3.10 (a, b) Modelled and observed aquifer heads and radiocarbon distribution in the Dilwyn confined aquifer obtained using the initial MODFLOW model. (c, d) Modelled and observed aquifer heads and radiocarbon distribution in the Dilwyn confined aquifer obtained using the final MODFLOW model.

intervals. Under complete mixing conditions in each cell, the recursive state equations for each tracer for a Δt time interval can be represented by:

$$\text{Tracer Mass}(t) = \text{Tracer Mass}(t-\Delta t) + \text{Incoming Mass Flux}(t) - \text{Outgoing Mass Flux}(t)$$

The equation above represent the mass of the tracer at each time step as a function of the incoming and outgoing mass flux. The method has been used widely for the simulation of isotopic and chemically-reactive transport (Campana and Mahin 1985; Yurtsever and Payne 1978; Van Ommen 1985; Simpson and Duckstein 1976).

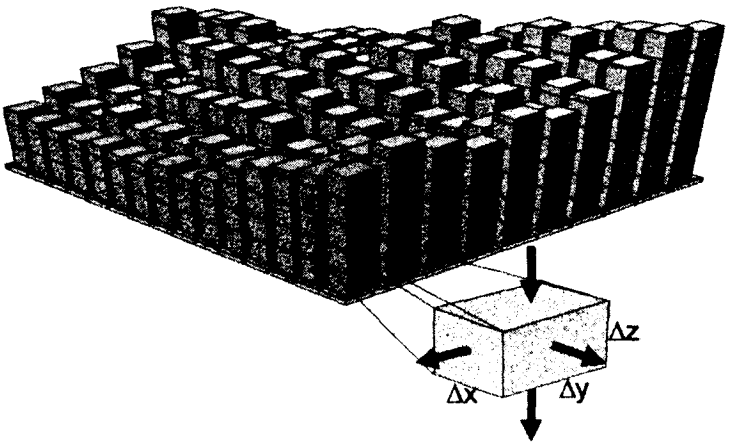

Fig.3.11 Representation of the hydrogeologic system by interconnected volumetric cells.

$$n\frac{\partial C}{\partial t} = -\left(\frac{\partial(q_x C_x)}{\partial x} + \frac{\partial(q_y C_y)}{\partial y} + \frac{\partial(q_z C_z)}{\partial z}\right) \tag{3.14}$$

The partial differential equation describing the advective transport (neglecting dispersion, diffusion, adsorption, reaction and decay) can be expressed as:
in which C is solute concentration (M/L^3), t is time (T), n is effective porosity, and q is the specific discharge in the direction of increasing x,y,z (L/T). The source and sink can also be included in the above equation. The solution of this three-dimensional (3-D) partial differential equation can be achieved by numerous numerical models based on either Eulerian or Lagrangian methods. In the Eulerian approach the transport equation is solved with a fixed grid such as in finite-difference (FD) or finite-element (FE) methods. In order to avoid numerical dispersion and oscillations, restrictively small grid size and time steps are required. In the Lagrangian method the equation is solved in either a deforming grid or deforming co-ordinate in a fixed grid through particle tracking. This method is free of numerical dispersion.

In a continuous flow domain, the mixing-cell algorithm is either an explicit or implicit backward finite-difference approximation of the advective term in the solute transport equation (Bajracharya and Bary 1994). The 1-D advective solute transport equation can be expressed as:

$$\frac{\partial C}{\partial t} = -\frac{q_x}{n}\frac{\partial C}{\partial x} \tag{3.15}$$

where C=C(x,t) is the concentration and (qx/n) is the average groundwater velocity. The advective term of this equation can be approximated by the following finite-difference scheme:

$$C_i^{t+\Delta t} = C_i^t + \frac{q_x \Delta t}{n\Delta x}\left(C_{i-1}^t - C_i^t\right) \tag{3.16}$$

where ($qx\Delta t/n\Delta x$) is the Courant number and should be less than 1 to affirm the finite-difference solution is stable. This scheme provides the same solution as the analytic solution of the advective solute transport equation (Van Ommen 1995).

Eq.3.14 at any cell, say (i,j,k) can be approximated by the concentration values at the neighbouring cell faces as:

$$n\frac{C_{i,j,k}^{t+\Delta t}-C_{i,j,k}^{t}}{\Delta t}=-\frac{q_{i,j+1/2,k}C_{i,j+1/2,k}-q_{i,j-1/2,k}C_{i,j-1/2,k}}{\Delta x_j}-\frac{q_{i+1/2,j,k}C_{i+1/2,j,k}-q_{i-1/2,j,k}C_{i-1/2,j,k}}{\Delta y_i}-\frac{q_{i,j,k+1/2}C_{i,j,k+1/2}-q_{i,j,k-1/2}C_{i,j,k-1/2}}{\Delta z_k} \quad (3.17)$$

where Δx_j, Δy_i, Δz_k are cell dimensions, and j+1/2, i+1/2, and k+1/2 denote the cell interfaces normal to the x, y, z directions (Fig.3.12). The cell interface concentration between two neighbouring nodes in a particular direction is set equal to the concentration at the upstream node along the same direction (Bear 1979; Zheng and Bennett 1995). This approach is called the upstream weighting scheme and provides oscillation free solutions:

$$C_{i,j-1/2,k}=\begin{cases}C_{i,j-1,k} & \text{if } q_{i,j-1/2,k}>0\\ C_{i,j,k} & \text{if } q_{i,j-1/2,k}<0\end{cases} \quad (3.18)$$

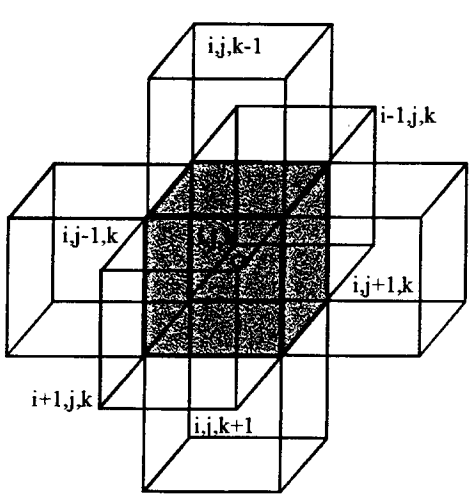

Fig.3.12 Cell (i,j,k) and indices for the adjacent cells

Eq.3.17 represents the 3-D recursive state equation for each cell in the flow domain considering the tracer mass in the cell and incoming and outgoing mass fluxes. Since the

mixing cell algorithm is the either an explicit or implicit backward FD approximation of the advective term in the solute transport equation, Eq.3.17 can be considered as an explicit form if the concentration terms at the right side of the equation represent the beginning of the time step (t) or as an implicit form if they represent the end of the time step (t+Δt). The explicit form of the equation can be solved directly for C(t+Δt)i,j,k. The implicit form requires the simultaneous solutions of the equation for all nodes by using a matrix solver.

The solution of Eq.3.17 requires the incoming and outgoing specific discharge rates between the cell i,j,k and the neighbouring cells. In the early applications of the mixing-cell method to isotopic transport, the flow was assumed as steady, so that incoming and outgoing flow rates were equal and there was no change in the volume of the water in the cell (Simpson and Duckstein 1976). For unsteady flow regimes, numerical groundwater flow models such as MODFLOW (McDonald and Harbauch 1988) can calculate the cell-by-cell flow rates.

Groundwater flow models generally require the continuous representation of the flow domain in terms of hydraulic parameters (K,T,S). In some cases, it is difficult to obtain all the parameters required by the numerical groundwater models. Additionally, in a karst aquifer system, such models cannot be used because of the discontinuities in the flow domain. In such cases the flow terms can be calculated by the flow routing technique based on linear reservoir theory (Tezcan, in press).

The flow routing technique uses the reservoir water balance equation. Each model cell represents linear or non-linear reservoirs in which the relationship between the storage (S) and outflow (Q) is given by:

$$S = KQ^n \tag{3.19}$$

where K and n represent the constants for the physical process. The water balance or the mass conservation within a time interval Δt for each cell can be expressed as:

Total Inflow - Total Outflow = Change in Storage

or:
$$R(t) - Q(t) = \frac{dS}{dt} \tag{3.20}$$

This relation can be rearranged for an input (R) to the linear reservoir (n=1) by continuity:

$$K + \frac{dQ}{dt} = R \tag{3.21}$$

The flow between the cells is then expressed by the following equation:

$$Q_t = e^{\frac{-\Delta T}{K}} Q_{t-\Delta t} + \left[1 - \frac{K}{\Delta T}\left(1 - e^{\frac{-\Delta T}{K}}\right)\right] R_t + \left[\frac{K}{\Delta T}\left(1 - e^{\frac{-\Delta T}{K}}\right) - e^{\frac{-\Delta T}{K}}\right] R_{t-\Delta t} \tag{3.22}$$

Eq.3.22 is the discrete form of the flow routing equation representing the outflow (Q_t) of the reservoir at time t as a function of the previous outflow (Q_{t-Dt}), the present (R_t), and the

previous (R_{t-Dt}) recharge rates (Fig.3.13). The parameter K is the storage constant that has the dimension of time. Under the no recharge condition, the equation becomes the well-known Maillet equation of the hydrograph recession curves.

3.4.2 MIXING-CELL MODEL OF FLOW AND TRANSPORT DYNAMİCS İN KARST AQUİFER SYSTEMS

We develop a distributed conceptual model to analyse groundwater flow and transport dynamics in large-scale karst aquifer systems by using the mixing-cell approach and the power of terrain analysis. The model is developed for aquifer systems in which knowledge about the hydraulic and the transport characteristics is limited. The aquifer system is discretised into a finite number of the cells in three dimensions, and the transport process is simulated by the mixing-cell approach whereas the surface and subsurface flow processes are simulated by flow routing. Special characteristics such as the distribution of the recharge, flow and storage properties of the karst terrain are considered in the dynamics of the flow.

Groundwater flow models are generally based on the prediction of the consequences of a proposed action to the flow system. In complex cases, models can be used as an explanatory tool to provide additional information and interpretation on the flow domain, which is especially important in karst terrain where the knowledge about the flow and transport system is limited.

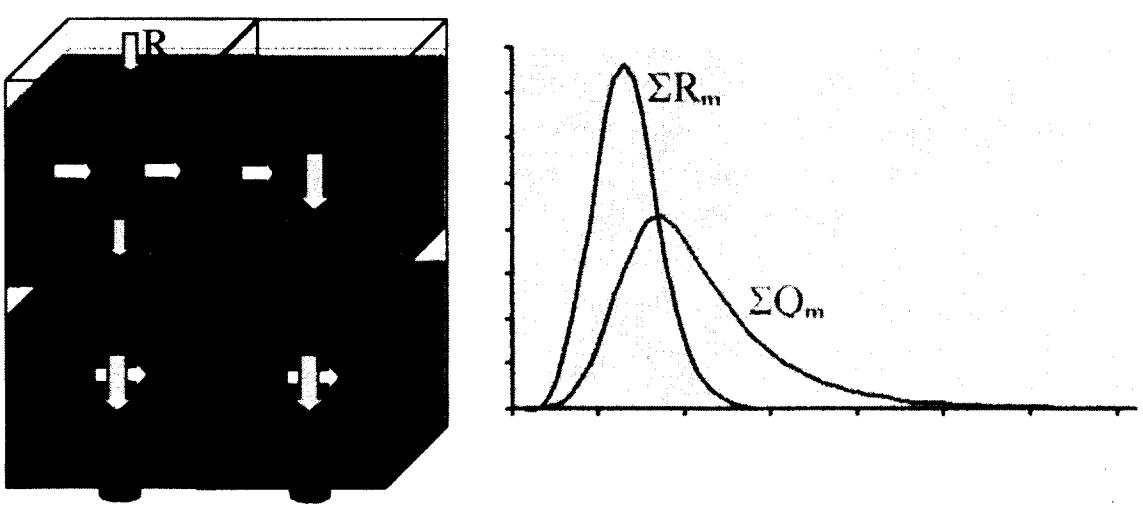

Fig.3.13 The convolution of the recharge to the discharge through interconnected reservoirs.

The complex organisation of the flow domain and the heterogeneous recharge distribution causes difficulties in understanding groundwater flow pattern in the karst aquifers. Groundwater flow models developed for the granular aquifers, based on Darcy's law, are not applicable for karst aquifers, where the groundwater generally moves through the conduits, and the velocity is higher than that through the granular systems. The discontinuity in the flow

domain limits the expression of the flow system by the differential equations based on the continuity and the representative elementary volume approach.

The model developed in this study is a first attempt to identify the karst groundwater flow system by a terrain-based distributed parameter hydrologic model coupled with the mixing-cell approach for environmental isotope transport. This distributed flow and transport model considers the spatial variations of the parameters in three dimensions and is applied to the highly karstified Beydaglari Aquifer system located at the Mediterranean coast of Turkey (Tezcan, in press).

3.4.2.1 PHYSICAL FRAMEWORK OF THE MODEL

The hydrogeologic system is simulated as though it is composed of interconnected reservoir systems. The flow system is discretised into volumetric cells ($\Delta V = \Delta x \cdot \Delta y \cdot \Delta z$) in a 3-D co-ordinate system and all the variables and parameters representing the flow and transport in the cell are defined as 3-D functions of the geographic (topographic) co-ordinate system. An equal grid spacing is used in x-y surface, whereas the thickness of the layers can vary and be assigned by the user for each layer at the beginning of the simulation. Then the number of the layers is calculated for each grid according to the topographic elevation of the grid. An additional layer may be located at the bottom of the system to consider dead storage, submarine discharge, or deep percolation.

Each cell is attributed by a cell type code ("GeoCode") representing the hydrogeologic properties of the cell based on the lithology (Fig.3.14). The cell type code is taken as negative for impervious (non-active) units, zero for constant head cells such as sea, and positive for pervious (active) units. Infiltration or groundwater circulation does not take place over the negative coded cells; instead, overland flow occurs according to the aspect and the slope of the terrain in these cells. The "GeoCode" is a 3-D array and it is read for all the layers as input to the model. The deeper extinction of the lithology that is outcropping can be estimated by using the depth of the cell/layer and the thickness, dip, and strike.

Structural features (faults, folds, and lineaments) are defined by their directions. The directions of these features are limited to eight directions: North, Northeast, East, Southeast, South, Southwest, West, and Northwest. The cells are attributed by the code ("StrCode") for structural features. If the cell is not crossed by any structural feature, the "StrCode" of the cell is assigned to zero. The "StrCode" is attributed with numbers from 1 to 8 (N, NE, E, SE, S, SW, W, NW) representing the direction of the groundwater flow controlled by the structure.

The location of the sinkholes and springs are expressed by similar codes ("SnkCode" and "SprCode"). The cells including a sinkhole/spring are assigned by the value 1, whereas all the remaining are expressed as zero.

The terrain slope represents the slope at any grid node on the surface and is reported in degrees from -90 (vertical downhill) to 90 (vertical uphill).

-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7
-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7
-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	1
-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	1
-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	1	1
-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	1	1	1
-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	1	1	1	1	1
-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	1	1	1	1	1	1	1
1	1	1	-7	-7	-7	-7	1	1	1	1	1	1	1	1	1	1
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
1	1	1	1	1	1	1	1	1	1	1	1	1	1	-7	-7	-7
1	1	1	1	1	1	1	1	1	1	1	1	1	-7	-7	-7	-7
1	1	1	1	1	1	1	1	1	1	1	1	-7	-7	-7	-7	-7
1	1	1	1	1	1	1	1	1	1	1	1	-7	-7	-7	-7	-7
1	1	1	1	1	1	1	1	1	1	1	1	-7	-7	-7	-7	-7
1	1	1	1	1	1	1	1	1	1	1	1	-7	-7	-7	-7	-7

Fig.3.14 The discretisation of the active (+) and non-active (-) cells by "Geocode".

For a particular point on the surface, the terrain slope is based on the direction of steepest descent or ascent at that point so that across the surface, the gradient direction can change.

The aspect of the terrain is the direction of the steepest slope at each grid node. It represents the direction that water would flow over the surface or the angle that is exactly perpendicular to the contour lines on the surface. Terrain aspect values are calculated as azimuth, where 0 degrees points due North, and 90 degrees points due East. In calculation of the overland flow the flow direction is expressed as one of eight major directions: N (337.5° – 22.5°), NE (22.5° – 67.5°), E (67.5° – 112.5°), SE (112.5° – 157.5°), S (157.5° – 202.5°), SW (202.5° – 247.5°), W (247.5° – 292.5°), and NW (292.5° – 337.5°).

3.4.2.2 HYDROLOGIC MODEL

The model is designed to simulate the surface water and groundwater circulation on the karst terrain. The terrain is described by topographic, geologic, and morphologic aspects as outlined above. The hydrologic system is expressed by the recharge, storage, and discharge events. The model considers precipitation and evaporation, infiltration, overland flow, surface storage, percolation, groundwater storage, and flow processes. The water balance is calculated for each cell at every time step by considering the recharge from precipitation, infiltration, percolation, evapotranspiration, overland flow, surface storage, and groundwater flow. The time step in the model is selected as one day, but selection of more frequent time steps is also possible. The general structure of the flow model is indicated in Fig.3.15.

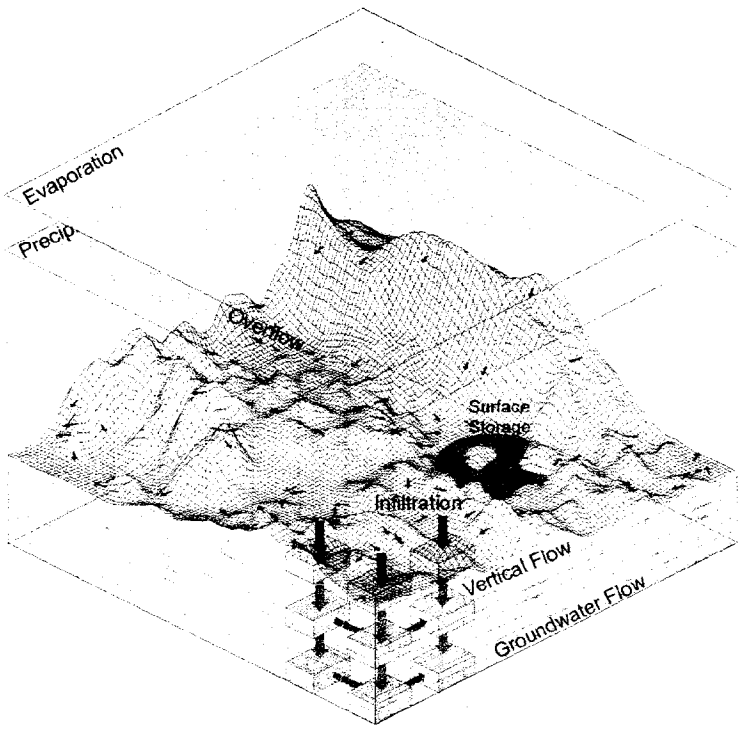

Fig.3.15 The structure of the model of karst groundwater flow and transport processes.

The precipitation observed in the meteorological observation stations is considered the recharge source of the model area. The stations are defined by their topographic co-ordinates in the model. The model checks the records of the precipitation stations at all time steps during the simulation to determine whether point rainfall events are recorded for these particular time steps. For every time step, if precipitation happens in one or more stations in the model area, the values are interpolated for each cell. Potential evapotranspiration is also given to the model for the observation sites and then extrapolated over the model area. The net recharge is calculated as precipitation surplus over evapotranspiration. In case of greater evapotranspiration than the precipitation amount, the deficiency is supplied from the surface storage (if any).

Infiltration takes place over the pervious geologic units as defined by positive "Geocode" values. The sources of infiltration are the precipitation surplus, the amount of water flowing from upstream cells as overland flow, and the surface storage of the previous time step in the cell. Infiltration is simulated in the model as either a concentrated or diffuse process. If the cell consists of sinkholes, all the recharge water will infiltrate to the top layer in that particular time interval as point/concentrated recharge, and the surface storage will be zero. In absence of the sinkholes, Hortonian infiltration will take place for the diffuse recharge.

Overland flow may occur in both negative and positive geocoded cells where surface storage is available. The negative "Geocode" means that the geologic unit does not allow the water to infiltrate, so all the water will flow over the surface. In positive geocoded cells, overland flow occurs if there is water remaining after the infiltration event in that particular time step. The

water at the surface may be the excess of the infiltration, but it may be the amount coming from upstream cells. The direction of the overland flow is due to the aspect value of the cell. The water may flow to the one of the eight neighbouring cells in the direction of the aspect of the cell. The overland flow for per unit width of the cell is calculated by the routing equation given above.

The volume of the water in a particular time step remaining after all the hydrologic events is called the surface storage, and is calculated by the balance equation at each time step:

$$Sstor = Sstor(t-\Delta t) + P(t) + OFlowUp(t) - Et(t) - I(t) - OFlowDown(t)$$

Overland flow coming from upstream cells (OFlowUp(t)) , precipitation (P(t)) and the surface storage of the previous time step (Sstor(t-Δt)) are the gains of the balance equation, whereas evapotranspiration (Et(t)), infiltration (I(t)), and overland flow to downstream cells (OFlowDown(t)) are the losses at the surface of the terrain.

The cell-by-cell flow process is simulated by Eq.3.22. The flow between the cells as a function of time is controlled by the storage constant (K), which represents the turnover time for the reservoir. Each cell can be recharged from or discharge to the neighbouring six cells. The partitioning of the flow between the neighbouring cells is estimated by the volumetric gradient between the cells. The model calculates the current volumes of neighbouring cells and compares them to the current cell's volume. If the neighbouring volumes are lower than the volume of the cell of interest, the flow partition to the cell is estimated by the percentage of the total gradient with the neighbouring cells. The flow does not occur to the neighbouring cell whose volume is higher than the cell of interest. If the volume of the any neighbouring cell is at its maximum value, flow will not take place to that cell.

The porosity of the cell is an important factor to define the karst circulation path. If a cave, conduit, or similar secondary porosity feature exists in the cell, the porosity may be as high as 100%. Any known value for the secondary porosity value may increase the representativeness of the model.

The model allows downward movement of groundwater from the lowest cell to outside of the model region, but does not allow an upward recovery. The release of the water from the model region to the outside may be interpreted as the deeper circulation, or dead storage for the modelled region. To simulate the interrelations with the neighbouring aquifers, the outer cells accept recharge as specified flux through the horizontal model boundaries.

The flow model outputs the discharge hydrographs of the cells representing the springs of interest. The calibration parameters are the storage constant (K) and the infiltration constant.

3.4.2.3 TRANSPORT MODEL

Karst groundwater flow is simulated by a flow routing technique whereas the transport process is simulated by the mixing-cell approach. The model is designed to simulate the

spatial and temporal distribution of the up to five conservative (non-reactive) tracers (isotopes, chlorofluorocarbons, electrical conductivity, chloride, etc.) in the groundwater. The model simulates only advective transport and does not consider dispersion and diffusion processes. The transport process is simulated by considering Eq.3.17 in explicit form:

$$C_{i,j,k}^{t+\Delta t} = C_{i,j,k}^{t} + \frac{\Delta t}{n}\left[\begin{array}{l} -\dfrac{q_{i,j+1/2,k}^{t+\Delta t} C_{i,j+1/2,k}^{t} - q_{i,j-1/2,k}^{t+\Delta t} C_{i,j-1/2,k}^{t}}{\Delta x_j} \\ -\dfrac{q_{i+1/2,j,k}^{t+\Delta t} C_{i+1/2,j,k}^{t} - q_{i-1/2,j,k}^{t+\Delta t} C_{i-1/2,j,k}^{t}}{\Delta y_i} \\ -\dfrac{q_{i,j,k+1/2}^{t+\Delta t} C_{i,j,k+1/2}^{t} - q_{i,j,k-1/2}^{t+\Delta t} C_{i,j,k-1/2}^{t}}{\Delta z_k} \end{array}\right] \qquad \textbf{(3.23)}$$

The explicit form of the equation can be solved directly for $C(t+\Delta t)_{i,j,k}$. The concentration value is calculated for every cell at each time step and the model outputs the concentration-time relation for specified cells.

The explicit scheme of the advective transport equation (Eq.3.23) is subject to numerical dispersion introduced by the truncation error of the partial differential transport equation (Eq.3.14). In order to minimise numerical dispersion a fine grid and smaller time steps are required. The transport time steps should be:

$$\Delta t \leq \frac{1}{\dfrac{q_x}{\Delta x} + \dfrac{q_y}{\Delta y} + \dfrac{q_x}{\Delta z}} \qquad \textbf{(3.24)}$$

The grid spacing and the model time interval are determined at the beginning of the simulation by the user and the specific discharge components calculated by these specified intervals. The transport time steps are then estimated by the model according to Eq.3.24 at each model time step. Depending upon the grid size and the groundwater velocity, the number of the transport time steps may increase enormously.

3.4.3 CONCLUSIONS

The mixing-cell approach together with the flow routing technique is used for the simulating the groundwater flow and transport dynamics in large-scale karst aquifer systems. The model is developed as compatible with the data processing structure of the GIS approach. The cell configuration, geologic and hydrogeologic system and the recharge and discharge events are all defined in space co-ordinates. This will help in further associations of the model to a GIS system.

Discrete-state compartmental models such as proposed by (Campana and Mahin 1985; Yurtsever and Payne 1978; Van Ommen 1985; Simpson and Duckstein 1976) are the initial works of distributed parameter modelling of environmental isotope data. These studies have

provided turnover time and dynamic volume of the compartments representing part of the groundwater system by calibrating the isotopic contents and additionally, the flow rate at the single outlet of the system. The model proposed in this study differs from these earlier works in that it produces output of the isotopic contents and flow rates for all the cells in the system and allows the estimation of the calibration variables at multiple outlet points (springs, wells, etc.). The structure of the model is similar to the finite-difference flow models such as MODFLOW (McDonald and Harbauch 1988) in terms of the grid design and the discrete structure of the flow and transport equations. As in the deterministic groundwater flow and transport models, the model imposes large requirements for data to define all the parameters at all nodes of the grid, and it is inherently impossible to obtain a unique solution and the parameters and the variables obtained by the model are not the real and unique values representing the physical system. They are approximate values based on limited knowledge about the system. Due to the size and the complexity of the aquifer system, knowledge of the spatial and temporal distribution of the input data (recharge, concentration) may not be satisfactory. Therefore, the model calibration does not necessarily produce an exact match of the observed data. Instead, a good representation of the observed discharge and concentration distributions should be achieved at all the observation points. The calibration may also be constrained by using several transport variables (isotopes, CFCs, hydrochemical variables, etc.) and by considering several outlets of the system.

The model program and sample data set can be requested by contacting the author at tezcan@hacettepe.edu.tr.

3.5 SUMMARY AND CONCLUSIONS

The three models described above illustrate the utility of and level of sophistication in compartmental or mixing-cell models. In this section we will summarise the results and speculate on the future of the compartmental model approach.

Campana's compartmental model is the simplest to use, but it is not as well-constrained as the other models. It can be used as a "stand-alone" model or coupled to a flow model. How successful it is relies heavily upon the skill of the modeller and his/her familiarity with the area being modelled. The model is appropriate to apply in an area with few data, perhaps to guide future data-collection and model-building efforts. Certainly, the model is improved and afforded a stronger physical basis by using a linear-reservoir routing algorithm to calculate intercellular discharges; use of a Darcy-type equation could also be used. Adar and colleagues have used such an approach as well as linear and non-linear programming to further constrain compartmental models. Campana's model has the advantage in that it can calculate age and residence time distributions, although the calculation of these must be extended to transient flow.

Harrington's approach shows one of the potential strengths of the compartmental model - environmental isotope approach: its utility in constraining a physically-based groundwater flow model. However, when conducting transient simulations covering thousands of years, the modeller may have difficulty estimating the ^{14}C inputs over that length of time. This adds additional uncertainty to the results. The use of other environmental isotopes will present similar problems. The next steps for Harrington's approach are a three-dimensional simulation and the use of other environmental isotopes (perhaps multiple ones).

Tezcan's model is a highly-integrated, powerful model in that it combines the mixing-cell approach for transport, linear reservoir theory for flow, surficial processes (infiltration, runoff, etc.), and terrain analysis, all in a GIS-type framework. Tezcan's model is particularly well-suited to karst and fractured-rock aquifers, where Darcy's Law may not apply and traditional REV-based approaches are questionable. A full-scale GIS approach is the next step for this approach.

Future research efforts should involve the following:

1) continued investigation of the linear and non-linear reservoir approach for the treatment of transient effects
2) more rigorous constraint of the Campana model parameter estimates
3) development of transient analogues to the steady-state residence-time distributions
4) further application of the Harrington approach, including its extension to three dimensions and application of multi-isotopic tracers
5) investigation of the compartmental model's utility in palaeoclimatic and palaeohydrologic investigations
6) use of compartmental models as contaminant transport models
7) coupling of geochemical models to compartmental models
8) availability of user-friendly software.

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4 USE OF NUMERICAL MODELS TO SIMULATE GROUNDWATER FLOW AND TRANSPORT

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4.1 INTRODUCTION

In the past, the main driving force for hydrogeologic studies has been the need to assess the water-supply potential of aquifers. During the past 20 years, however, the emphasis has shifted from water-supply problems to water-quality problems. This has driven a need to predict the movement of contaminants through the subsurface environment. One consequence of the change in emphasis has been a shift in perceived priorities for scientific research and data collection. Formerly, the focus was on developing methods to assess and measure the water-yielding properties of high-permeability aquifers. The focus is now largely on transport and dispersion processes, retardation and degradation of chemical contaminants, the effects of heterogeneity on flow paths and travel times, and the ability of low-permeability materials to contain contaminated groundwater.

The past 20 years or so have also seen some major technological breakthroughs in groundwater hydrology. One technological growth area has been in the development and use of deterministic, distributed-parameter, computer simulation models for analysing flow and solute transport in groundwater systems. These developments have somewhat paralleled the development and widespread availability of faster, larger memory, more capable, yet less expensive computer systems. Another major technological growth area has been in the application of isotopic analyses to groundwater hydrology, wherein isotopic measurements are being used to help interpret and define groundwater flow paths, ages, recharge areas, leakage, and interactions with surface water (Coplen 1993).

Because isotopes move through groundwater systems under the same driving forces and by the same processes as do dissolved chemicals, it is natural that the groundwater flow and solute-transport models applied to groundwater contamination problems be linked to and integrated with isotopic measurements and interpretations. Many previous applications of isotopic

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[1] Chapter largely based on Konikow (1996) and Konikow and Reilly (1998); Y.Yurtsever and T.E.Reilly are gratefully acknowledged for contributions and support.

analyses to groundwater systems, however, have assumed overly simplified conceptual models for groundwater flow and transport of dissolved chemicals--either plug flow (with piston-like displacement and no mixing) or a well-mixed reservoir (which unrealistically overestimates the mixing effects of dispersion and diffusion). If the interpretations of isotopic analyses are coupled with more realistic conceptual models of flow and transport, then it is anticipated that the synergistic analysis will lead to a more accurate understanding of the hydrogeologic system being studied. Dinçer and Davis (1984) provide a review of the application of environmental isotope tracers to modelling in hydrology, and Johnson and DePaolo (1994) provide an example of applying such a coupled approach in their analysis of a proposed high-level radioactive waste repository site (Dinçer and Davis 1984; Johnson and Depaolo 1994).

The purpose of this chapter is to review the state of the art in deterministic modelling of groundwater flow and transport processes for those who might want to merge the interpretation of isotopic analyses with quantitative groundwater model analysis. This chapter is aimed at practitioners and is intended to help define the types of models that are available and how they may be applied to complex field problems. It will discuss the philosophy and theoretical basis of deterministic modelling, the advantages and limitations of models, the use and misuse of models, how to select a model, and how to calibrate a model. However, as this chapter is only a review, it cannot offer comprehensive and in-depth coverage of this very complex topic; but it does guide the reader to references that provide more details. Other recent comprehensive reviews of the theory and practice of deterministic modelling of groundwater processes are provided by Anderson and Woessner (1992) and Bear and Verruijt (1987) (Anderson and Woessner 1992; Bear and Verruyt 1987).

4.2 MODELS

The word model has so many definitions and is so overused that it is sometimes difficult to discern the meaning of the word (Konikow and Bredehoeft 1992). A model is perhaps most simply defined as a representation of a real system or process. A conceptual model is a hypothesis for how a system or process operates. This hypothesis can be expressed quantitatively as a mathematical model. Mathematical models are abstractions that represent processes as equations, physical properties as constants or coefficients in the equations, and measures of state or potential in the system as variables.

Most groundwater models in use today are deterministic mathematical models. Deterministic models are based on conservation of mass, momentum, and energy and describe cause and effect relations. The underlying assumption is that given a high degree of understanding of the processes by which stresses on a system produce subsequent responses in that system, the system's response to any set of stresses can be predetermined, even if the magnitude of the new stresses falls outside of the range of historically observed stresses.

Deterministic groundwater models generally require the solution of partial differential equations. Exact solutions can often be obtained analytically, but analytical models require that

the parameters and boundaries be highly idealised. Some deterministic models treat the properties of porous media as lumped parameters (essentially, as a black box), but this precludes the representation of heterogeneous hydraulic properties in the model. Heterogeneity, or variability in aquifer properties, is characteristic of all geologic systems and is now recognised as playing a key role in influencing groundwater flow and solute transport. Thus, it is often preferable to apply distributed-parameter models, which allow the representation of more realistic distributions of system properties. Numerical methods yield approximate solutions to the governing equation (or equations) through the discretisation of space and time. Within the discretised problem domain, the variable internal properties, boundaries, and stresses of the system are approximated. Deterministic, distributed-parameter, numerical models can relax the rigid idealised conditions of analytical models or lumped-parameter models, and they can therefore be more realistic and flexible for simulating field conditions (if applied properly).

The number and types of equations to be solved are determined by the concepts of the dominant governing processes. The coefficients of the equations are the parameters that are measures of the properties, boundaries, and stresses of the system; the dependent variables of the equations are the measures of the state of the system and are mathematically determined by the solution of the equations. When a numerical algorithm is implemented in a computer code to solve one or more partial differential equations, the resulting computer code can be considered a generic model. When the grid dimensions, boundary conditions, and other parameters (such as hydraulic conductivity and storativity), are specified in an application of a generic model to represent a particular geographical area, the resulting computer program is a site-specific model. The ability of generic models to solve the governing equations accurately is typically demonstrated by example applications to simplified problems. This does not guarantee a similar level of accuracy when the model is applied to a complex field problem.

If the user of a model is unaware of or ignores the details of the numerical method, including the derivative approximations, the scale of discretisation, and the matrix solution techniques, significant errors can be introduced and remain undetected. For example, if the groundwater flow equation is solved iteratively, but the convergence criterion is relatively too coarse, then the numerical solution may converge, but to a poor solution. The inaccuracy of the solution may or may not be reflected in the mass-balance error. Unrecognized errors in numerical groundwater models are becoming more possible as "user-friendly" graphical interfaces make it easier for models to be used (and to be misused). These interfaces effectively place more "distance" between the modeller and the numerical method that lies at the core of the model.

4.3 FLOW AND TRANSPORT PROCESSES

The process of groundwater flow is generally assumed to be governed by the relations expressed in Darcy's law and the conservation of mass. Darcy's law does have limits on its range of applicability, however, and these limits must be evaluated in any application.

The purpose of a model that simulates solute transport in groundwater is to compute the concentration of a dissolved chemical species in an aquifer at any specified time and place. The theoretical basis for the equation describing solute transport has been well documented in the literature (Bear 1997; Domenico and Schwartz 1998). Reilly et al. (1987) provide a conceptual framework for analysing and modelling physical solute-transport processes in groundwater (Reilly et al. 1987). Changes in chemical concentration occur within a dynamic groundwater system primarily due to four distinct processes:

1) advective transport, in which dissolved chemicals are moving with the flowing groundwater;
2) hydrodynamic dispersion, in which molecular and ionic diffusion and small-scale variations in the flow velocity through the porous media cause the paths of dissolved molecules and ions to diverge or spread from the average direction of groundwater flow
3) fluid sources, where water of one composition is introduced into and mixed with water of a different composition
4) reactions, in which some amount of a particular dissolved chemical species may be added to or removed from the groundwater as a result of chemical, biological, and physical reactions in the water or between the water and the solid aquifer materials or other separate liquid phases.

The subsurface environment constitutes a complex, three-dimensional, heterogeneous hydrogeologic setting. This variability strongly influences groundwater flow and transport, and such a reality can be described accurately only through careful hydrogeologic practice in the field. Regardless of how much data are collected, however, uncertainty always remains about the properties and boundaries of the groundwater system of interest. Stochastic approaches have resulted in many significant advances in characterising subsurface heterogeneity and dealing with uncertainty (Gelhar 1993).

4.4 GOVERNING EQUATIONS

The development of mathematical equations that describe the groundwater flow and transport processes may be developed from the fundamental principle of conservation of mass of fluid or of solute. Given a representative volume of porous medium, a general equation for conservation of mass for the volume may be expressed as:

(rate of mass inflow) – (rate of mass outflow) +

+ (rate of mass production/consumption) = (rate of mass accumulation) **(4.1)**

This statement of conservation of mass (or continuity equation) may be combined with a mathematical expression of the relevant process to obtain a differential equation describing flow or transport (Bear 1997; Domenico and Schwartz 1998; Freeze and Cherry 1979).

4.4.1 GROUNDWATER FLOW EQUATION

The rate of flow of water through a porous media is related to the properties of the water, the properties of the porous media, and the gradient of the hydraulic head, as represented by Darcy's law, which can be written as:

$$q_i = -K_{ij} \frac{\partial h}{\partial x_j} \tag{4.2}$$

where q_i is the specific discharge, LT^{-1}; K_{ij} is the hydraulic conductivity of the porous medium (a second-order tensor), LT^{-1}; and h is the hydraulic head, L.

A general form of the equation describing the transient flow of a compressible fluid in a non-homogeneous anisotropic aquifer may be derived by combining Darcy's law with the continuity equation. A general groundwater flow equation may be written in Cartesian tensor notation as:

$$\frac{\partial}{\partial x_i}\left(K_{ij} \frac{\partial h}{\partial x_i}\right) = S_S \frac{\partial h}{\partial t} + W^* \tag{4.3}$$

where S_S is the specific storage, L^{-1}; t is time, T; W* is the volumetric flux per unit volume (positive for outflow and negative for inflow), T^{-1}; and x_i are the Cartesian co-ordinates, L. The summation convention of Cartesian tensor analysis is implied in Eqs.4.2 and 4.3. Eq.4.3 can generally be applied if isothermal conditions prevail, the porous medium only deforms vertically, the volume of individual grains remains constant during deformation, Darcy's law applies (and gradients of hydraulic head are the only driving force), and fluid properties (density and viscosity) are homogeneous and constant. Aquifer properties can vary spatially, and fluid stresses (W*) can vary in space and time.

If the aquifer is relatively thin compared to its lateral extent, it may be appropriate to assume that groundwater flow is areally two-dimensional. This allows the three-dimensional flow equation to be reduced to the case of two-dimensional areal flow, for which several additional simplifications are possible. The advantages of reducing the dimensionality of the equation include less stringent data requirements, smaller computer memory requirements, and shorter computer execution times to achieve numerical solutions.

An expression similar to Eq.4.3 may be derived for the two-dimensional areal flow of a homogeneous fluid in a confined aquifer and written as:

$$\frac{\partial}{\partial x_i}\left(T_{ij} \frac{\partial h}{\partial x_i}\right) = S\frac{\partial h}{\partial t} + W \tag{4.4}$$

where T_{ij} is the transmissivity,L^2T^{-1}; and $T_{ij} = K_{ij}\, b$; b is the saturated thickness of the aquifer, L; S is the storage coefficient (dimensionless); and $W = W^*b$ is the volume flux per unit area, LT^{-1}.

When Eq.4.4 is applied to an unconfined (water-table) aquifer system, it must be assumed that flow is horizontal and equipotential lines are vertical, that the horizontal hydraulic gradient equals the slope of the water table, and that the storage coefficient is equal to the specific yield (S_y) (Anderson and Woessner 1992). Note that in an unconfined system, the saturated thickness changes as the water-table elevation (or head) changes. Thus, the transmissivity also can change over space and time (i.e. $T_{ij} = K_{ij}b$; $b(x,y,t) = h - h_b$, and h_b is the elevation of the bottom of the aquifer).

In some field situations, fluid properties such as density and viscosity may vary significantly in space or time. This may occur where water temperature or dissolved-solids concentration changes significantly. When the water properties are heterogeneous and (or) transient, the relations among water levels, hydraulic heads, fluid pressures, and flow velocities are neither simple nor straightforward. In such cases, the flow equation is written and solved in terms of fluid pressures, fluid densities, and the intrinsic permeability of the porous media (Konikow and Grove 1977).

4.4.2 SEEPAGE VELOCITY

The migration and mixing of chemicals dissolved in groundwater will obviously be affected by the velocity of the flowing groundwater. The specific discharge calculated from Eq.4.2 is sometimes called the Darcy velocity. However, this nomenclature can be misleading because q_i does not actually represent the speed of water movement. Rather, q_i represents a volumetric flux per unit cross-sectional area. Thus, to calculate the actual seepage velocity of groundwater, one must account for the actual cross-sectional area through which flow is occurring, as follows:

$$V_i = \frac{q_i}{\varepsilon} = -\frac{K_{ij}}{\varepsilon}\frac{\partial h}{\partial x_j} \qquad \textbf{(4.5)}$$

where V_i is the seepage velocity (also commonly called average linear velocity or average interstitial velocity), LT^{-1}; and ε is the effective porosity of the porous medium.

4.4.3 SOLUTE-TRANSPORT EQUATION

An equation describing the transport and dispersion of a dissolved chemical in flowing groundwater may be derived from the principle of conservation of mass (Eq.4.1), just as a general flow equation was so derived (Bear 1979; Domenico and Schwartz 1998; Konikow and Grove 1977; Bear 1972; Bredehoeft and Pinder 1973; Reddell and Sunada 1970). The principle of conservation of mass requires that the net mass of solute entering or leaving a specified volume of aquifer during a given time interval must equal the accumulation or loss of mass stored in that volume during the interval. This relationship may then be expressed mathematically by considering all fluxes into and out of a representative elementary volume (REV), as described by Bear (1972, p.19).

A generalised form of the solute-transport equation is presented by Grove (1976), in which terms are incorporated to represent chemical reactions and solute concentration both in the pore fluid and on the solid surface, as:

$$\frac{\partial(\varepsilon C)}{\partial t} = \frac{\partial}{\partial x_i}\left(\varepsilon D_{ij}\frac{\partial C}{\partial x_j}\right) - \frac{\partial}{\partial x_i}(\varepsilon C V_i) - C'W^* + CHEM \qquad \textbf{(4.6)}$$

where CHEM equals :

$-\rho_b \frac{\partial \overline{C}}{\partial t}$ for linear equilibrium controlled sorption or ion-exchange reactions,

$\sum_{k=1}^{s} R_k$ for s chemical rate-controlled reactions, and (or)

$-\lambda(\varepsilon C + \rho_b \overline{C})$ for decay,

and where D_{ij} is the coefficient of hydrodynamic dispersion (a second-order tensor), L^2T^{-1}, C' is the concentration of the solute in the source or sink fluid, $\overline{C}$ is the concentration of the species adsorbed on the solid (mass of solute/mass of solid), ρ_b is the bulk density of the sediment, ML^{-3}, R_k is the rate of production of the solute in reaction k, $ML^{-3}T^{-1}$, and λ is the decay constant (equal to $\ln 2/T_{1/2}$), T^{-1} (Grove 1976).

The first term on the right side of Eq.4.6 represents the change in concentration due to hydrodynamic dispersion. This expression is analogous to Fick's Law describing diffusive flux. This Fickian model assumes that the driving force is the concentration gradient and that the dispersive flux occurs in a direction from higher concentrations towards lower concentrations. However, this assumption is not always consistent with field observations and is the subject of much ongoing research and field study. The second term represents advective transport and describes the movement of solutes at the average seepage velocity of the flowing groundwater. The third term represents the effects of mixing with a source fluid that has a different concentration than the groundwater at the location of the recharge or injection. The fourth term lumps all of the chemical, geochemical, and biological reactions that cause transfer of mass between the liquid and solid phases or conversion of dissolved chemical species from one form to another. The chemical attenuation of inorganic chemicals can occur by sorption/desorption, precipitation/dissolution, or oxidation/reduction; organic chemical can adsorb or degrade by microbiological processes. There has been considerable progress in modelling these reaction processes; however, a comprehensive review of the reaction processes and their representation in transport models is beyond the scope of this chapter.

If reactions are limited to equilibrium-controlled sorption or exchange and first-order irreversible rate (decay) reactions, then the general governing equation (Eq.4.6) can be written as:

$$\frac{\partial C}{\partial t}+\frac{\rho_b}{\varepsilon}\frac{\partial \overline{C}}{\partial t}=\frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial C}{\partial x_j}\right)-\frac{\partial}{\partial x_i}(CV_i)+\frac{C'W^*}{\varepsilon}-\lambda C-\frac{\rho_b}{\varepsilon}\lambda\overline{C} \quad \textbf{(4.7)}$$

The temporal change in sorbed concentration in Eq.4.7 can be represented in terms of the solute concentration using the chain rule of calculus, as follows:

$$\frac{d\overline{C}}{dt}=\frac{d\overline{C}}{dC}\frac{\partial C}{\partial t} \quad \textbf{(4.8)}$$

For equilibrium sorption and exchange reactions $d\overline{C}/dC$, as well as $\overline{C}$, is a function of C alone. Therefore, the equilibrium relation for $\overline{C}$ and $d\overline{C}/dC$ can be substituted into the governing equation to develop a partial differential equation in terms of C only. The resulting single transport equation is solved for solute concentration. Sorbed concentration can then be calculated using the equilibrium relation. The linear-sorption reaction considers that the concentration of solute sorbed to the porous medium is directly proportional to the concentration of the solute in the pore fluid, according to the relation

$$\overline{C}=K_dC \quad \textbf{(4.9)}$$

where K_d is the distribution coefficient, L^3M^{-1}. This reaction is assumed to be instantaneous and reversible. The curve relating sorbed concentration to dissolved concentration is known as an isotherm. If that relation is linear, the slope (derivative) of the isotherm, $d\overline{C}/dC$, is known as the equilibrium distribution coefficient, K_d. Thus, in the case of a linear isotherm,

$$\frac{d\overline{C}}{dt}=\frac{d\overline{C}}{dC}\frac{\partial C}{\partial t}=K_d\frac{\partial C}{\partial t} \quad \textbf{(4.10)}$$

After substituting this relation into Eq.4.7, we can then rewrite Eq.4.7 as:

$$\frac{\partial C}{\partial t}+\frac{\rho_bK_d}{\varepsilon}\frac{\partial C}{\partial t}=\frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial C}{\partial x_j}\right)-\frac{\partial}{\partial x_i}(CV_i)+\frac{C'W^*}{\varepsilon}-\lambda C-\frac{\rho_bK_d}{\varepsilon}\lambda C \quad \textbf{(4.11)}$$

Factoring out the term $(1+\rho_b K_d/\varepsilon)$ and defining a retardation factor, Rf (dimensionless), as:

$$R_f=1+\frac{\rho_bK_d}{\varepsilon} \quad \textbf{(4.12)}$$

and substituting this relation into Eq.4.11, results in:

$$R_f\frac{\partial C}{\partial t}=\frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial C}{\partial x_j}\right)-\frac{\partial}{\partial x_i}(CV_i)+\frac{C'W^*}{\varepsilon}-R_f\lambda C \quad \textbf{(4.13)}$$

Because Rf is constant under these assumptions, the solution to this governing equation is identical to the solution for the governing equation with no sorption effects, except that the velocity, dispersive flux, and source strength are reduced by a factor R_f. The transport process thus appears to be "retarded" because of the instantaneous equilibrium sorption onto the

porous medium.

In the conventional formulation of the solute-transport equation (Eq.4.6), the coefficient of hydrodynamic dispersion is defined as the sum of mechanical dispersion and molecular diffusion (Bear 1997). The mechanical dispersion is a function both of the intrinsic properties of the porous media (such as heterogeneities in hydraulic conductivity and porosity) and of the fluid flow. Molecular diffusion in a porous media will differ from that in free water because of the effects of porosity and tortuosity. These relations are commonly expressed as:

$$D_{ij} = \alpha_{ijmn} \frac{V_m V_n}{|V|} + D_m, \qquad i, j, m, n = 1,2,3 \qquad \textbf{(4.14)}$$

where α_{ijmn} is the dispersivity of the porous medium (a fourth-order tensor), L; V_m and V_n are the components of the flow velocity of the fluid in the m and n directions, respectively, LT^{-1}; D_m is the effective coefficient of molecular diffusion, L^2T^{-1}; and |V| is the magnitude of the velocity vector, LT^{-1}, defined as $|V| = \sqrt{V_x^2 + V_y^2 + V_z^2}$ (Bear 1979; Domunico and Schwartz 1998; Scheidegger 1961). The dispersivity of an isotropic porous medium can be defined by two constants. These are the longitudinal dispersivity of the medium, α_L, and the transverse dispersivity of the medium, α_T . These are related to the longitudinal and transverse dispersion coefficients by $D_L = \alpha_L|V|$ and $D_T = \alpha_T|V|$. Most applications of transport models to groundwater problems that have been documented to date have been based on this conventional formulation.

Although conventional theory holds that α_L is generally an intrinsic property of the aquifer, it is found in practice to be dependent on and proportional to the scale of the measurement. Most reported values of α_L fall in a range from 0.01 to 1.0 times the scale of the measurement, although the ratio of α_L to scale of measurement tends to decrease at larger scales (Anderson 1984; Gelhar et al. 1992). Field-scale dispersion (commonly called macrodispersion) results from large-scale spatial variations in hydraulic properties. Consequently, the use of relatively large values of dispersivity together with uniform hydraulic properties (K_{ij} and ε) is inappropriate for describing transport in geological systems Smith and Schwartz 1980). If a model applied to a system having variable hydraulic conductivity uses mean values and thereby does not explicitly represent the variability, the model calibration will likely yield values for the dispersivity coefficients that are larger than would be measured locally in the field area. Similarly, representing a transient flow field by a mean steady-state flow field, as is commonly done, inherently ignores some of the variability in velocity and must be compensated for by using increased values of dispersivity (primarily transverse dispersivity) (Goode and Konikow 1990). Overall, the more accurately a model can represent or simulate the true velocity distribution in space and time, the less of a problem will be the uncertainty concerning representation of dispersion processes.

A special form of the solute-transport equation can be used for direct simulation of groundwater age (Goode 1996; 1999). This is accomplished by adding a zero-order growth term, which would represent internal production of the solute, $ML^{-3}T^{-1}$. In developing an age transport equation, concentrations are replaced with corresponding ages, which represent a volume-averaged groundwater age in the aquifer; the zero-order growth rate has a unit value; decay and sorption reactions are assumed to be not present; and, in general, the age of incoming water (analogous to C') is specified as zero. This type of analysis allows a direct comparison of groundwater modelling results with environmental tracer information while accounting for effects of dispersion and other transport processes.

4.5 NUMERICAL METHODS TO SOLVE EQUATIONS

The partial differential equations describing groundwater flow and transport can be solved mathematically using either analytical solutions or numerical solutions. The advantages of an analytical solution, when it is possible to apply one, are that it usually provides an exact solution to the governing equation and is often relatively simple and efficient to obtain. Many analytical solutions have been developed for the flow equation; however, most applications are limited to well hydraulics problems involving radial symmetry (Walton 1962; Lohman 1972; Reed 1980). The familiar Theis type curve represents the solution of one such analytical model. Analytical solutions are also available to solve the solute-transport equation (Bear 1979; Javandel et al. 1984; Van Genuchten and Alves 1982; Wexler 1992). In general, obtaining the exact analytical solution to the partial differential equation requires that the properties and boundaries of the flow system be highly and perhaps unrealistically idealised. For most field problems, the mathematical benefits of obtaining an exact analytical solution are probably outweighed by the errors introduced by the simplifying assumptions of the complex field environment that are required to apply the analytical model.

Alternatively, for problems where the simplified analytical models are inadequate, the partial differential equations can be approximated numerically. In so doing, the continuous variables are replaced with discrete variables that are defined at grid blocks (or nodes). Thus, the continuous differential equation, which defines hydraulic head or solute concentration everywhere in the system, is replaced by a finite number of algebraic equations that defines the hydraulic head or concentration at specific points. This system of algebraic equations generally is solved using matrix techniques. This approach constitutes a numerical model.

The equations describing groundwater flow and solute transport are second-order differential equations, which can be classified on the basis of their mathematical properties. There are basically three types of second-order differential equations, which are parabolic, elliptic, and hyperbolic (Peaceman 1977). Such equations can be classified and distinguished based on the nature and magnitude of the coefficients of the equation. This is important because the numerical methods for the solution of each type have should be considered and developed separately for optimal accuracy and efficiency in the solution algorithm.

Two major classes of numerical methods have come to be well accepted for solving the groundwater flow equation. These are the finite-difference methods and the finite-element methods. Each of these two major classes of numerical methods includes a variety of subclasses and implementation alternatives. Comprehensive treatments of the application of these numerical methods to groundwater problems are presented by (Remson et al. 1971; Wang and Anderson 1982). Both of these numerical approaches require that the area of interest be subdivided by a grid into a number of smaller subareas (cells or elements) that are associated with node points (either at the centres of peripheries of the subareas).

Finite-difference methods approximate the first derivatives in the partial differential equations as difference quotients (the differences between values of variables at adjacent nodes, both in space and time, with respect to the interval between those adjacent nodes). There are several advanced text books that focus primarily on finite-difference methods (Peaceman 1977; Remson et al. 1971; Von Rosenberg 1969). Finite-element methods use assumed functions of the dependent variables and parameters to evaluate equivalent integral formulations of the partial differential equations. Huyakorn and Pinder (1983) present a comprehensive analysis and review of the application of finite-element methods to groundwater problems (Huyakorn and Pinder 1983). In both numerical approaches, the discretisation of the space and time dimensions allows the continuous boundary-value problem for the solution of the partial differential equation to be reduced to the simultaneous solution of a set of algebraic equations. These equations can then be solved using either iterative or direct matrix methods.

Each approach has advantages and disadvantages, but there are very few groundwater problems for which either is clearly superior. In general, the finite-difference methods are simpler conceptually and mathematically, and are easier to program for a computer. They are typically keyed to a relatively simple, rectangular grid, which also eases data entry tasks. Finite-element methods generally require the use of more sophisticated mathematics but, for some problems, may be more accurate numerically than standard finite-difference methods. A major advantage of the finite-element methods is the flexibility of the finite-element grid, which allows a close spatial approximation of irregular boundaries of the aquifer and (or) of parameter zones within the aquifer when they are considered. However, the construction and specification of an input data set is much more difficult for an irregular finite-element grid than for a regular rectangular finite-difference grid. Thus, the use of a model preprocessor, which includes a mesh generator and a scheme to efficiently number the nodes and elements of the mesh and to specify the spatial co-ordinates of each node, is valuable to effectively utilise the advantageous features of a finite-element model. Fig.4.1 illustrates a hypothetical aquifer system, which has impermeable boundaries and a well field of interest (Fig.4.1a), which has been discretised using finite-difference (Fig.4.1b) and finite-element (Fig.4.1c) grids. Figs.4.1b and 4.1c illustrate conceptually how their respective grids can be adjusted to use a finer mesh spacing in selected areas of interest. The rectangular finite-difference grid approximates the aquifer boundaries in a step-wise manner, resulting in some nodes or cells outside of the aquifer, whereas sides of the triangular elements of the finite-element grid can closely follow

the outer boundary using a minimal number of overall nodes.

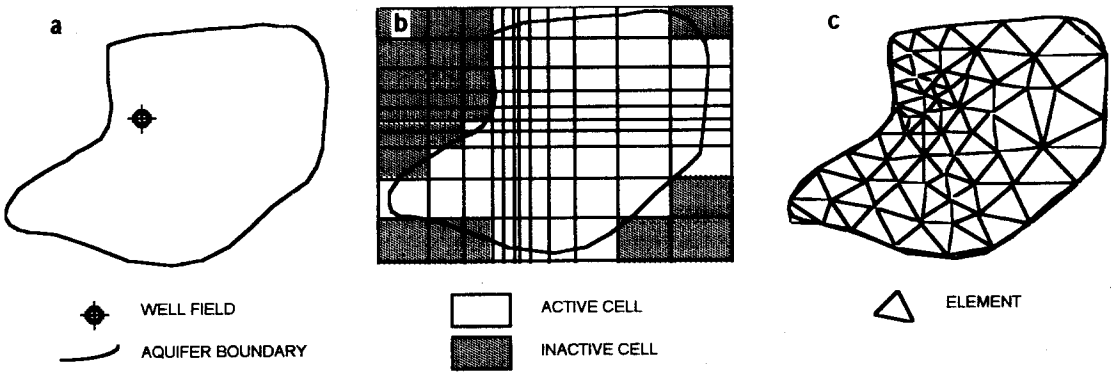

Fig.4.1 Hypothetical application of finite-difference and finite-element grids to an irregularly bounded aquifer (Konikow 1996).

The solute-transport equation is in general more difficult to solve numerically than the groundwater flow equation, largely because the mathematical properties of the transport equation vary depending upon which terms in the equation are dominant in a particular situation. When solute transport is dominated by advective transport, as is common in many field problems, then Eq.4.6 approximates a hyperbolic type of equation (similar to equations describing the propagation of a wave or of a shock front). But if a system is dominated by dispersive fluxes, such as might occur where fluid velocities are relatively low and aquifer dispersivities are relatively high, then Eq.4.6 becomes more parabolic in nature (similar to the transient groundwater flow equation).

The numerical methods that work best for parabolic partial differential equations are not best for solving hyperbolic equations, and vice versa. Thus, no one numerical method or simulation model will be ideal for the entire spectrum of groundwater transport problems likely to be encountered in the field. Further compounding this difficulty is the fact that in the field, the seepage velocity of groundwater is highly variable, even if aquifer properties are relatively homogeneous (because of the effects of complex boundary conditions). Thus, in low permeability zones or near stagnation points, the velocity may be close to zero and the transport processes will be dominated by dispersion processes; in high permeability zones or near stress points (such as pumping wells), the velocity may be several meters per day and the transport processes will be advection dominated. In other words, for the same system, the governing equation may be more hyperbolic in one area (or at one time) and more parabolic in nature in another area (or at another time). Therefore, no matter which numerical method is chosen as the basis for a simulation model, it will not be ideal or optimal over the entire domain of the problem, and significant numerical errors may be introduced somewhere in the solution. The transport modelling effort must recognise this inherent difficulty and strive to

minimise and control the numerical errors.

Although finite-difference and finite-element models are commonly applied to transport problems, other types of numerical methods have also been applied to transport problems, including method of characteristics, particle tracking, random walk, Eulerian-Lagrangian methods, and adaptive grid methods. All of these have the ability to track sharp fronts accurately with a minimum of numerical dispersion. Documented models based on variants of these approaches include Konikow and Bredehoeft (1978), Sanford and Konikow (1985), Prickett et al. (1981), and Zheng (1990).

Finite-difference and finite-element methods also can be applied to solve the transport equation, particularly when dispersive transport is large compared to advective transport. However, problems of numerical dispersion and oscillations may induce significant errors for some problems. The numerical errors can generally be reduced by using a finer discretisation (either time steps or spatial grid). Examples of documented three-dimensional, transient, finite-difference models that simultaneously solve the fluid pressure, energy-transport, and solute-transport equations for non-homogeneous miscible fluids include Kipp (1987) and Reeves et al. (1986). A two-dimensional finite-element transport model is documented by Voss (1984). Because none of the standard numerical methods are ideal for a wide range of transport problems, there is currently still much research on developing better mixed or adaptive methods that aim to minimise numerical errors and combine the best features of alternative standard numerical approaches (Carrera and Melloni 1987; Neuman 1984; Celia et al. 1990; Gottardi and Venutelli 1994.

The conventional solute-transport equation is a Fickian model. However, most mechanical dispersion actually arises from variations in velocity about the mean, so at least partly is an advective-based process. Transport in stratified porous media may be non-Fickian in nature (Gelhar et al. 1979; Matheron and De Marsily 1980). Thus, no matter how accurately we can solve the governing solute-transport equation, that equation itself is not necessarily a definitive and sufficient description of the processes controlling solute transport at the scale of most field problems. In general, the more accurately a model can represent or simulate the true velocity distribution, the less of a problem will be the uncertainty concerning representation of dispersion processes.

There are additional complications when the solutes of interest are reactive. The reaction terms included in Eq.4.6 are mathematically simple ones. They do not necessarily represent the true complexities of many reactions. Also, particularly difficult numerical problems arise when reaction terms are highly non-linear, or if the concentration of the solute of interest is strongly dependent on the concentration of other chemical constituents. In reality, isotherms may not be linear and may not be equilibrium controlled. Rubin (1983) discusses and classifies the chemical nature of reactions and their relation to the mathematical problem formulation. Bahr and Rubin (1987) compare kinetic and local equilibrium formulations for solute transport affected by surface reactions. For field problems in which reactions are significantly affecting

solute concentrations, simulation accuracy is less limited by mathematical constraints than by data constraints. That is, the types and rates of reactions for the specific solutes and minerals in the particular groundwater system of interest are rarely known and require an extensive amount of data to assess accurately. Yeh and Tripathi (1989) review hydrogeochemical transport models and discuss various mathematical approaches to modelling transport of multiple reacting species.

4.5.1 BASICS OF FINITE-DIFFERENCE METHODS

The partial differential equations describing the flow and transport processes in groundwater include terms representing derivatives of continuous variables. Finite-difference methods are based on the approximation of these derivatives (or slopes of curves) by discrete linear changes over small discrete intervals of space or time. If the intervals are sufficiently small, then all of the linear increments will represent a good approximation of the true curvilinear surface.

Considering the observation wells in a confined aquifer, as illustrated in Fig.4.2a, Bennett (1976) shows that a reasonable approximation for the derivative of head, $\partial h/\partial x$, at a point (d) midway between wells 1 and 0 is:

$$\left(\frac{\partial h}{\partial x}\right)_d \approx \frac{h_0 - h_1}{\Delta x} \tag{4.15}$$

Note that the observation wells are spaced an equal distance apart. Similarly, a reasonable approximation for the second derivative, $\delta^2 h/\delta x^2$, at point 0 (the location of the centre well) can be given as:

$$\left(\frac{\partial^2 h}{\partial x^2}\right) \approx \frac{\left(\frac{\partial h}{\partial x}\right)_e - \left(\frac{\partial h}{\partial x}\right)_d}{\Delta x} = \frac{\frac{h_2 - h_0}{\Delta x} - \frac{h_0 - h_1}{\Delta x}}{\Delta x} = \frac{h_1 + h_2 - 2h_0}{(\Delta x)^2} \tag{4.16}$$

If we also consider wells 3 and 4 shown in Fig.4.2b, located on a line parallel to the y-axis, we can similarly approximate $\partial^2 h/\partial y^2$ at point 0 (the same point 0 as in Fig.4.2a) as (Bennett 1976):

$$\left(\frac{\partial^2 h}{\partial y^2}\right) \approx \frac{h_3 + h_4 - 2h_0}{(\Delta y)^2} \tag{4.17}$$

If the spacing of the wells in Fig.4.2b is uniform (that is, $\Delta x = \Delta y = a$), then we can develop the following approximation:

$$\frac{\partial^2 h}{\partial x^2} + \frac{\partial^2 h}{\partial y^2} \approx \frac{h_1 + h_2 + h_3 + h_4 - 4h_0}{a^2} \tag{4.18}$$

These approximations can also be obtained through the use of Taylor series expansions. A certain error is involved in approximating the derivatives by finite-differences, but this error will generally decrease as a (or Δx and Δy) is given smaller and smaller values. This error is called a "truncation error" because the replacement of a derivative by a difference quotient is equivalent to using a truncated Taylor series, so that the exact solution of a difference equation differs from the solution of the corresponding differential equation (Peaceman 1977). Also, it may not be possible to achieve an "exact" solution of the difference equation because of limits of precision in storing numbers in a digital computer. In solving a large set of difference equations, many arithmetic operations are performed, and round-off errors may sometimes accumulate.

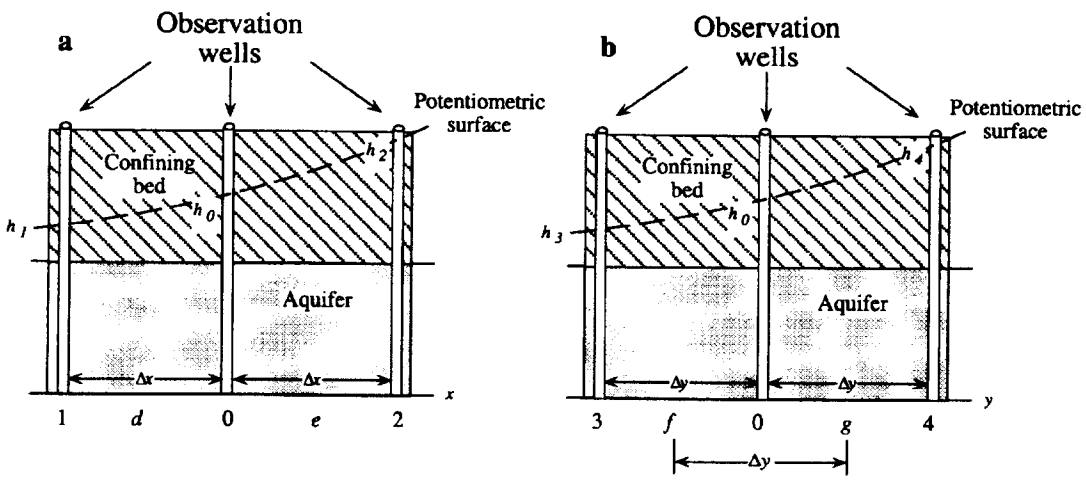

Fig.4.2 Schematic cross section through confined aquifer to illustrate numerical approximation to derivatives of head, $\partial h/\partial x$ (a) and $\partial h/\partial y$ (b) (modified from Bennett, 1976).

We must also consider the discretisation of time, which may be viewed as another dimension, and hence represented by another index. If we consider a representative segment of a hydrograph (see Fig.4.3), in which head is plotted against time for a transient flow system, n is the index or subscript used to denote the time at which a given head value is observed. The slope of the hydrograph at any point is the derivative of head with respect to time, and it can be approximated as $\partial h/\partial t \approx \Delta h/\Delta t$. In terms of the heads calculated at specific time increments (or time nodes), the slope of the hydrograph at time n can be approximated by:

$$\left(\frac{\partial h}{\partial t}\right)_{n\Delta t} \approx \frac{h_{n+1} - h_n}{\Delta t} \qquad \textbf{(4.19)}$$

or

$$\left(\frac{\partial h}{\partial t}\right)_{n\Delta t} \approx \frac{h_n - h_{n-1}}{\Delta t} \qquad \textbf{(4.20)}$$

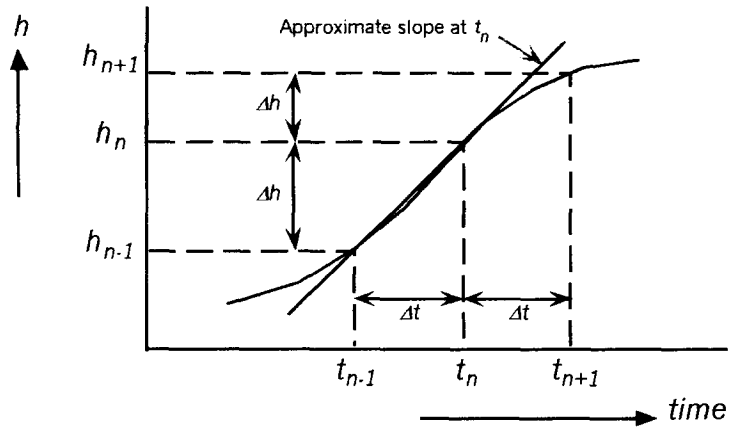

Fig.4.3 Part of a hydrograph showing that the derivative (or slope, $\partial h/\partial t$) at time node t_n may be approximated by $\Delta h/\Delta t$ (Konikow 1996).

We are calculating the derivative at $t = n\Delta t$ in Eq.4.19 by taking a "forward difference" from time n to time n+1, and by taking a "backward difference" in Eq.4.20. In terms of solving the groundwater flow equation for a node (i,j) of a finite-difference grid, we have to consider heads at five nodes and at two time levels, as illustrated in Fig.4.4. In Fig.4.4a, we have expressed the spatial derivatives of head at time level n, where all values are known, and the time derivative as a forward difference to the unknown head at time step n+1. Then for every node of the grid we will have a separate difference equation, each of which contains only one unknown variable. Thus, these equations can be solved explicitly. Explicit finite-difference equations are thus simple and straightforward to solve, but they may have stability criteria associated with them. That is, if time increments are too large, small numerical errors or perturbations may propagate into larger errors at later stages of the computations.

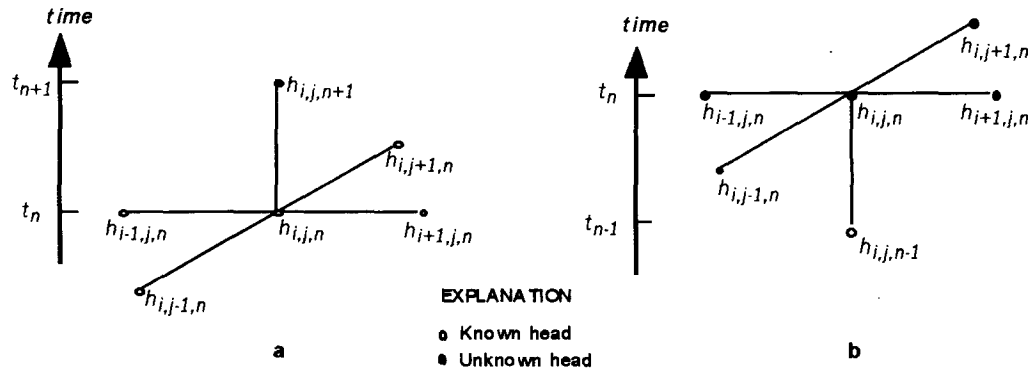

Fig.4.4 Grid stencil showing discretisation of time at node (i,j) in two-dimensional finite-difference grid: (a) explicit (forward-difference) formulation and (b) implicit (backward-difference) formulation (Konikow 1996).

In Fig.4.4b we have expressed the time derivative as a backward difference from the heads at time level n, which are thereby the unknown heads, whereas the heads at the previous time level, n-1, are known. The spatial derivatives of head are written at time level n, where all values are unknown, so for every node of the grid we will have one difference equation that contains five unknowns, which cannot be solved directly. However, for the entire grid, which contains N nodes, we would have a system of N equations containing a total of N unknowns. Such a system of simultaneous equations, together with specified boundary conditions, can be solved implicitly. Although implicit solutions are more complicated, they also have the advantage of generally being unconditionally stable. Most available groundwater flow models solve an implicit finite-difference approximation to the flow equation.

We may next consider a two-dimensional groundwater flow equation for a heterogeneous, anisotropic aquifer, in which the co-ordinate system is aligned with the major axes of the transmissivity tensor. This may be approximated by the following finite-difference equation for representative node (i,j) as:

$$\begin{aligned} & T_{xx[i-1/2,j]}\left(\frac{h_{i-1,j,n}-h_{i,j,n}}{(\Delta x)^2}\right)+T_{xx[i+1/2,j]}\left(\frac{h_{i+1,j,n}-h_{i,j,n}}{(\Delta x)^2}\right) \\ & +T_{yy[i,j-1/2]}\left(\frac{h_{i,j-1,n}-h_{i,j,n}}{(\Delta y)^2}\right)+T_{yy[i,j+1/2]}\left(\frac{h_{i,j+1,n}-h_{i,j,n}}{(\Delta y)^2}\right) \\ & =S\left(\frac{h_{i,j,n}-h_{i,j,n-1}}{\Delta t}\right)+\frac{q_{i,j}}{\Delta x\Delta y}-\frac{K_z}{m}\left(H_{s[i,j]}-h_{i,j,n}\right) \end{aligned} \qquad \textbf{(4.21)}$$

where $q_{i,j}$ is the volumetric rate of withdrawal or recharge at the i,j node, L^3T^{-1}. This formulation inherently assumes that any stresses, such as represented by $q_{i,j}$, are applied over the entire surface area of cell i,j rather than at a point (or at node i,j). This implies that if a pumping well is represented at node i,j, then the head will be calculated as if it were being withdrawn from a well that had a borehole surface area equal to $\Delta x\Delta y$ rather than its actual value. In Eq.4.21 the transmissivity terms represent the harmonic means of the transmissivity of the two adjacent cells. The harmonic mean can be shown to be appropriate and consistent with the assumption that transmissivity is constant and uniform within each cell but may be different between cells. Other types of means for interblock transmissivity may be more appropriate for other assumptions about the transmissivity distribution, such as smoothly varying transmissivity (Goode and Appel 1992).

4.5.2 BASICS OF FINITE-ELEMENT METHODS

The finite-element method (FEM) is a numerical analysis technique for obtaining approximate solutions to a wide variety of problems in physics and engineering. The method was originally applied to structural mechanics but is now used in all fields of continuum mechanics. Huebner (1975) describes four different approaches to formulate the finite-element method for a problem, which are: the direct approach, the variational approach, the weighted residual

approach, and the energy balance approach (Huebner 1975). In groundwater problems, the approach frequently used is either the weighted residual or variational approach.

The finite-element method (FEM) uses a concept of "piecewise approximation". The domain of the problem, that is the extent of the aquifer to be simulated, is divided into a set of elements or pieces. In theory, the elements can be of different shapes and sizes. Most FEM computer programs use one shape element, most commonly either triangular or quadrilateral elements. In the groundwater model MODFE (Torak 1993; Cooley 1992) triangular elements are used, whereas in the groundwater model SUTRA (Voss 1984) quadrilateral elements are used. Point values of the dependent variable (for example, head, pressure, or concentration) are calculated at nodes, which are the corners or vertices of the elements, and a simple equation is used to describe the value of the dependent variable within the element. This simple equation is called a basis function and each node that is part of an element has an associated basis function. The simplest basis functions that are usually used are linear functions. The solution to the differential equation for flow (Eq.4.3) or transport (Eq.4.6) is approximated by a set of elements in which the dependent variable only varies linearly within the element, but the entire set of elements approximates the complex distribution of head or concentration. Huyakorn and Pinder (1983), Huebner (1975), Zienkiewicz (1971), Wang and Anderson (1982), and Cooley (1992) provide more comprehensive explanations of the method.

4.5.3 MATRIX SOLUTION TECHNIQUES

As indicated, the finite-difference and finite-element approximations lead to an algebraic equation for each node point. The set of algebraic equations may be solved numerically by one of two basic methods: direct or iterative. In direct methods, a sequence of operations is performed only once to solve the matrix equation, providing a solution that is exact, except for machine round-off error. Iterative methods arrive at a solution by a process of successive approximation. They involve making an initial guess at the solution, then improving this guess by some iterative process until an error criterion is satisfied. Therefore, in these techniques, convergence and the rate of convergence are of concern.

Direct methods can be further subdivided into:

1) solution by determinants,

2) solution by successive elimination of the unknowns, and

3) solution by matrix inversion.

Direct methods have two main disadvantages. The first problem is one of computer resource requirements, including large storage (memory) requirements and long computation times for large problems. The matrix is sparse (contains many zero values) and to minimise computational effort, several techniques have been proposed. However, for finite-difference and finite-element methods, storage requirements may still prove to be unavoidably large for three-dimensional problems. The second problem with direct methods is round-off error.

Because many arithmetic operations are performed, round-off errors can accumulate for certain types of matrices.

Iterative schemes avoid the need for storing large matrices, which make them attractive for solving problems with many unknowns. Numerous schemes have been developed; a few of the more commonly used ones include successive over-relaxation methods, iterative alternating-direction implicit procedure, and the strongly implicit procedure.

Because iterative methods start with an initial estimate for the solution, the efficiency of the method depends somewhat on this initial guess. To speed up the iterative process, relaxation and acceleration factors are used. Unfortunately, the definition of best values for these factors commonly is problem dependent. In addition, iterative approaches require that an error tolerance be specified to stop the iterative process. An optimal value for the tolerance, which is used to evaluate when the iterative calculations have converged on a solution, may also be problem dependent. If the tolerance is set too large, then the iterations may stop before adequate numerical accuracy is achieved. If the tolerance is set too small, then the iterative process may consume excessive computational resources in striving for numerical precision that may be orders of magnitude smaller than the precision of the field data, or the iterative process may even fail to converge.

More recently, a semi-iterative method, or class of methods, known as conjugate-gradient methods, has gained popularity. One advantage of the conjugate-gradient method is that it does not require the use or specification of iteration parameters, thereby eliminating this partly subjective procedure.

4.5.4 BOUNDARY AND INITIAL CONDITIONS

To obtain a unique solution of a partial differential equation corresponding to a given physical process, additional information about the physical state of the process is required. This information is supplied by boundary and initial conditions. For steady-state problems, only boundary conditions are required, whereas for transient problems, boundary and initial conditions must be specified.

Mathematically, the boundary conditions include the geometry of the boundary and the values of the dependent variable or its derivative normal to the boundary. In physical terms, for groundwater model applications, the boundary conditions are generally of three types:

1) specified value (head or concentration),
2) specified flux (corresponding to a specified gradient of head or concentration), or
3) value-dependent flux (or mixed boundary condition, in which the flux across a boundary is related to both the normal derivative and the value) (Mercer and Faust 1981.

The third type of boundary condition might be used, for example, to represent leakage or exchange between a stream and an adjacent aquifer, in which the leakage may change over time as the head in the aquifer changes, even though the head in the stream might remain fixed.

A no-flow boundary is a special case of the second type of boundary condition. The types of boundaries appropriate to a particular field problem require careful consideration.

The initial conditions are simply the values of the dependent variable specified everywhere inside the boundary at the start of the simulation. Normally, the initial conditions are specified to be a steady-state solution. If, however, initial conditions are specified so that transient flow is occurring in the system at the start of the simulation, it should be recognised that heads will change during the simulation, not only in response to the new pumping stress, but also due to the initial conditions (Franke et al. 1987).

4.6 MODEL DESIGN, DEVELOPMENT AND APPLICATION

The first step in model design and application is to define the nature of the problem and evaluate the purpose of the model. Although this may seem obvious, it is an important first step that is sometimes overlooked in a hasty effort to take action. This step is closely linked with the formulation of a conceptual model, which again is required prior to development of a simulation model. In formulating a conceptual model, the analyst must evaluate which processes are significant in the system being investigated for the particular problem at hand. Some processes may be important to consider at one spatial or temporal scale of study, but negligible or irrelevant at another scale. The analyst must similarly decide on the appropriate dimensionality for the numerical model. Good judgement is required to evaluate and balance the trade-offs between accuracy and cost, with respect to both the model and to data requirements. The key to efficiency and accuracy in modelling a system probably is more affected by the formulation of a proper and appropriate conceptual model than by the choice of a particular numerical method or code.

Once a decision to develop a model has been made, a code (or generic model) must be selected (or modified or constructed) that is appropriate for the given problem. Next, the generic code must be adapted to the specific site or region being simulated. Development of a numerical deterministic, distributed-parameter, simulation model involves selecting or designing spatial grids and time increments that will yield an accurate solution for the given system and problem. The analyst must then specify the properties of the system (and their distributions), stresses on the system (such as recharge and pumping rates), boundary conditions, and initial conditions (for transient problems). All of the parameter specifications and boundary conditions are really part of the overall conceptual model of the system, and the initial numerical model reflects the analyst's conceptual model of the system.

It must always be remembered that a model is an approximation of a very complex reality, and a model is used to simplify that reality in a manner that captures or represents the essential features and processes relative to the problem at hand. In the development of a deterministic groundwater model for a specific area and purpose, we must select an appropriate level of complexity (or, rather, simplicity). Although finer resolution in a model will generally yield greater accuracy, there also exists the practical constraint that even when appropriate data are

available, a finely discretised three-dimensional numerical model may be too large to run on available computers, especially if transport processes are included. The selection of the appropriate model and appropriate level of complexity remains subjective and dependent on the judgement and experience of the analysts, the objectives of the study, and level of prior information on the system of interest. The trade-off between model accuracy and model cost will always be a difficult one to resolve, but will always have to be made. In any case, water managers and other users of model results must be made aware that these trade-offs and judgements have been made and may affect the reliability of the model.

In general, it is more difficult to calibrate a solute-transport model of an aquifer than it is to calibrate a groundwater flow model. Fewer parameters need to be defined to compute the head distribution with a flow model than are required to compute concentration changes using a solute-transport model. Because the groundwater seepage velocity is determined from the head distribution, and because both advective transport and hydrodynamic dispersion are functions of the seepage velocity, a model of groundwater flow is often calibrated before a solute-transport model is developed. In fact, in a field environment perhaps the single most important key to understanding a solute-transport problem is the development of an accurate definition (or model) of the flow system. This is particularly relevant to transport in fractured rocks, where simulation is commonly based on porous-media concepts. Although the potential (or head) field can often be simulated, the required velocity field may be greatly in error.

4.6.1 GRID DESIGN

The dimensionality of the model should be selected during the formulation of the conceptual model. If a one- or two-dimensional model is selected, then it is important that the grid be aligned with the flow system so that there is no unaccounted flux into or out of the line or plane of the grid. For example, if a two-dimensional areal model is applied, then there should be no significant vertical components of flow and any vertical leakage or flux must be accounted for by boundary conditions; if a two-dimensional profile model is applied, then the line of the cross section should be aligned with an areal streamline, and there should not be any lateral flow into or out of the plane of the cross section.

To minimise a variety of sources of numerical errors, the model grid should be designed using the finest mesh spacing and time steps that are possible, given limitations on computer memory and computational time. To the extent possible, the grid should be aligned with the fabric of the rock and with the average direction of groundwater flow. The boundaries of the grid also should be aligned, to the extent possible, with natural hydrologic and geologic boundaries of the system of interest. Where it is impractical to extend the grid to a natural boundary, then an appropriate boundary condition should be imposed at the edge of the grid to represent the net effects of the continuation of the system beyond the grid. This can typically be accomplished using head-dependent leakage (third type) boundary conditions. These boundaries should also be placed as far as possible away from the area of interest and areas of stresses on the system, so as to minimise any impact of conceptual errors associated with these artificial boundary

conditions.

In designing the grid, the length to width ratio (or aspect ratio) of cells or elements should be kept as close to one as possible. Long linear cells or elements can lead to numerical instabilities or errors, and should be avoided, particularly if the aspect ratio is greater than about five (Anderson and Woessner 1992).

In specifying boundary conditions for a particular problem and grid design, care must be taken to not overconstrain the solution. That is, if dependent values are fixed at too many boundary nodes, at either internal or external nodes of a grid, the model may have too little freedom to calculate a meaningful solution. At the extreme, by manipulating boundary conditions, one can force any desired solution at any given node. While this may assure a perfect match to observed data used for calibration, it is of course not an indicator of model accuracy or reliability, and in fact is meaningless.

To optimise computational resources in a model, it is generally advisable to use an irregular (or variably-spaced) mesh in which the grid is finest in areas of point stresses, where gradients are steepest, where data are most dense, where the problem is most critical, and (or) where greatest numerical accuracy is desired. It is generally advisable to increase the mesh spacing by a factor no greater than about two between adjacent cells or elements. Similarly, time steps can often be increased geometrically during a simulation. At the initial times or after a change in the stress regime, very small time steps should be imposed, as that is when changes over time are the greatest. With increased elapsed time, the rate of change in head typically decreases, so time steps can often be safely increased by a factor of two or more.

Because transmissivity is a property of the porous media, the cross-product terms of the transmissivity tensor can typically be dropped out of the governing flow equation that is solved in a model by aligning the model grid with the major axes of the transmissivity tensor. However, this cannot typically be done for the dispersion tensor in the transport equation because it is related to, and depends on, the flow direction, which changes orientation over space and time. There is, in general, no way to design a fixed grid that will always be aligned with a changing flow field.

4.6.2 MODEL CALIBRATION

Deterministic groundwater simulation models impose large requirements for data to define all of the parameters at all of the nodes of a grid. To determine uniquely the parameter distribution for a field problem would require so much expensive field testing that it is seldom feasible either economically or technically. Therefore, the model typically represents an attempt, in effect, to solve a large set of simultaneous equations having more unknowns than equations. It is inherently impossible to obtain a unique solution to such a problem.

Uncertainty in parameters logically leads to a lack of confidence in the interpretations and predictions that are based on a model analysis, unless it can be demonstrated that the model is a reasonably accurate representation of the real system. To demonstrate that a deterministic

groundwater simulation model is realistic, it is usual to compare field observations of aquifer responses (such as changes in water levels for flow problems or changes in concentration for transport problems) to corresponding values calculated by the model. The objective of this calibration procedure is to minimise differences between the observed data and calculated values. Usually, the model is considered calibrated when it reproduces historical data within some acceptable level of accuracy. What level is acceptable is, of course, determined subjectively. Although a poor match provides evidence of errors in the model, a good match in itself does not prove the validity or adequacy of the model (Konikow and Bredehoeft 1992).

Because of the large number of variables in the set of simultaneous equations represented in a model, calibration will not yield a unique set of parameters. Where the match is poor, it suggests (i) an error in the conceptual model, (ii) an error in the numerical solution, or (iii) a poor set of parameter values. It may not be possible to distinguish among the several sources of error (Konikow and Bredehoeft 1992). Even when the match to historical data is good, the model may still fail to predict future responses accurately, especially under a new or extended set of stresses than experienced during the calibration period.

The calibration of a deterministic groundwater model is often accomplished through a trial and error adjustment of the model's input data (aquifer properties, sources and sinks, and boundary and initial conditions) to modify the model's output. Because a large number of interrelated factors affect the output, this may become a highly subjective and inefficient procedure. Advances in parameter identification procedures help to eliminate some of the subjectivity inherent in model calibration (Cooley 1982; Knopman and Voss 1987; Neuman 1980; Wagner and Gorelick 1986; Yeh 1986). The newer approaches tend to treat model calibration as a statistical procedure. Thus, multiple regression approaches allow the simultaneous construction, application, and calibration of a model using uncertain data, so that the uncertainties are reflected as estimated uncertainties in the model output and hence in predictions or assessments to be made with the model (Cooley et al. 1986).

Even with regression modelling, however, the hydrologic experience and judgement of the modeller continues to be a major factor in calibrating a model both accurately and efficiently, even if automated procedures are used. In any case, the modeller should be very familiar with the specific field area being studied to know that both the data base and the numerical model adequately represent prevailing field conditions. The modeller must also recognise that the uncertainty in the specification of sources, sinks, and boundary and initial conditions should be evaluated during the calibration procedure in the same manner as the uncertainty in aquifer properties. Failure to recognise the uncertainty inherent both in the input data and in the calibration data may lead to "fine-tuning" of the model through artificially precise parameter adjustments strictly to improve the match between observed and calculated variables. This may only serve to falsely increase the confidence in the model without producing an equivalent (or any) increase in its predictive accuracy.

Fig.4.5 illustrates in a general manner the use and role of deterministic models in the analysis of

groundwater problems. The value of the modelling approach is its capability to integrate site-specific data with equations describing the relevant processes as a quantitative basis for predicting changes or responses in a groundwater system. There must be allowances for feedback from the stage of interpreting model output both to the data collection and analysis phase and to the conceptualisation and mathematical definition of the relevant governing processes. One objective of model calibration should be to improve the conceptual model of the system. Because the model numerically integrates the effects of the many factors that affect groundwater flow or solute transport, the calculated results should be internally consistent with all input data, and it can be determined if any element of the conceptual model should be revised. In fact, prior concepts or interpretations of aquifer parameters or variables, such as represented by potentiometric maps or the specification of boundary conditions, may be revised during the calibration procedure as a result of feedback from the model's output.

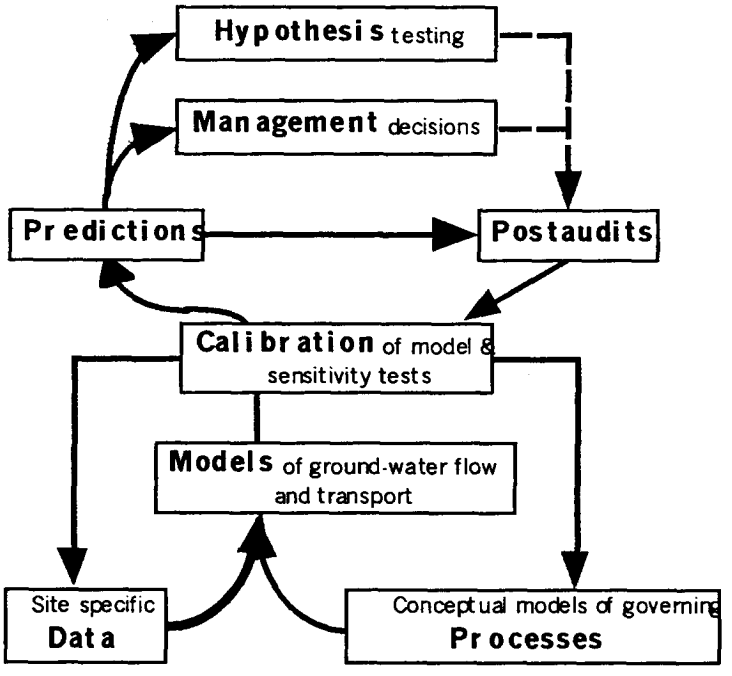

Fig.4.5 The use and role of models in the analysis of groundwater problems (Konikow 1996).

Automated parameter-estimation techniques improve the efficiency of model calibration and have two general components--one part that calculates the best fit (sometimes called automatic history matching) and a second part that evaluates the statistical properties of the fit. The objective of automatic history matching is to obtain the estimates of system parameters that yield the closest match (minimises deviations) between observed data and model calculations. Least squares deviation is usually chosen as a criteria. The minimisation procedure uses sensitivity coefficients that are based on the change in calculated value divided by the change in the parameter. For groundwater flow, for example, this may take the specific form of $\partial h/\partial t$,

that is the change in head with changing transmissivity. The sensitivity coefficients themselves may be useful in the consideration of additional data collection.

A recently documented computer program, UCODE, performs inverse modelling, posed as a parameter-estimation problem, using non-linear regression (Poeter and Hill 1998). UCODE is extremely general and powerful because it can be used with almost any application model or set of models. An estimated parameter can be a quantity that appears in the input files of the application model(s), or that can be used in conjunction with user-defined functions to calculate a quantity that appears in the input files. UCODE calculates sensitivities as well as statistical measures that evaluate estimated parameter values and quantify the likely uncertainty of model simulated values. Hill (1998) documents methods and guidelines for modern model calibration using inverse modelling such that the resulting model is as accurate and useful as possible (Hill 1998). Hill notes that obtaining useful results with inverse modelling depends on (i) defining a tractable inverse problem using simplifications appropriate to the system under investigation and (ii) wise use of statistics generated using calculated sensitivities and the match between observed and simulated values.

4.6.3 MODEL ERROR

Discrepancies between observed and calculated responses of a system are the manifestation of errors in the mathematical model. In applying groundwater models to field problems, there are three sources of error (Konikow and Bredehoeft 1992). One source is conceptual errors--that is, theoretical misconceptions about the basic processes that are incorporated in the model. Conceptual errors include both neglecting relevant processes as well as representing inappropriate processes. Examples of such errors include the application of a model based upon Darcy's Law to media or environments where Darcy's Law is inappropriate, or the use of a two-dimensional model where significant flow or transport occurs in the third dimension. A second source of error involves numerical errors arising in the equation-solving algorithm. These include truncation errors, round-off errors, and numerical dispersion. A third source of error arises from uncertainties and inadequacies in the input data that reflect our inability to describe comprehensively and uniquely the aquifer properties, stresses, and boundaries. In most model applications conceptualisation problems and uncertainty concerning the data are the most common sources of error.

Numerical methods in general yield approximate solutions to the governing equations. There are a number of possible sources of numerical error in the solution. If the modeller is aware of the source and nature of these errors, they can control them and interpret the results in light of them. In solving advection dominated transport problems, in which a relatively sharp front (or steep concentration gradient) is moving through a system, it is numerically difficult to preserve the sharpness of the front. Obviously, if the width of the front is narrower than the node spacing, then it is inherently impossible to calculate the correct values of concentration in the vicinity of the sharp front. Even in situations where a front is less sharp, however, the numerical solution technique can calculate a greater dispersive flux than would occur by

physical dispersion alone or would be indicated by an exact solution of the governing equation. That part of the calculated dispersion introduced solely by the numerical solution algorithm is called numerical dispersion, as illustrated in Fig.4.6. Because the hydrologic interpretation of isotopic data is sensitive to mixing phenomena in an aquifer, numerical mixing (or dispersion) can have the same effect on the interpretation of model-calculated isotopic values. Therefore, care must be taken to assess and minimise such numerical errors that would artificially add "numerical" mixing to the calculated mixing attributable to physical and chemical processes.

Fig.4.6 illustrates calculated breakthrough curves for a hypothetical problem of uniform flow and transport to the right, at some time and distance after a tracer having a relative concentration of 1.0 was injected at some point upstream. Curve A represents the breakthrough curve and position of a sharp front for a case having no dispersion (plug flow). Curve B represents an exact analytical solution for a nonzero dispersivity. Curve C illustrates the breakthrough curve calculated using a numerical method that introduces numerical dispersion.

Numerical dispersion can be controlled by reducing the grid spacing (Δx and Δy). However, reduction to a tolerable level may require an excessive number of grid points for a particular region to be simulated and render the computational costs unacceptably high (Peaceman 1977). It may also be controlled in finite-element methods by using higher order basis functions or by

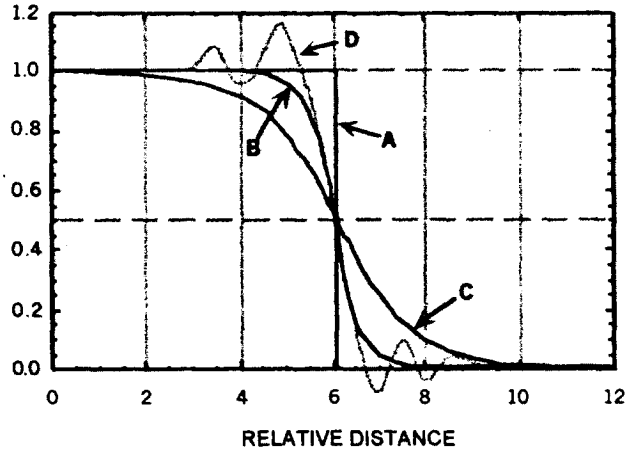

Fig.4.6 Representative breakthrough curves for a simple flow and transport problem to illustrate types of numerical errors that may occur in numerical solution to transport equation: (A) plug flow having no dispersion, (B) "exact" solution for transport with dispersion, (C) numerical solution for case B that exhibits effects of numerical dispersion, and (D) numerical solution for case B that exhibits oscillatory behaviour (Konikow 1996).

adjusting the formulation of the difference equations (using different combinations of forward, backward, or centred in time and/or space, or using different weighting functions). Unfortunately, many approaches that eliminate or minimise numerical dispersion introduce

oscillatory behaviour, causing overshoot behind a moving front and undershoot ahead of the front (see curve D in Fig.4.6), and vice versa. Undershoot can result in the calculation of negative concentrations, which are obviously unrealistic. However, overshoot can introduce errors of equal magnitude that may go unnoticed because the value is positive in sign (although greater than the source concentration, so still unrealistic). Oscillations generally do not introduce any mass-balance errors, and often dampen out over time. In some cases, however, oscillatory behaviour can become unbounded, yielding an unstable solution or failure to converge numerically.

In solving the advective-dispersive transport equation, some numerical errors (mainly oscillations) can be related to two dimensionless parameter groups (or numbers). One is the Peclet number, P_e, which may be defined as $P_e = \Delta l/\alpha$, where Δl is a characteristic nodal spacing (although it should be noted that there are several alternative, though essentially equivalent, ways to define P_e). Anderson and Woessner (1992) recommend that the grid be designed so that $\Delta l < 4\alpha$ (or $P_e < 4$), although Ségol (1994) recommends a criteria of $P_e \leq 2$ (Anderson and Woessner 1992; Ségol 1994). Similarly, time discretisation can be related to the Courant number, C_o, which may be defined as $C_o = V\Delta t/\Delta l$ (Anderson and Woesser 1992). Anderson and Woessner (1992) also recommend that time steps be specified so that $\Delta t < \Delta l/V$ (or $C_o<1.0$), which is equivalent to requiring that no solute be displaced by advection more than one grid cell or element during one time increment. The deviations of curves C and D from the exact solution can be significant in some locations, although such errors tend to be minimal at the centre of a front (relative concentration of 0.5).

In solving the transport equation, classical numerical methods exhibit the proportionately largest numerical errors where the relative (or dimensionless) concentrations (C/C_{max}) are lowest. Dougherty and Bagtzoglou (1993) show that the error-to-signal (or noise-to-signal) ratio can become quite large (>0.1) where the relative concentrations are less than 0.01. In isotope analyses of groundwater systems, the samples from areas of interest frequently reflect concentrations less than 0.01 of the source concentration, so caution is warranted.

In transport models there may also be a grid-orientation effect, in which the solute distribution, calculated for the same properties and boundary conditions, will vary somewhat depending on the angle of the flow relative to the grid. This phenomena is largely related to the cross-product terms in the governing equation, and generally is not a serious source of error, but the model user should be aware of it.

4.6.4 MASS BALANCE

One measure of model accuracy is how well the model conserves mass. This can be measured by comparing the net fluxes calculated or specified in the model (e.g. inflow and sources minus outflow and sinks) with changes in storage (accumulation or depletion). Mass-balance calculations should always be performed and checked during the calibration procedure to help

assess the numerical accuracy of the solution. As part of these calculations, the hydraulic and chemical fluxes contributed by each distinct hydrologic component of the flow and transport model should be itemised separately to form hydrologic and chemical budgets for the system being modelled. The budgets are valuable assessment tools because they provide a measure of the relative importance of each component to the total budget.

Errors in the mass balance for flow models should generally be less than 0.1%. However, because the solute-transport equation is more difficult to solve numerically, the mass-balance error for a solute may be greater than for the fluid, but this will depend also on the nature of the numerical method implemented. Finite-difference and finite-element methods are inherently mass conservative, while some implementations of the method of characteristics and particle tracking approaches may not be (or their mass-balance calculations themselves are only approximations). It must also be remembered that while a large mass-balance error provides evidence of a poor numerical solution, a perfect mass balance in itself does not and cannot prove that a true or accurate solution has been achieved or that the overall model is valid. That is, a perfect mass balance can be achieved if the model includes compensating errors. For example, the solutions C and D in Fig.4.6 that exhibit significant numerical dispersion or oscillatory behaviour arise from solutions that show a near-perfect mass balance, but they are still wrong.

4.6.5 SENSITIVITY TESTS

Assuming various values for given parameters also helps to achieve another goal of the calibration procedure, namely to determine the sensitivity of the model to factors that affect groundwater flow and transport and to errors and uncertainty in data. Evaluating the relative importance of each factor helps determine which data must be defined most accurately and which data are already adequate or require only minimal further definition. If additional data can be collected in the field, such a sensitivity analysis helps you decide which types of data are most critical and how to get the best information return on the costs of additional data collection. If additional data cannot be collected, then the sensitivity tests can help to assess the reliability of the model by demonstrating the effect of a given range of uncertainty or error in the input data on the output of the model. The relative sensitivities of the parameters that affect flow and transport will vary from problem to problem. Furthermore, sensitivities may change over time as the stress regime imposed on a system evolves. Thus, one generalisation is that a sensitivity analysis should be performed during the early stages of a model study.

The sensitivity of the solution to the grid design (or spacing), time-step criteria, nature and placement of boundary conditions, and other numerical parameters should also be evaluated, even if an inverse or regression modelling approach has been used. This is frequently overlooked, but failure to do so may cause critical design flaws to remain undetected. For example, parameter-estimation models cannot calculate the sensitivity to grid spacing or certain boundary conditions that are fixed in the model by the user. A general approach that works is after a preliminary calibration has be achieved with a model, it should be rerun for the

same stresses and properties using a finer grid, smaller time steps, and perhaps alternative boundary conditions. If such a test yields significantly different results, then the model should be recalibrated using design criteria that yield a more accurate numerical solution. If such a test yields no significant differences, then the coarser design is probably adequate for that particular problem.

4.6.6 CALIBRATION CRITERIA

Model calibration may be viewed as an evolutionary process in which successive adjustments and modifications to the model are based on the results of previous simulations. The modeller must decide when sufficient adjustments have been made to the representation of parameters and processes and at some time accept the model as being adequately calibrated (or perhaps reject the model as being inadequate and seek alternative approaches). This decision is often based on a mix of subjective and objective criteria. The achievement of a best fit between values of observed and computed variables is a regression procedure and can be evaluated as such. That is, the residual errors should have a mean that approaches zero and the deviations should be minimised. Cooley (1977) discusses several statistical measures that can be used to assess the reliability and "goodness of fit" of groundwater flow models. The accuracy tests should be applied to as many dependent variables as possible. The types of observed data that are most valuable for model calibration include head and concentration changes over space and time, and the quantity and quality of groundwater discharges from the aquifer.

While it is necessary to evaluate the accuracy of the model quantitatively, it is equally important to assure that the dependent variables that serve as a basis for the accuracy tests are reliable indicators of the computational power and accuracy of the model. For example, if a particular dependent variable was relatively insensitive to the governing parameters, then the existence of a high correlation between its observed and computed values would not necessarily be a reflection of a high level of accuracy in the overall model.

Similarly, caution must be exercised when the "observed data" contain an element of subjective interpretation. For example, matching an observed potentiometric surface or concentration distribution is sometimes used as a basis for calibrating groundwater models. However, a contoured surface is itself interpretive and can be a weak basis for model calibration because it includes a variability or error introduced by the contouring process, in addition to measurement errors present in the observed data at the specific points.

4.6.7 PREDICTIONS AND POSTAUDITS

As model calibration and parameter estimation are keyed to a set of historical data, the confidence in and reliability of the calibration process is proportional to the quality and comprehensiveness of the historical record. The time over which predictions are made with a calibrated model should also be related to, and limited by, the length of the historical record. A reasonable guideline is to predict only for a time comparable to the period that was matched.

The accuracy of a model's predictions is the best measure of its reliability. However, predictive accuracy can be evaluated only after the fact. Anderson and Woessner (1992) summarise several published studies in which the predictive accuracy of a deterministic groundwater model was evaluated several years after the prediction had been made. The results suggest that extrapolations into the future were rarely very accurate. Predictive errors often were related to having used a time period for history matching that was too short to capture an important element of the model or of the system, or to having an incomplete conceptual model. For example, processes and boundary conditions that are negligible or insignificant under the past and present stress regime may become nontrivial or even dominant under a different set of imposed stresses. Thus, a conceptual model founded on observed behaviour of a groundwater system may prove to be inadequate in the future, when existing stresses are increased or new stresses are added. A major source of predictive error is sometimes attributable primarily to the uncertainty of future stresses, which is often controlled by demographic, political, economic, and (or) social factors. But if the range or probability of future stresses can be estimated, then the range or probability of future responses can be predicted. An encouraging trend is that many analysts are now attempting to place confidence bounds on predictions arising out of the uncertainty in parameter estimates. However, these confidence limits still would not bound errors arising from the selection of a wrong conceptual model or from problems in the numerical solution algorithms (Bredehoeft and Konikow 1993).

If a model is to be used for prediction relating to a problem or system that is of continuing interest or significance to society, then field monitoring should continue and the model should be periodically postaudited, or recalibrated, to incorporate new information, such as changes in imposed stresses or revisions in the assumed conceptual model. A postaudit offers a means to evaluate the nature and magnitude of predictive errors, which may itself lead to a large increase in the understanding of the system and in the value of a subsequently revised model. Revised predictions can then be made with greater reliability.

4.6.8 MODEL VALIDATION

It is natural for people who apply groundwater models, as well as those who make decisions based on model results, to want assurance that the model is valid. Groundwater models are embodiments of various scientific theories and hypotheses. Karl Popper (1959) argues that "as scientists we can never validate a hypothesis, only invalidate it". The same philosophy has been applied specifically to groundwater models (Konikow and Bredehoeft 1992; Oreskes et al. 1994).

The criteria for labelling a model as validated are inherently subjective. In practice, validation is attempted through the same process that is typically and more correctly identified as calibration--that is, by comparing calculations with field or laboratory measurements. However, the non-uniqueness of model solutions means that a good comparison can be achieved with an inadequate or erroneous model. Also, because the definition of "good" is subjective, under the common operational definitions of validation, one competent and

reasonable scientist may declare a model as validated while another may use the same data to demonstrate that the model is invalid. To the general public, proclaiming that a groundwater model is validated carries with it an aura of correctness that many modellers would not claim (Bredehoeft and Konikow 1993). Because labelling a model as having been "validated" has very little objective or scientific meaning, such "certification" does little beyond instilling a false sense of confidence in such models. Konikow and Bredehoeft (1992) recommend that the term validation not be applied to groundwater models.

4.7 CASE HISTORY: LOCAL-SCALE FLOW AND TRANSPORT IN A SHALLOW UNCONFINED AQUIFER

Reilly et al. (1994) combined the application of environmental tracers and deterministic numerical modelling to analyse and estimate recharge rates, flow rates, flow paths, and mixing properties of a shallow groundwater system near Locust Grove, in eastern Maryland, U.S.A. The study was undertaken as part of the U.S. Geological Survey's National Water Quality Assessment Program to provide flow paths and travel time estimates to be used in understanding and interpreting water-quality trends in monitoring wells and stream base flows. The study area encompassed about 2.6×10^7 m^2 of mostly agricultural land on the Delmarva Peninsula. The surficial aquifer includes unconsolidated permeable sands and gravel that range in thickness from less than 6 m to more than 20 m. This surficial aquifer is underlain by relatively impermeable silt and clay deposits, which form a confining unit.

In this study, chlorofluorocarbons (CFCs) and tritium were analysed from a number of water samples collected from observation wells to estimate the age of groundwater at each sampling location and depth. Because errors and uncertainty are associated with estimates of age based on environmental tracers, just as errors and uncertainty are associated with deterministic models of groundwater flow and transport, the authors applied a feedback or iterative process based on comparisons of independent estimates of travel time. Their approach is summarised and outlined in Fig.4.7. Each task shown was designed to improve either the estimates of parameters or the conceptualisation of the system.

The preliminary calculations (first task) were used to set bounds on the plausibility of the results of the more complex simulations and chemical analyses. The first-level calibration of a groundwater flow model (second task) provided the initial system conceptualisation. The third task was a second-level calibration and analysis involving simulation of advective transport, which provided quantitative estimates of flow paths and time of travel to compare with those obtained from the CFC analyses. The fourth task involved the application of a solute-transport model to simulate tritium concentrations in the groundwater flow system as influenced by the processes of advection, dispersion, radioactive decay, and time-varying input (source concentration) functions.

The sampling wells were located approximately along an areal flow line, and a two-dimensional cross-sectional model was developed for the simulation of processes occurring along this flow

line. The MODFLOW model (McDonald and Harbauch 1988) was used to simulate groundwater flow and advective transport. The finite-difference grid consisted of 24 layers and 48 columns of nodes, with each cell having dimensions of 1.14 by 50.80 m, as shown in Fig.4.8, which also shows the wells that lie in the cross section. The simulation was designed to represent average steady-state flow conditions.

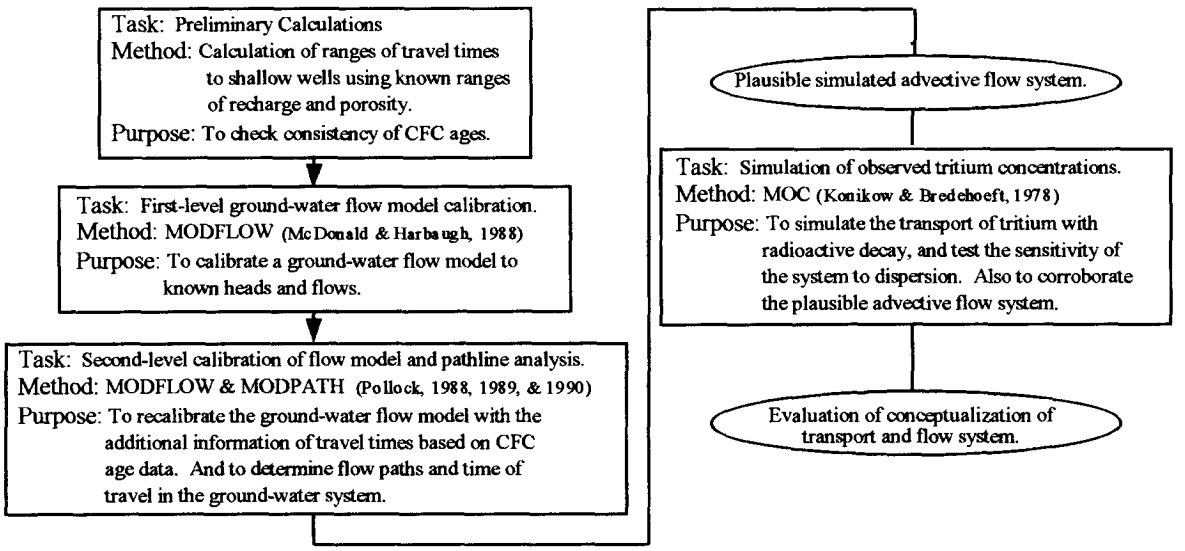

Fig.4.7 Flow diagram of the steps taken to quantify the flow paths in the Locust Grove, Maryland, groundwater flow system (modified from Reilly et al. 1994).

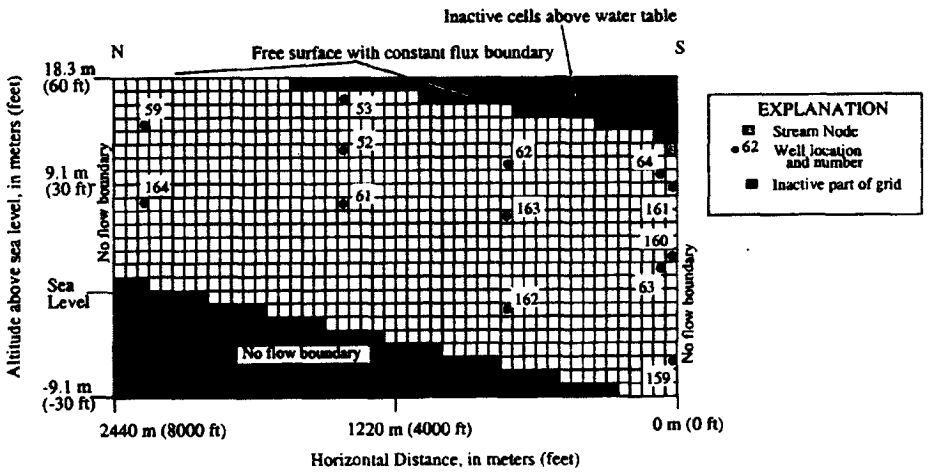

Fig.4.8 Model grid used to simulate Locust Grove cross section, showing well locations (modified from Reilly et al. 1994).

After the flow model was calibrated, pathline and travel time analysis was undertaken and comparisons to CFC age estimates were made. Fig.4.9 shows the pathlines calculated using MODPATH (Pollock 1989) after the second-level calibration with MODFLOW. The comparison with CFC estimates were generally good. However, Reilly et al. (1994) note that close to the stream, many flow lines converge, and the convergence of pathlines representing the entire range of travel times present in the aquifer causes waters of different ages to be relatively near each other. Thus, at the scale and grid spacing of the model, in the area near the stream the convergent flow lines cannot be readily differentiated in the model and the locations of individual well screens cannot be accurately represented directly under the stream. After the second-level calibration, the root mean squared error between the simulated ages and the CFC ages for the 10 wells farthest from the stream (i.e., excluding wells 159, 160, and 161) was 3.4 years.

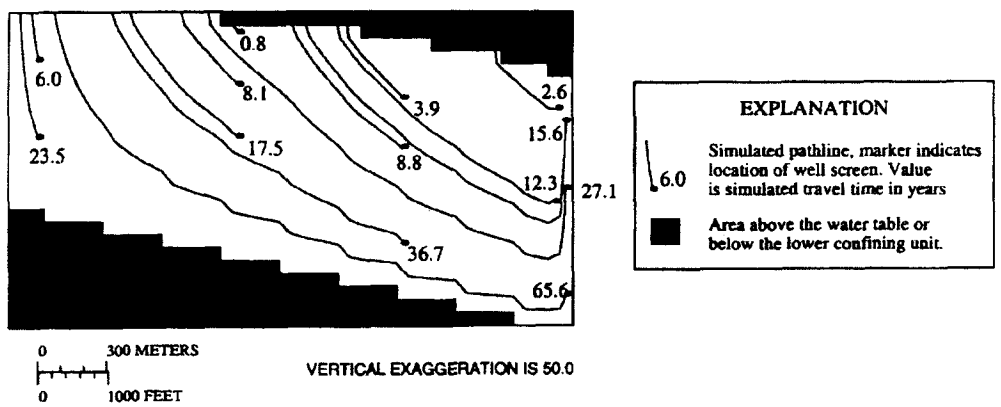

Fig.4.9 Pathlines (calculated using MODPATH after second-level calibration) in Locust Grove cross section to observation wells showing time of travel (in years) from the water table (modified from Reilly et al., 1994).

^{3}H concentrations of recharge waters have varied considerably over the last 40 years. Thus, the time of travel would not always be readily apparent from the ^{3}H concentration in a water sample. Also, mixing of waters recharged during periods of these relatively sharp changes of input concentrations can make the interpretation of time of travel from ^{3}H concentrations even more uncertain. Thus, the investigators simulated solute transport of ^{3}H within the system using a model that accounts for mixing (dispersion), radioactive decay, and transient input functions, which also allowed a further evaluation of consistency with the results of the previous flow and advective transport model. They applied the MOC solute-transport model of Konikow and Bredehoeft (1978) and Goode and Konikow (1989) for this purpose.

The results of the simulations of the ^{3}H distribution assuming (i) no dispersion and (ii) α_L of 0.15 m and α_T of 0.015 m are shown in Fig.4.10. The limiting case simulation of no dispersion

yielded acceptable results and was used as the best estimate of the ^3H distribution in November 1990 (Reilly et al. 1994). This case reproduces the sharp concentration gradients required to reproduce the low tritium values that were observed. The MOC model was advantageous for this problem because it minimises numerical dispersion and it can solve the governing equations for α_L of 0.0, which transport models based on finite-difference or finite-element methods generally cannot do. The results of the solute-transport simulation are consistent with the advective flow system determined by the second-level calibration and thus strengthen the case for the conceptual model. The coupling of the ^3H analyses and the transport model indicates where discrepancies between the measured and simulated concentrations occur, where additional data collection would be most useful, and where refinement of the conceptual model may be warranted.

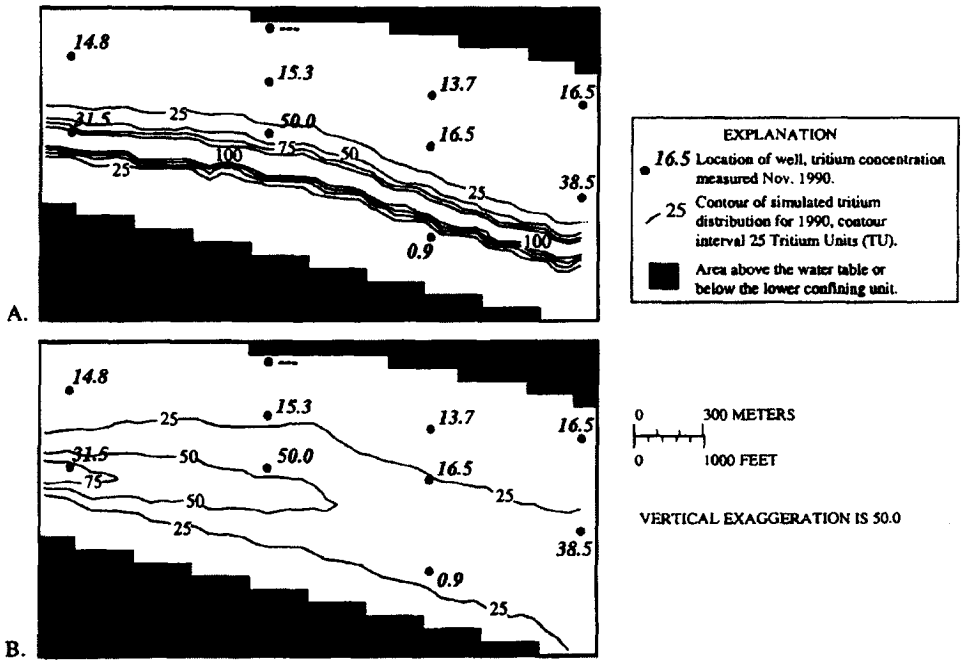

Fig.4.10 Simulated ^3H distribution at the end of 1990: (A) with dispersivity α_L = 0.0 m and α_T = 0.0 m, and (B) with dispersivity α_L = 0.15 m and α_T = 0.015 m. Contour interval 25 TU. Measured concentrations from samples obtained from wells in November 1990 are given for their location in bold italics (modified from Reilly et al., 1994).

This case study illustrates that environmental tracers and numerical simulation methods in combination are effective tools that complement each other and provide a means to estimate the flow rate and path of water moving through a groundwater system. Reilly et al. (1994) found that the environmental tracers and numerical simulation methods also provide a "feedback" that allows a more objective estimate of the uncertainties in the estimated rates and

paths of movement. Together the two methods enabled a coherent explanation of the flow paths and rates of movement while identifying weaknesses in the understanding of the system that require additional data collection and refinement of conceptual models of the groundwater system.

4.8 AVAILABLE GROUNDWATER MODELS

A large number of generic deterministic groundwater models, based on a variety of numerical methods and a variety of conceptual models, are available. The selection of a numerical method or generic model for a particular field problem depends on several factors, including accuracy, efficiency/cost, and usability. The first two factors are related primarily to the nature of the field problem, availability of data, and scope or intensity of the investigation. The usability of a method may depend partly on the mathematical background of the modeller, as it is preferable for the model user to understand the nature of the numerical methods implemented in a code. It may be necessary to modify and adapt the program to the specific problem of interest, and this can sometimes require modifications to the source code. In selecting a model that is appropriate for a particular application, it is most important to choose one that incorporates the proper conceptual model; one must avoid force fitting an inappropriate model to a field situation solely because of the model's convenience, availability, or familiarity to the user. Usability is also enhanced by the availability of pre-processing and post-processing programs or features, and by the availability of comprehensive yet understandable documentation.

A large number of public and private organisations distribute public domain and (or) proprietary software for groundwater modelling. Anderson et al. (1992), in their review of groundwater models, list 19 separate software distributors and provide brief descriptions of several codes (Anderson et al. 1992). The availability of models on the internet is growing. Some World Wide Web sites allow computer codes to be downloaded at no cost whereas other sites provide catalogue information, demonstrations, and pricing information. The International Ground Water Modelling Center, Golden, CO (http://www.mines.edu/igwmc/) maintains a clearing-house and distribution centre for groundwater simulation models. Many U.S. Geological Survey public domain codes are available over the internet (http://water.usgs.gov/software/).

The Hydrogeologist's Home Page (http://www.thehydrogeologist.com/) is an example of a general groundwater-oriented Web site that provides links to a large number of software resources.

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CONSTANTS

a	year = 3.1558×10^{7} s
amu	atomic mass unit = $1.660\ 54\times10^{-27}$ kg
c	velocity of light (in vacuum) = $2.997\ 925\times10^{8}$ m·s^{-1}
cal	calorie = 4.184 J
e	elementary/electron/proton charge = $1.602\ 18\times10^{-19}$ C
eV	electronvolt = $1.602\ 18\times10^{-19}$ J
g	acceleration of free fall = 9.806 65 m·s^{-2}
h	Planck constant = $6.626\ 08\times10^{-34}$ J·s
J	Joule = 0.2390 cal
k	Boltzmann constant = $1.380\ 54\times10^{-23}$ J/K
m_e	electron mass = $9.109\ 39\times10^{-31}$ kg
m_n	neutron mass = $1.674\ 93\times10^{-27}$ kg
m_p	proton mass = $1.672\ 62\times10^{-27}$ kg
M/E eq.	mass/energy equivalence: 1 amu ≡ 931.5 MeV
N_A	Avogadro constant = $6.022\ 14\times10^{23}$ mol^{-1}
π	= 3.141 592 6535
R	gas constant = 8.314 51 J·K^{-1}·mol^{-1}
T	thermodynamic temperature = t (^{0}C) + 273.15 K
V_m	molar volume (= 22.41 L·mole^{-1} at STP)

SUBJECT INDEX

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