

Interim Report

R&D Project 0295

Geochemical Process Modelling

British Geological Survey

October 1992

R&D 0295/8/A

Geochemical process modelling:
Review of models

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Interim Report 0295/8/A

This report has been produced
under contract to the
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EXECUTIVE SUMMARY

This is a report of the *Geochemical Process Modelling* project, which is concerned with the modelling of contaminant transport in the subsurface. The aim of this document is to present a review of models that can be used to help understand, predict, and control the migration of pollutants in the subsurface. The next report in this series (0295/9/A) provides a directory of models.

Approaches to modelling the processes that affect subsurface contaminants are described and discussed in terms of their applicability under various circumstances.

Although some specific recommendations are made on the choice of model codes, it is emphasized that model choice is a complex issue that will be covered in detail later in the project.

Analytical solutions can in some circumstances be more useful than complex numerical models, however it is numerical models that are of primary concern.

Simple flow models which can provide flow directions and travel times are well established and can be used with some confidence. For the immediate future these may be the most suitable models in many circumstances. Numerous codes exist and they are (mostly) reliable, therefore consideration of support and user-friendliness are of paramount importance in model choice. Codes worthy of particular consideration are: MODFLOW (with MODPATH), FLOWPATH, and QUICKFLOW.

To obtain concentrations, simple transport models (often referred to as 'convection-dispersion' models) can often be useful. These include advection, dispersion and (linear) sorption processes. There are many codes in this category, the better known ones include: MOC, SUTRA, Random Walk, HST3D and AQUA. Significant problems exist with the ability of models to solve the equations involving both advection (convection) and dispersion, and a variety of quite distinct numerical methods are used. The relationship between aquifer heterogeneity and dispersion parameters is still a controversial research area.

For fractured porous rocks, such as the Chalk, the process of molecular diffusion into the relatively immobile matrix water is probably the dominant dispersive process under most conditions. Particularly suitable models fall into the 'double porosity' category and codes worth considering include: SWIFTII, FRACFLOW and TRAFRAP-WP. But further code development specifically for the Chalk aquifer would be useful, provided efforts are made to collect validation data.

Multiphase flow modelling is still in its infancy in hydrogeology. In particular, satisfactory modelling of dense non-aqueous phase liquid (DNAPL) must await a better conceptual picture of their subsurface behaviour. The modelling of lighter than water liquids, such as oil, is likely to be more successful; SWANFLOW is a leading but limited code. Where the pollutant (often DNAPL) forms an immobile source via dissolution, simple advection-dispersion models can be applied, but research is needed to establish the nature of

the 'source term'. Models suitable for modelling multiphase flow in fractured rock have yet to be developed into tools suitable for use other than in the petroleum industry or for fundamental research.

The different approaches and capabilities of geochemical models are discussed and the more popular programs are highlighted. Recommended programs are MINTEQA2 (USEPA) for chemical speciation especially for the transition and heavy metals, NETPATH (USGS) for backward in time modelling especially of aquifer systems, and PHREEQE (USGS) for forward in time modelling including mass transfer and reaction path simulation. PHREEQM which is PHREEQE in a mixing cell flowtube looks promising for 1-D simulations of solute transport with reaction. These programs are all available free of charge or can be bought at a nominal cost. A review of up-to-date sources of thermodynamic data is also given. Geochemical models should prove useful for sensitivity analyses, for interpreting groundwater quality data, for designing monitoring programmes and in providing a solid foundation for the formulation of aquifer protection policy.

Few models have been developed for microbial transport; however, the combination of the model BIOPLUME II with the decision support system OASIS is an interesting development.

There are many areas of uncertainty which require further research. Mostly the needs are for field and laboratory work to provide data for model validation and parameters for process equations. Research sites similar to those established in North America would greatly benefit the research community. Broad areas worthy of attention include: characterization of fractured rock, practical (field-scale) models of the unsaturated zone and multiphase processes.

Model development effort would probably be best directed to: the Chalk aquifer, field-scale models of the unsaturated zone, and the coupling of chemical and biochemical process models with transport models.

1. INTRODUCTION

Groundwater models are tools of growing importance for understanding and managing groundwater systems. Models provide a rational approach to predicting the behaviour of groundwater based on physical, chemical and biochemical laws and available data (which are used in model calibration and validation).

1.1 Scope of the report

This report reviews models not 'modelling'. It is intended that by the end of the current project the reports, taken as a whole, will have covered all important aspects of modelling; however, at this stage modelling methodology, in particular, remains to be covered. Methodology includes such issues as: model choice, data needs, problem formulation, risk analysis, verification, calibration, and validation. These are not peripheral issues for broader-minded practitioner of modelling: without due consideration to these aspects of the process of model application the results obtained will be at best questionable and often misleading.

Most groundwater models can be described either as site-specific ('bespoke') models, or as generic models. Many bespoke models are in use in the UK having been developed for a particular customer (e.g. water authority) - most early models were of this type. More recently, general-purpose codes that could be adapted to many sites with similar geological and geochemical characteristics have been developed. It is this latter group of 'generic' models that is of primary interest here although it is understood that models will (outside research endeavours) usually be applied to site-specific problems.

Analytical, semi-analytical and numerical models have all been considered in the study, although the latter class is of dominant importance (see Appendix A).

Another model classification is based on model use, three categories are normally recognized: *prediction models*, *management models*, and *identification models* (see Appendix A). Mostly, this review is concerned with prediction models.

1.2 Suitable models

The rate of production of groundwater models is so high that it gave rise as early as 1978 to the establishment of The International Ground Water Modeling Center (IGWMC), which is supported largely by the US Environmental Protection Agency (EPA). The IGWMC, which now has offices both in the USA and Europe, aims to help list, evaluate and distribute those models. There are also a growing number of independent groundwater software distributors which provide similar services on a commercial basis.

There are many models because of the many special circumstances that can arise in the subsurface and because of the different specialized approaches that have been developed in order to handle those circumstances as efficiently as possible. In principle, there would seem no bar to formulating a single model which would include all of the subsurface

processes that are included in existing models. The problem would then be to code such a model and to find a computer large and powerful enough to run that code. Even as a long-term goal, the construction of such a model appears at present to be totally impractical.

For the foreseeable future it will be necessary to work with a family of models and to exploit the special (simplifying) features of the hydrogeological situation under study in order to produce practical tools.

1.3 Model choice

The choice of a model is a sufficiently complex task that it has always been the intention within this project to deal with it under 'Modelling Methodology' which will be reported on later. While not wanting to pre-empt that work, it is perhaps helpful to indicate the nature of the task. It involves consideration of: model use, project funding, data availability, data quality, user experience, project deadlines, code validation, quality assurance practices. This complexity is widely recognized in environmental modelling and some groups have begun producing 'decision support' software to aid the modeller in making a choice.

Given this situation it is not easy to provide clear-cut recommendations on which models should be adopted by the NRA. It is not suggested that such decisions could not be made, but that it requires much more interaction and discussion. Despite these comments, we have tried to provide some initial indications of models worthy of particular consideration. Most of these are widely-used, well-supported, generic models.

A recent survey of model use in was briefly reported on by Geraghty & Miller (1992), and that report is summarized in Appendix C. It identifies the ten most widely used software packages. Such surveys are valuable indicators of model suitability. Apart from implicitly being a useful tool, a widely used model will be well-tested and corrected (as updated versions appear), it will be worthwhile for developers to add user-friendly facilities to the code, documentation and support will be good, and the results from such a code will be more readily accepted than those from a more obscure code (even though that latter code might be more applicable to the problem under consideration).

1.4 Database of models

Models can be sorted into many groups depending on the priority of characteristics considered important. For example, models could be first sorted according to whether they are analytical or numerical (computer) models, and then into subgroups depending on how many spatial dimensions (one, two or three) can be simulated. Clearly there is no unique method of sorting and a single model will fall into a number of groups. Therefore, as part of this project it was decided to create a computer database of models. With such a method of storage, models can be sorted into groups according to virtually any set of criteria (depending on the characteristics recorded) with any hierarchy of those criteria.

At present the database is on a personal computer in dBase IV, but it could easily be transferred to another database system. The database is still being developed and updated. It will eventually be handed over to the NRA with a set of 'macros' to allow some standard forms of search to be carried out with ease.

Maintenance of the database is potentially an unending task as new and updated models appear continually. The database is, however, likely to have only a limited lifetime as it is inevitable that electronically accessible databases of models held by international organisations will eventually become available.

1.5 Directory of models

Since an electronic database is not always a convenient source of information, a directory of models has been produced as the next report in this series (R&D 0295/9/A). The directory is partly based on the database mentioned above and is partly a collation of information gathered from a variety of other sources. The directory has three parts: (i) it lists model names by a variety of application areas (*Category Tables*), (ii) it provides two tables of model features (*Features Tables*), and (iii) it gives brief descriptions of models (*Model Descriptions*). The tables are all in alphabetical order for ease of access, although it is recognized that that will not always be a convenient format.

It is intended that the directory should be updated at least once before the end of the project. The first version is very much a first draft: it certainly has omissions and could be improved in a number of other ways.

The directory and - to a lesser extent - this review, mention many models which have not been widely used. It is useful to know about such models since: (i) they may contain a novel approach which could be emulated, (ii) the codes could be suitable for incorporation into modelling packages being developed (even though they are not adequately supported or user-friendly for use in their own right), (iii) the models may be used (or proposed for use) by contractors to the NRA, and (iv) they point to researchers (and their publications) which could be relevant to similar investigations.

1.6 Follow-up and future work

Inevitably, there are a number of inadequacies in the current model review and the associated model directory; some have already been mentioned. Some models will have been overlooked and not all features have been included in the features table (it has not yet been possible to obtain adequate information for many models). Also, model development is rapid: new models are continually being introduced and the features of models are being modified and added to. It is therefore intended that the model database, the model directory will be updated continually through the rest of the project and a revised review reflecting those changes will be presented towards the end of the project. Therefore any constructive criticism of the review would be of value.

Appendix B provides a list of specific follow-up topics that we consider require some further coverage. Comments on those suggestions would also be welcomed.

The reader may not find all topics of interest covered in this report. More detail on processes is to be found in the previous report (R&D 0295/7/A) in this series. Details on specific models is given in tabular form in the model directory report (R&D 0295/9/A). Also, as mentioned above, it is intended that a wide variety of model related topics are to be covered in later reports from the current project. Mostly these relate to 'Modelling Methodology' which is seen as a separate and important topic. Appendix B gives a tentative list of subjects to be covered. The reader is encouraged to suggest further items to add to that list.

1.7 Structure of this report

The modelling of physical, chemical and biochemical processes are discussed separately, and specific models are discussed within those sections.

Separate attention is given to modelling of the unsaturated zone, multiphase transport and transport in fractured rock. This inevitably leads to some overlap and to topics not necessarily appearing where the reader might expect to see them covered. We use the term 'simple transport models' to cover all models that at least include advection but exclude chemical or biochemical reactions. This includes the important class of models often referred to as 'convection-dispersion' models.

Research needs are listed in a separate section towards the end of the report. Those needs include basic research on processes which is necessary for model development and use.

The first appendix provides a brief discussion of models according to their use and formulation. The second appendix is concerned with future work of the project. And the last appendix gives the results of a recent survey on model use.

2. PHYSICAL PROCESS MODELS

2.1 Introduction

The current project is concerned with contaminant transport arising from typical pollution problems. In order to understand and predict contaminant transport, an understanding of the groundwater flow system is a necessary prerequisite. Also, a particularly useful approach to pollutant modelling is to establish the flow field, ignoring the influence on flow of the pollutant, and then to apply some technique of 'particle-tracking' to establish the paths and travel times of pollutants. Because well-calibrated flow models are often the key to understanding groundwater pollution, it has been decided to list flow models alongside contaminant transport models, but not to dwell on their detailed descriptions or relative merits. Of course, when the pollutant is an immiscible fluid (e.g. oil or solvent), it is the flow of the contaminant itself that is important.

2.2 Flow models

2.2.1 Saturated flow of water

The equation describing three-dimensional fluid flow through a saturated porous medium is normally obtained by combining Darcy's law with the principle of mass conservation giving:

$$S_s \frac{\partial h}{\partial t} - \nabla \cdot (K \nabla h) - q_s = 0 \quad (2.1)$$

where h is the head, t is time, S_s is the specific storage, K is the hydraulic conductivity (tensor) and q_s is a volumetric source term (per unit volume). The equation is not sufficient to describe a system (and construct a model), also required are: (i) a set of initial conditions (the head distribution, h_0 , at some particular time, t_0):

$$h(x, y, z, t_0) = h_0(x, y, z) \quad (2.2)$$

and (ii) the boundary conditions. These boundary conditions will normally consist either of specified boundary heads:

$$h = h_i \quad (x, y, z) \in \Gamma_i \quad (2.3)$$

for a given section of boundary, Γ_i , or specified head gradients normal to the boundary:

$$\frac{\partial h}{\partial n} = g_i \quad (x, y, z) \in \Gamma_i \quad (2.4)$$

The head gradient can be replaced by a flux using Darcy's law.

Equation (2.1) is often integrated vertically through an aquifer or formation to give:

$$S \frac{\partial h}{\partial t} - \nabla \cdot (T \nabla h) - Q_s = 0 \quad (2.5)$$

where S is the storage coefficient, T is the transmissivity, and Q_s is the volumetric flux (per unit area) into the system. Again, both initial and boundary conditions are also required.

Most commonly, the term Q_s will derive from recharge, R , and a set of point sinks (e.g. wells), Q_{si} , at points (x_i, y_i) :

$$Q = R - \sum_i Q_{si} \delta(x_i - x) \delta(y_i - y) \quad (2.6)$$

2.2.2 Unsaturated flow

When air and water coexist in a porous medium, there is a pressure difference at the interface known as the capillary pressure, P_c ; the negative value of this pressure is known as the 'suction' or 'tension'. A quantity known as the capillary pressure head, ψ , is defined by:

$$\psi = \frac{P_c}{\rho g} = z - h \quad (2.7)$$

where z is elevation above some (arbitrary) datum, ρ is the density and g is the acceleration due to gravity. The capillary pressure head is a function of the volumetric water content, θ .

As the degree of saturation, θ , of a rock changes, so does the head (or suction pressure), h . Rocks with small pores will have higher saturations for a given suction than rocks with large pores. Therefore the suction-saturation curve, $\theta(h)$ (also known as the 'soil-water characteristic curve') is an important characteristic of an unsaturated rock. It is not a unique function because of hysteresis.

Also, as a generalization of saturated flow, Darcy's law is taken to pertain but with a hydraulic conductivity which is highly sensitive to head or water content. Darcy's law and mass conservation give the Richards equation:

$$F \frac{\partial h}{\partial t} - \nabla \cdot (K \nabla h) = 0 \quad (2.8)$$

The moisture capacity, F , is defined by:

$$F = \frac{d\theta}{dh} = - \frac{d\theta}{d\psi} \quad (2.9)$$

which plays the same role as the specific storage in the flow equations for the saturated zone.

Because of the interdependence of the characterizing parameters, formulations of the flow equations are variously given in terms of two of the three 'independent' parameters h , θ and ψ .

A major difficulty in modelling unsaturated flow is in establishing theoretical and empirical relationships $\theta(h)$ and $K(h)$, or the equivalent functions; these vary greatly from one rock type to another. A variety of functional forms, with varying numbers of empirical parameters, have been suggested for these relationships (El-Kadi 1985a,b). Similarly, models differ in the manner in which the functions need to be described: normally either via a set of empirical parameters or a computer routine.

Ignoring hysteresis, soil moisture is often expressed in the form:

$$\begin{aligned}\theta(h) &= \theta_r + (\theta_s - \theta_r) f_\theta(h) & h < h_0 \\ &= 0 & h \geq h_0\end{aligned}\quad (2.10)$$

where θ_s is the saturated water content (the porosity), and θ_r is the residual water content. Some examples of the functions f_θ (which range in value from zero to unity) are given in Table 2.1.

Table 2.1 Commonly used two-parameter functions $f_\theta(h)$.

| $f_\theta(h)$ | h_0 | Source |
|-------------------------------|-------|-------------------------|
| $a/(a + h ^b)$ | 0 | Brutsaert (1966) |
| $a/(a + (\ln h)^b)$ | -1 | Haverkamp et al. (1977) |
| $(a + h ^b)^{\frac{1}{b}-1}$ | 0 | van Genuchten (1980) |
| $(a/ h)^b$ | a | |

There are even more expressions for $K(h)$ and these tend to vary greatly in their mathematical form. However, most commonly, hydraulic conductivity is expressed in the general form:

$$\begin{aligned}K(h) &= K_s f_K(h) & h < h_0 \\ &= K_s & h \geq h_0\end{aligned}\quad (2.11)$$

where K_s is the saturated conductivity. Some examples of the dimensionless functions f_K (which range in value from zero to unity) are given in Table 2.2.

Table 2.2 Some commonly used $f_K(h)$ functions for equation (2.11)

| $f_K(h)$ | h_0 | Source |
|-----------------------------|----------|-------------------------|
| $\exp(-\alpha h)$ | ∞ | Gardner (1958) |
| $ h / h_{cr})^{-b}$ | h_{cr} | Brooks and Corey (1966) |
| $\alpha / (\alpha + h ^b)$ | 0 | Haverkamp et al. (1977) |

While the classical Richards equation - equation (2.8) - remains the most popular description of water flow in the unsaturated (vadose) zone, the value of that formulation for application at the field scale has been questioned and several alternative formulations have been proposed. Those alternatives have specifically been aimed at overcoming problems associated with preferential flow and heterogeneity.

It is generally agreed that preferential flow through macropores (normally defined as those wider than about one millimetre) does not follow the traditional Richards equation. Instead this rapid flow phenomenon has been approximated (e.g. Levy and Germann 1988) by a kinematic wave equation of the form $q = bw^\alpha$, where q is the flux, b is a constant conductance, w is the water content, and α is a dimensionless exponent.

Preferential flow is a particular problem when considering the transport of highly toxic substances, for which even a very small percentage of fast transport to the water table can have harmful consequences.

Unsaturated flow is one form of multiphase flow, and the problem is sometimes formulated as one of air flow as well as water flow (e.g. Pinder and Gray 1977).

2.2.3 Multiphase flow

Many contaminants, such as organic solvents and oil, enter groundwater systems in the immiscible phase. Although multiphase systems have long been studied in the petroleum field, in the hydrogeological field progress has only just reached the point where models are being produced. But there are differences in the two fields including: financial constraints on model size and complexity, and physical differences such as with unsaturated behaviour and DNAPL migration.

For reviews of ('groundwater') modelling multiphase transport in the subsurface see Abriola (1984), Allen (1985), Pinder and Abriola (1986) and Abriola (1988). Reviews with less emphasis on modelling were given by Parker (1989) and Mercer and Cohen (1990).

Two broad classes of model are in use: those which only consider migration in the miscible phase and those which consider two or more fluids. When considering only miscible-phase transport, standard solute transport codes can be applied (Section 2.3), although special consideration will have to be given to: the source term, biodegradation and sorption.

Dense organics may pass through the unsaturated zone and the saturated zone so rapidly that there would be little value in modelling that downward migration. Such liquids may simply become trapped and then provide a fairly constant pollution source as a result of dissolution at the water/organic liquid interface. This is a common case where miscible phase models are of value.

For multiple fluids, models usually assume the existence of a continuum in which the fluids coexist. One fluid flow equation is required for each phase, and these equations are coupled by the (capillary force controlled) relative saturation and permeability relationships for the fluids in the porous medium. Unfortunately, this complex description is further complicated by transfer between phases; for example, volatile organic liquids will both dissolve into groundwater and assume a gaseous phase: this transfer is characterized by 'partition coefficients'. Models for multiple fluids can thus be (hierarchically) subdivided into: sharp interface models, those that include capillarity, and those which also include transfer between phases.

When fluid saturations become small the phase becomes discontinuous and consists of isolated bodies of fluid ('globules' or 'blobs'). Most models cannot represent the transport of such blobs since the permeability functions usually reduce to zero once the phase becomes discontinuous.

In fractured media capillary effects can be dominant. The wetting phase (often water) tends to occupy the smaller pores while the non-wetting phase tends to occupy the larger pores and fractures, and is thus susceptible to a larger permeability. The physical parameters affecting such flows are: density; viscosity; interfacial tension; wetting properties; and fracture widths, wall roughnesses, and dips. There is as yet very inadequate data on the characteristic parameters for real fracture systems (e.g. Chilton et al. 1989). Multiphase flow modelling of double-porosity formations is still in its infancy in hydrogeology. However, almost identical problems have been studied by petroleum reservoir engineers with regard to the processes of gas/oil drainage and water/oil imbibition (which are analogous to the hydrogeological processes of unsaturated flow and pollution by immiscible fluids, respectively). There are however continuing difficulties; in particular, there is disagreement over the degree of capillary continuity between neighbouring matrix blocks. A recent paper by Rossen and Shen (1989) provides a brief review of the modelling literature, while Van Golf-Racht (1982) and Torsaeter et al. (1987) provided descriptions of the processes involved.

Johnson et al. (1990) considered the problem of removal of volatile organic chemicals from the subsurface by air-phase movement. They presented simple mathematical models that can be employed as screening tools to evaluate the potential for remediation by in situ soil venting.

One problem that has attracted attention recently is that of using models to estimate the volumes of liquid spills, which is obviously important in planning clean-up (e.g. Farr et al. 1990, Parker and Lenhard 1990).

Saline intrusion can often be adequately modelled as a two-phase (saltwater and freshwater) problem with negligible capillary forces (the first class of multiple-fluid models). Similarly, water flow in the unsaturated zone can be considered as a two-phase (water and air) problem (the second class).

It must be stressed that present multiphase models remain speculative since adequate laboratory and field validation has yet to be performed, especially in heterogeneous media. Also, much work remains to be done in order to establish constitutive relations for use in models. Most important are the permeability-saturation-pressure (k-S-P) relations. Researchers are now beginning to introduce relations that include hysteresis (e.g. Lenhard et al. 1989). The effects of wettability on hydrological properties has been reviewed by Anderson (1987a, b, c), who covers phenomena observed in studies of oil production but which are of more general applicability.

The ARMOS and FEDAR models can be applied to light hydrocarbons in an unconfined aquifer. SWANFLOW is a more general three dimensional code which is used to aid clean-up work.

2.2.4 Flow in fractured rock

Fracturing is important in both of the two major aquifer of the UK: the Chalk and the Triassic Sandstones. It is therefore appropriate that significant attention should be given to the problems of describing and modelling flow and transport (Section 2.5) in fractured rock.

Two types of models have been studied in relation to flow through fractured *porous* media. In 'double porosity' models, flow is assumed to take place only in the fractures (or fissures) with the matrix water being effectively immobile. In double permeability models, flow takes place in both the fissure and matrix systems (Figure 2.1).

Models of transport in fractured porous rock often consider the matrix water to be immobile. This is a reasonable assumption for the Chalk under most circumstances. From tracer tests it is known that rates of movement of groundwater through the Chalk's secondary fissure system can often be in excess of 100 metres per day. In the primary fissure system, a hydraulic conductivity, K , of the order of 0.01 m/d to 1 m/d, and a porosity of 1% and a head gradient of 10^{-3} gives rates of movement of the order of a few millimetres a day. For

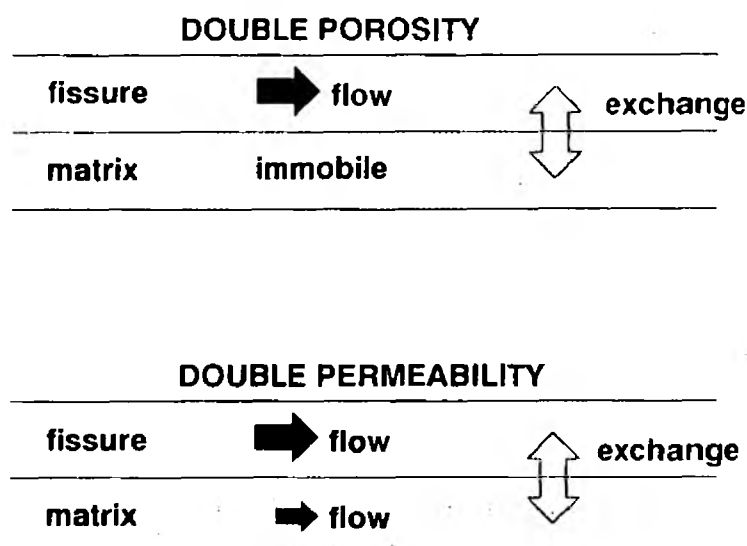


Figure 2.1 Schematic representation of the difference between double-porosity and double-permeability models.

the same gradient, the rate of movement in the matrix (assuming K is 0.001 m/d and the porosity 35%) will only be of the order of a millimetre per year. (Whether or not a double porosity model can be used for solute transport, as opposed to water flow, is discussed later.)

The behaviour of groundwater in *unsaturated* fractured rock is significantly different from that in the saturated zone, mostly as a result of capillary forces. The flow patterns can be exceedingly complex even in idealized laboratory systems or in computer simulations. Exotic theories - involving such concepts as percolation, fractal geometry and chaos - have been brought to bear on these problems. In the face of such difficulties, practical models have had to be based on fairly crude physical concepts. This topic is well covered by Evans and Nicholson (1987) and Dykhuizen (1987).

2.3 Simple transport models

2.3.1 Types

For many applications (for example, protection-zone delineation and pollution source identification) all that is required from a model is an indication of the flow pattern and times of flow along various flow paths. Many simple hydraulic models have the capability to carry out such flow-path computations built into them, but there are also a number of special codes available for post-processing the head distributions produced by other models to generate flow-paths. These types of models will also be of interest to the NRA.

Models at one level of complexity above the hydraulic models include solute transport of a single species via a advection-dispersion (convection-dispersion) equation. These models often include linear source and loss (decay) terms and are based on an assumption of local chemical equilibrium.

2.3.2 Advection

Let J_a be the advective flux of a solute (contaminant) in water flowing through a saturated system with velocity v and dynamic porosity n , then:

$$J_a = nvc \quad (2.12)$$

where c is the mass per unit volume of solution (concentration) of the solute.

2.3.3 Pathline models

Models which include just advection in the flowing groundwater are normally solved by tracking individual particles through a previously determined flow field; such models are normally referred to as 'pathline models'.

In a short project funded by the NRA, BGS undertook to evaluate models that might be suitable for the delineation of protection zones around individual groundwater sources. The recommendation from that work (Barker et al. 1991) was that a pathline model would be adequate and, more specifically, the FLOWPATH model (Figure 2.2) should be used (although it was noted that it had not been possible to evaluate the WHPA model). One of the reasons for this recommendation was the flexibility in outputting results from FLOWPATH to other packages. Other pathline models worth considering include: ASM, CAPTURE, GWPATH, MODFLOW with MODPATH, QUICKFLOW. Also, the long-established public domain code RESSQ, written in Fortran, can readily be adapted for simple problems that arise at the beginning of a field investigation: RESSQ is distributed as part of the AGU-10 package of software.

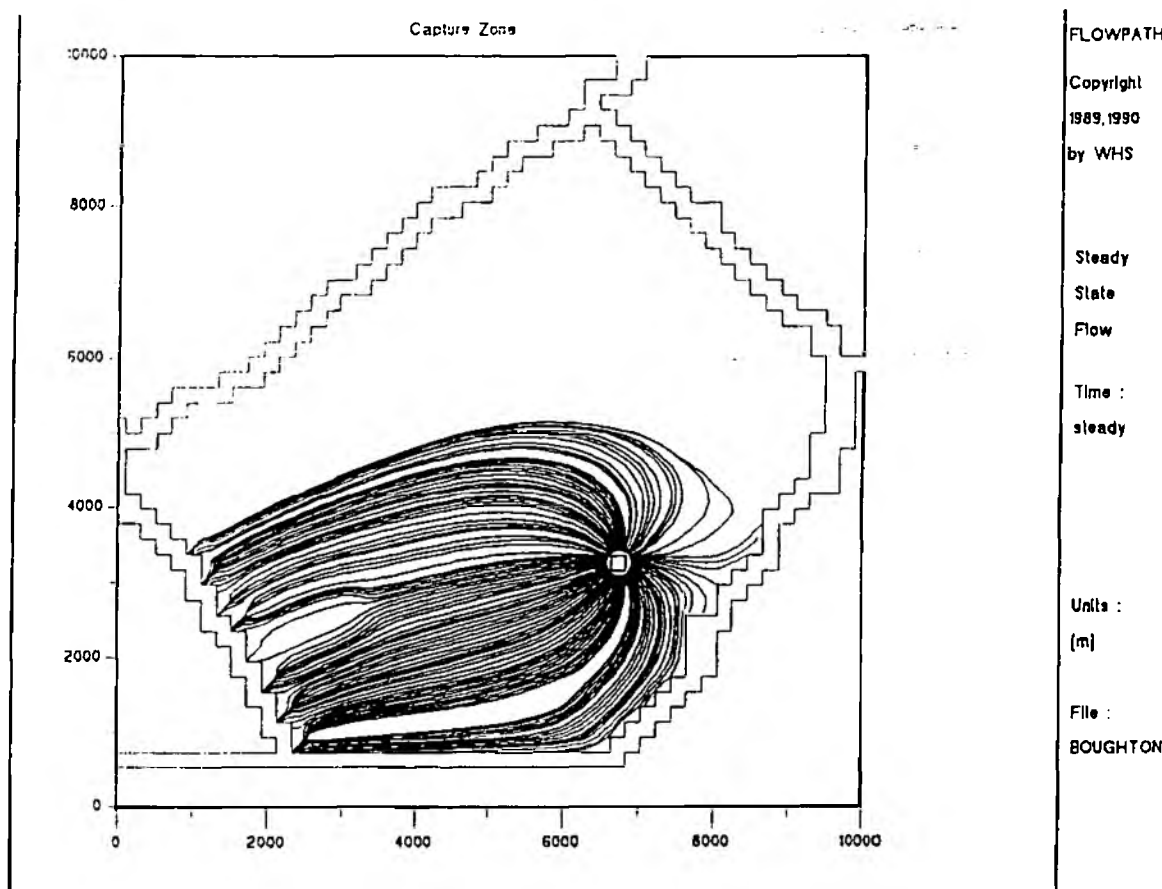


Figure 2.2 Typical example of output from the FLOWPATH model.

2.3.4 Density coupling of flow and solute transport

When the density of water is near constant through the region of interest (the solute is dilute), the equations of flow and solute transport are effectively uncoupled and the equations given previously for flow and transport can be applied. In a significant number of circumstance, however, the solute(s) significantly effect the flow regime; for example, in coastal regions where freshwater and saltwater meet. This is mostly due to the change in density with concentration, which is usually described by the equation:

$$\rho(c) = \rho_0 + \frac{\partial \rho}{\partial c}(c - c_0) \quad (2.13)$$

where ρ_0 and c_0 are 'base' density and concentration such that $\rho(c_0) = \rho_0$; normally the base concentration is zero and the density that of pure water. The density gradient $\partial \rho / \partial c$ is usually assumed to be constant; for example, a value of about 700 kg/m^3 (for c in dimensionless units) is appropriate for saline intrusion problems.

The flow and solute transport equations are also coupled by the very weak dependence of viscosity on density, since hydraulic conductivity is inversely proportional to viscosity. However, this complication is invariably ignored.

If density depends on concentration and concentration itself varies spatially, Darcy's law must be expressed in a form which can account for the effect of a spatial density variation:

$$q = -\frac{k}{\mu} \cdot (\nabla p - \rho g) \quad (2.14)$$

where q is the volumetric flux vector, k is the permeability tensor, μ is the dynamic viscosity of the fluid, p is the pressure, and g is the downward gravity vector. Note that the density and viscosity are also functions of temperature, but we are here restricting our attention to isothermal systems.

The above equations for the density/concentration relationship and Darcy's law must be taken into account in the mass balance equations both for the fluid and the solute. The equation for time-dependent concentration needs no significant modification but the fluid flow equation can no longer be expressed in terms of head. The equivalent equation is normally expressed in terms of the time derivatives of both the pressure and the density (or concentration). Different models make different approximations and include a variety of extra processes such as rock compression and variable saturation: the resulting equations are complex and unlikely to enlighten the reader. For details, the reader is advised to consult the manual for the model of interest.

SUTRA is an important example of a model that includes this coupling.

2.3.5 Hydrodynamic dispersion

In any heterogeneous medium a solute spreads during advective transport due to velocity variations.

The dispersive flux is normally expressed by a 'Fickian' equation:

$$J_D = -nD\nabla c \quad (2.15)$$

where D is the dispersion coefficient (or, more generally, tensor) which includes contributions from both hydrodynamic (mechanical) dispersion and molecular diffusion.

The above equation has attracted the attention of theoreticians in recent times because it has been found empirically that the dispersive phenomenon cannot normally be characterized by a constant Fickian dispersion coefficient: the term 'non-Fickian' dispersion is then applied.

For isotropic media the components of the dispersion tensor (ignoring molecular diffusion) are often written in the form:

$$D_{ij} = \alpha_T V \delta_{ij} + (\alpha_L - \alpha_T) V_i V_j / V \quad (2.16)$$

where α_T and α_L are the longitudinal and transverse dispersivities, V_i is the velocity in the i direction and V is the (absolute) magnitude of the velocity. For Cartesian coordinates with flow in the x direction this becomes simply:

$$D_L = D_{xx} = \alpha_L V \quad (2.17)$$

$$D_T = D_{yy} = D_{zz} = \alpha_T V$$

where D_L and D_T are referred to as the coefficients of longitudinal and transverse dispersion, respectively. Analytical models of dispersion normally make the assumption of one of the coordinates being parallel to the flow direction.

In pollution studies the dispersion phenomenon is normally beneficial as it tends to reduce concentrations, and the view is sometimes taken that it should be ignored in modelling studies and regarded as providing an added safety factor. It has certainly proved difficult to make a rational choice of parameter values to put into dispersion models (particularly because of scale-dependent behaviour), which also tends to negate the value of including dispersion. Perhaps a middle path is to include dispersion in some relatively simple manner (to avoid computational problems associated with accurate modelling of the dispersion-convection equation) and then to present results for a range of characteristic dispersion parameters.

Field and laboratory dispersion experiments have shown that the scale of measurement is typically between 1 and 100 times the dispersivity (e.g. Anderson 1984). This at least gives a starting point for choosing values in 'what-if' simulations when no field investigation (e.g. tracer test) is possible. In double-porosity media, such as the Chalk, molecular diffusion into the relatively immobile matrix water is likely to be the dominant dispersion mechanism and should be included explicitly in models of such systems.

2.3.6 Decay

The rate of loss of contaminant due to simple decay (characterized by a decay constant λ or, equivalently, a half life) is

$$r_{\text{decay}} = -n\lambda c \quad (2.18)$$

2.3.7 Linear sorption

The rate of loss due to sorption described by a simple linear isotherm (characterized by a distribution coefficient, K_d , is

$$r_{\text{sorption}} = -\rho K_d \frac{\partial c}{\partial t} \quad (2.19)$$

2.3.8 Advection-dispersion equation

The above expressions can be combined into a mass balance equation stating that the rate of change of mass within any volume must equal the net flux into that volume less the losses within the volume.

$$\frac{\partial c}{\partial t} = \nabla \cdot (J_a + J_D) - r_{decay} - r_{sorption} \quad (2.20)$$

Inserting expressions for the individual flux and loss terms into this equation, and rearranging gives:

$$R \frac{\partial c}{\partial t} = \nabla \cdot (D \nabla c) - \nabla \cdot (vc) - n\lambda c - r_{chem} \quad (2.21)$$

where r_{chem} is introduced to represent all losses due to chemical reaction and R is known as the retardation factor:

$$R = 1 + \rho K_d / n \quad (2.22)$$

Equation (2.20), with or without the decay and sorption terms, is referred to as the 'advection-dispersion' or 'convection-dispersion' equation.

2.3.9 Solving the transport equations

From a mathematical point of view the advection-dispersion equation can behave as: a 'parabolic equation', if the advective term is negligible; as a 'hyperbolic equation', if the dispersive term is negligible; or anywhere between those extremes. Unfortunately, different numerical formulations are appropriate to solving parabolic and hyperbolic equations. Standard finite difference and finite element techniques are suited to parabolic equations while the 'method of characteristics' and 'particle tracking' methods (Appendix A) are appropriate to hyperbolic equations. Therefore different model formulations are appropriate in different situations and in some cases no formulation will be well suited to conditions across the whole region of interest. Much current research is aimed at producing hybrid or adaptive methods which are applicable over a wide range of scenarios.

This is an issue that will be addressed further in the part of this project concerned with modelling 'methodology'.

2.3.10 Advection-dispersion models

Numerous models are concerned with solving the advection-dispersion equation. Most of these include decay and linear sorption as these terms can be very easily included in the analytical or numerical simulation.

The most popular 2-D models are: MOC, SUTRA and Random Walk. If a 3-D code is necessary, particular consideration should certainly be given to: the USGS code HST3D, CFEST, FTWORK (which is compatible with MODFLOW) and to SWIFT. However, other codes should not be ignored and may have particular features suitable to the problem in hand. The (proprietary) PC code AQUA is becoming popular due to its user-friendliness and marketing; a similar but far less well-known German code is FEFLOW (there are two codes with that name).

2.4 Saline intrusion models

2.4.1 Saline intrusion

Intrusion of sea water into aquifers is a problem of concern in several coastal aquifers in the UK. The situation is perhaps most accurately described as one of solute transport in water. The transport equation then takes the form of the convection-dispersion equation so the models mentioned above can be applied. However, if the interface between saltwater (at ocean concentrations) and freshwater is relatively sharp, details of the dispersion process are of little practical interest. Therefore it is often assumed in modelling saline intrusion that a sharp interface exists and then the problem is analogous to multiphase flow: but dissimilar in that both 'phases' (seawater and freshwater) are highly mobile and also because the interfacial (capillary) forces can be ignored. It is normally assumed that a sharp interface correspond to the isochlor corresponding to a salinity which is the average of that of the 'freshwater' and the saltwater.

Where the freshwater from the aquifer meets the seawater there is a 'transition zone'. The width of the transition zone is determined by a number of factors. The primary geological factor will normally be the branching nature of the flow paths in the rock which gives rise to the mixing of water with different salinities (dispersion). Other factors affecting the transition zone are changes in pumping regimes, tides and recharge variations. Note that the seawater beyond the transition zone is mobile outside the transition zone, although rates of movement are normally expected to be small.

The main division of these models is between 'Fully Mixed' and 'Sharp Interface' models. Fully mixed models solve the density-coupled equations of flow and transport and these are exactly the same equations described previously. Indeed, general purpose solute transport codes (especially SUTRA) have been applied to coastal aquifer problems.

Sharp interface models are further divided into two groups: 'Hydrodynamic' and 'Hydraulic'. Hydrodynamic models are multiphase models which envisage three-dimensional flow but, unlike general multiphase models, ignore the capillary effects at the interface. Hydraulic models only differ from hydrodynamic models in that the flow equations are vertically integrated. This gives separate (at each areal point) equations for the movement of the freshwater and saltwater, or one of those and the elevation of the interface. Only two of those three need be computed as the third can be found by application of the

Ghyben-Herzberg approximation (see below), which is valid for horizontal flow conditions (with no vertical head gradients). The SWIM model of Sa da Costa and Wilson (1979) is a hydraulic model.

The hydraulic models are very effective for cases where saline intrusion is areally extensive and the interface is either known to be thin or there are insufficient data to warrant a dispersed interface simulation.

Assuming both a sharp interface and that hydrostatic conditions prevail through any vertical column of freshwater and throughout the saltwater, then the saltwater and freshwater pressures at the interface can be equated to give a relationship between the freshwater elevation above sea level, h_f , and the interface depth z_i below sea level:

$$z_i = \frac{h_f}{(\rho_s / \rho_f - 1)} \quad (2.23)$$

where ρ_s / ρ_f is the ratio of the densities of the saltwater and freshwater. The above equation is known as the Ghyben-Herzberg approximation. For typical seawater densities, the Ghyben-Herzberg approximation gives an interface depth, z_i , about forty times the freshwater elevation, h_f . This equation is the basis of nearly all analytical solutions to coastal aquifer flow as well as being fundamental to 'hydraulic' numerical models.

Special problems arise in fissured, coastal aquifers because of the rapid movement through the fissures and damping effect on solute transport of diffusion into the rock matrix. Double porosity models (discussed elsewhere in this report) can be relevant to such situations, but have rarely been applied.

Publications which review saline intrusion modelling include: Sa da Costa and Wilson (1979); Volker (1980); and Custodio (1985), who emphasizes the complex geological controls that make modelling difficult. Numerous case studies, including many model applications, can be found in a set of proceedings of the Saline Intrusion Meetings (SWIM) which have been held every two or three years since 1968.

None of the saline intrusion codes identified appears to be either well-supported or user-friendly. The SWSOR code is a 2-D hydraulic model worth some consideration. MOC DENSE (a variant of the popular MOC code) is applicable to saline intrusion. SUTRA is applicable to two-dimensional problems if the sharp-interface approximation is not considered valid, as is often the case when considering upconing to wells. For three-dimensional problems the USGS code HST3D could be applied. Because of local geological controls, saline intrusion models are very often site-specific codes.

2.5 Fractured rock flow and transport models

2.5.1 Major categories of fractured-rock models

To a great extent the differences between the various models in use reflect the different conceptualizations of the geometry of the fractures under consideration. Although the conceptual models are normally quite simple, the details of the mathematical and numerical formulation are formidable for fractured media. Only the general conceptual ideas will be described and discussed here.

An attempt has been made to divide models into distinct categories. This is only partly successful since many combinations of the various conceptual features of the models are compatible, so a specific model may fall into two or more of the categories specified below.

Models of fractured rock, both analytical and numerical, fall into one of two classes: spatially deterministic or spatially stochastic (random). In the former class all geometrical parameters (fracture positions, sizes, etc.) are given specific values, but in the latter class only distributions of values with specified statistics are given.

Three very distinct conceptualizations can be identified in fractured-rock models: 'equivalent porous medium', 'double-porosity', and 'discrete fracture'. Discrete fracture models are often spatially stochastic while the other two types are normally deterministic.

2.5.2 Equivalent porous medium (EPM) models

When the fracture density is high on the scale of interest, fractured rocks are often assumed to behave as would unfractured systems. Then models that have been developed for homogeneous rocks can be employed provided appropriate parameter values are used. Such models are termed *equivalent porous* (or *homogeneous* or *continuous*) *medium* models. This approach seems reasonable when it is recalled that even sedimentary aquifers can be regarded as *fractured* at the scale of the grains. However, Sagar and Runchal (1982) provide a cautionary analysis: in particular, a system of fractures might be well represented in terms of flow by an EPM model, but such a model may give very poor estimates of solute travel times. So these models are more likely to be effective in predicting groundwater flows than other transport processes.

Khaleel (1989) considers fractured basaltic rocks where the fractures are defined by the columns of matrix material. For uniform fractures he concludes that EPM models are applicable on a scale about 6 times the column diameter, but for a lognormal aperture this can be 20 to 30 times the diameter. Long et al. (1982) proposed that the EPM is acceptable provided a plot of the measured directional permeability has the form of an ellipsoid. Troisi et al. (1989), who considered only hydrodynamics, proposed a criterion for accepting the EPM approximation based on a point of discontinuity in a plot of Reynolds number against friction factor. Pankow et al. (1986) compared two contaminated sites in fractured rock and concluded the combination of characteristics made only one suitable for modelling using an EPM model.

These models can be employed provided either the fissures act independently of the matrix or the two act in unison, the latter condition is more likely than the former. For example, regional water resources models of the Chalk aquifer (Nutbrown 1975, Morel 1981) can replace the fissured system by a homogeneous one with storage and permeability values characteristic of the matrix and fissures combined.

2.5.3 Double porosity (DP) models

When a significant proportion of the total storage capacity of the system is provided by the rock matrix, while the fractures provide the dominant path for regional transport, a detailed study of the interaction of the fracture and matrix *phases* is required. Perhaps the simplest conceptualization of such systems is provided by double porosity models (sometimes confused with dual permeability models, Figure 2.1). One of the, several, origins of the concept appears to have been the paper by Barenblatt et al. (1960) who, in modelling pumping tests in fractured porous rock, envisaged two overlapping continuous media (the matrix and fracture phases corresponding to the *primary and secondary porosity*, respectively) with an exchange mechanism.

Double porosity models can be divided into two categories depending on the physical (and mathematical) description of that mechanism:-

Diffusive type. Diffusive DP models are those for which solute transport in the blocks of rock matrix can be described by Fick's law. The concentration within a matrix block is controlled by the variations within the fissure system, and the two concentrations are assumed equal at the surface of the blocks (unless there is a surface coating - fracture skin - on the blocks. The shapes and size distribution of the matrix blocks affect the behaviour; Barker (1985a, 1985b) introduced a mathematical formulation capable of covering all cases.

Fissured rocks have often been represented by sets of identical, equally-spaced parallel conduits (e.g. Grisak and Pickens 1980; Barker 1982). These models are mathematically equivalent to and correctly described as double porosity models. Bibby (1981) used such a (numerical) model to investigate pollution of the Chalk in East Kent, and Muller (1987) applied a very similar model to pollution in the Chalk in Cambridgeshire. Barker and Foster (1981) applied a numerical double-porosity model to transport in the unsaturated zone of the Chalk.

Quasi-steady-state (QSS) type. In QSS models, the matrix is characterized by a single local concentration and the diffusive flux, F , between the matrix and fissures is taken to be proportional to the difference between their concentrations:

$$F = \alpha (c_f - c_m) \quad (2.24)$$

where α is an exchange coefficient and c_f and c_m are the concentrations of the fracture and matrix phases, respectively. This is sometimes referred to as a quasi-steady-state (QSS) approximation, as the equation describes diffusive steady-state transport between two systems at fixed concentrations. (Some writers prefer to reserve the term dual-porosity for systems with this simple exchange process.)

This type of model was proposed by Coats and Smith (1964) for solute diffusion into dead-end pores.

When viewed as an approximation to a diffusive model, the QSS model is only valid when changes within the fractures are slow in relation to the time for diffusive equilibrium across a matrix block or other immobile fluid zone: the exchange coefficient, α , can then be related to the block geometry (Barker 1985a and 1985b), but the diffusive and quasi-steady-state models are incompatible for relatively fast changes within the fractures. The diffusive and quasi-steady-state models are incompatible for relatively fast changes within the fractures.

The well-known Water Research Centre model of nitrate transport (Oakes 1982 and 1989) includes the effect of matrix diffusion by an exchange term of the quasi-steady-state type. Black and Kipp (1983) described a tracer experiment on an irrigated plot on the Lower Chalk and a quasi-steady-state double-porosity model fitted the data well.

There is some evidence that the effective value of the coefficient, α , varies with the flow velocity, and this has been taken to indicate that the exchange mechanism is, at least partly, advective rather than diffusive (Raven et al. 1988).

Double permeability models. In double (or *dual*) permeability models the advective velocity in the matrix, although small compared to that in the fissures, is not regarded as negligible.

The term dual (or double) permeability is sometimes used synonymously with double porosity. However, it is better to reserve the term for the case where there is significant regional transport in the rock matrix (Figure 2.1). Unfortunately, the term has also been adopted to describe a specific type of numerical model (Miller and Clempson 1988) where large fractures are modelled discretely and smaller fractures are modelled as a continuum.

Narasimhan (1982) pointed out the suitability of the integrated finite difference method (IFDM) for fractured porous media. Baca et al. (1984) presented a method for modelling double permeability rock with discrete fractures; they use finite elements to represent the blocks but line elements for the fractures. A similar boundary integral formulation was presented by Rasmussen et al. (1989)

Based on the later discussion of Peclet numbers (Section 2.5.5), these models should be useful for solute transport in very porous chalk with large blocks (and hence large diffusion

times). However, double permeability concepts are more applicable to the interaction between the primary and secondary fissure systems of chalk than to that between the matrix and fissures, for which the permeability contrast is much larger.

Liu and Chen (1990) generalized double porosity and permeability models to multiple porosity and permeability models.

Numerical double porosity models. Barker (1985b) gave a general mathematical formulation of the double porosity and QSS models as a partial integro-differential equation. The various numerical models of double-porosity behaviour that have been developed can be regarded as numerical formulations of that equation. Bibby (1981) presented a model with parallel fractures (effectively a double-porosity model with slab-shaped matrix blocks) which combined a finite-element fracture formulation with an analytical solution for the matrix diffusion. Preuss and Narasimhan (1985) introduced a multiple interacting continua (MINC) model, based on the double-porosity medium approach, where the matrix material is divided into layers of various distances from the fracture/matrix block surface. This conceptual model was extended by Neretnieks and Rasmuson (1984) to model mixtures of blocks of various shapes and sizes. They added contributions from all blocks, of whatever shape and size, into an equivalent single block, referred to as a *pseudobody*.

NAMSOL is a very general transport code developed at Harwell which includes matrix diffusion (Cherrill et al. 1987). It uses the approach introduced by Huyakorn et al. (1983) where each fracture node is connected to a set of nodes extending into the matrix blocks, which may be either planar or spherical.

2.5.4 Discrete fracture models

A number of modelling concepts have been specifically developed for the study of groundwater in hard rocks. (Much of this work has been in response to recent interest in radioactive waste disposal.) Such systems differ from those of interest to the hydrogeologist mainly in that fractures are generally less frequent and hard-rocks have little intrinsic porosity, although they do often contain a dense network of micro-fissures concentrated near the fractures which can impart a double-porosity character. Such models are valuable when considering rapid flow in karstic conditions when matrix porosity may not be significant.

In any continuum model of a porous medium it is assumed that at the scale of the spatial discretization (e.g. finite elements) average hydraulic properties (e.g. hydraulic conductivity) are meaningful. For fractured media the validity of such an assumption is questionable (Schwartz and Smith 1987). For sparsely fractured media, the size of the minimum averaging volume may be greater than the size of the region of interest. If the rock has a hierarchical structure - with small fractures feeding bigger fractures which themselves feed

bigger fractures, and so on - average parameter values will change continually with sampling volume. These problems indicate why much effort has gone into discrete as opposed to continuum fracture modelling approaches.

Network models.

Various geometric forms are used when modelling fracture networks, including: infinite fractures, finite fractures (in two and three dimensions), fractures on a grid (e.g. Smith and Schwartz 1984), and self-similar (fractal) networks.

When the number of fractures is relatively large it can be appropriate to regard the system as being characterized by various statistics (e.g. the average fracture length and aperture width). Stochastic network modelling involves the generation of fracture networks conforming to these statistics in a random manner. Specific realizations are created using computer programs with random number generators (the Monte-Carlo method). The transport processes of interest is then modelled on each realization, and the results from many realizations are combined to form a stochastic description of the behaviour of the system.

One such model developed at the Harwell Laboratory is called NAMNET (Robinson 1982). The Stripa Project has funded the development of the NAPSAC code, also developed at Harwell. Perhaps the widest studies of these models has been carried out at the Lawrence Berkeley Laboratory in California (e.g. Long et al. 1982, Long and Witherspoon 1985). Chiles (1989) reviewed the models from the point of view of the statistical description of a fracture system.

Once the flow pattern has been established, solute transport can be simulated; various numerical methods can be applied but particle tracking is particularly convenient. It has been found that dispersion does not conform to a Fickian-type description (characterized by a dispersion coefficient).

The great difficulty with stochastic network models is that of calibration against field results. This is a topic into which much research effort continues to be directed (for example, Long and Billaux 1987).

Andersson et al. (1984) presented a model which is partly deterministic and partly stochastic: observed fracture interceptions with boreholes are employed but additional fractures are added with a density determined by the observed fractures. This approach serves to quantify uncertainty in flow problems and also provides guidance on how to acquire additional information.

The behaviour of flow at fracture junctions is important in determining the transverse or lateral spread (dispersion) of solutes or particles being transported through a network of fractures. Most simulation models assume complete mixing at the intersections, while others route the streamlines across junctions. Laboratory studies lead Hull and Koslow (1986) to propose rules for the routing of streamlines in models.

These discrete concepts are described as they might be applied to the chalk macrofissures, which are typically of three types: pipe or channel fissures, vertical or high angle cracks or joints and bedding plane fissures.

Channel models

Channel models are somewhat less general and less complex than network models. Such models were introduced as a result of various observations that indicate that flow in fractured rock is often restricted to relatively small channels within the rock. These models are very sensitive to aperture variations along their length (Tsang and Tsang 1987). Channelling is important because it reduces the dynamic porosity and hence increases velocities; also, it limits the contact area between mobile and immobile water, which controls the amount of sorption and diffusion into the rock matrix. The possibility of channelled flow in chalk should be taken into account when estimating travel times for pollutants.

Neretnieks et al. (1982) used such a model to reproduce experimentally measured breakthrough curves. Abelin (1986) interpreted a tracer test over 5 metres in an in situ fracture using both channel and advection-dispersion models; they gave equally good comparisons with the data. Tsang and Tsang (1987) introduced a variable-aperture channel model. Characterization of the roughness of fracture surfaces is important in applying such models and is a topic of recent interest; studies have included descriptions in terms of fractal dimensions (see Brown (1989) and references therein).

An important effect of channelling is that individual flows may not meet and their waters may not mix over significant distances, consequently a Fickian description of dispersion may not be appropriate even on a large scale.

Some difficulties with discrete fracture models

Geological and geophysical techniques are incapable of fully describing fracture network geometries in the field. The best that can be attained is a set of approximate statistical distributions of fracture apertures, lengths, densities, orientations and connection patterns. Stochastic modelling techniques must therefore be applied (e.g. Smith and Freeze 1979a, b), but because of the combined uncertainties in the parameters predictions will tend to be uncertain. Much work needs to be done on natural fractured systems before the validity and accuracy of the models can be assessed.

To obtain realistic simulations, it may be necessary to generate three dimensional distributions of thousands of individual fractures, which gives rise to very imposing computational problems.

Discrete models cannot currently be regarded as practical tools for hydrogeologist, other than perhaps those working in specialized fields such as radioactive waste disposal. They can, however, be used to investigate fundamental problems of transport in fractured rock.

2.5.5 Regimes of behaviour in fissured systems and model choice

In order to better understand why various types of model are used to simulate fissured systems, and to decide which type might be appropriate for a given situation, it is necessary to consider how the behaviour of a fissured system is related to the time scales of the transport processes.

It is particularly important to establish whether advection or molecular diffusion is the dominant transport mechanism in the matrix. The time taken for diffusion over a distance x is of the order of x^2/D where D is the diffusion coefficient. The time for advection through a matrix block of dimension x in the direction of flow is simply xn/Ki where n is the porosity, K is the hydraulic conductivity and i is the hydraulic gradient. The ratio of these two times, often referred to as the Peclet number, is therefore xKi/nD . Diffusion is dominant when the Peclet number has a value much less than unity. For example taking relatively large values for chalk matrix of $K=0.01$ m/d and $i=0.01$, the Peclet number for solute transport is less than unity for block sizes, x , less than about 10 cm.

Whenever the Peclet number is much less than unity the assumption of immobile matrix water is valid and the *double porosity* models are appropriate. If on the other hand the rate of advection in the matrix is not negligible, *double permeability* models are preferable.

All double-porosity systems, with advective transport in the fissures and diffusive transport in the matrix, exhibit different forms of behaviour depending on the time scale of the process under consideration in relation to the characteristic times for diffusion across a fissure or a matrix block. The *time scale* referred to here might, for example, be a period of oscillation (as in a tidally influenced aquifer) or a half-life (as for transport of a radioactive isotope). Many systems will exhibit a range of time scales, and for those the shortest time scale will normally be the one of interest.

Four regimes of double-porosity behaviour can be identified:-

I. If the time scale is small with respect to the characteristic time for diffusion across the fissure width, the effects of the porous matrix can be ignored. (Both because of the restricted diffusion out of the fissure and the small volume of matrix accessed, in relation to the fissure volume). Under such conditions an *equivalent porous medium* (EPM) model can be applied with a porosity equal to the fissure porosity.

II. If the time scale is a small fraction of the time for diffusion across a matrix block, then only the matrix/fissure surface area per unit volume of the rock is important, not the block size or shape. *Diffusive-type double-porosity* (DP) models, simplified by assuming an infinite matrix, are appropriate.

III. If the two times are similar, the sizes and shapes of the matrix blocks become important. Then a general *diffusive-type double-porosity* (DP) model should be used, although a *quasi-steady-state* (QSS) DP model may be adequate over some periods.

IV. If the time taken for diffusive equilibrium between fissures and matrix is small in relation to the time for any significant change in the fissure system, then the rock will behave as a (locally) homogeneous medium characterized by the total porosity. A QSS-DP model should prove to be more than adequate and a EPM model might also be suitable.

For some processes there is a very wide distribution of characteristic time scales, and only the diffusive DP models can then be used with confidence.

2.5.6 Models available

Analytical

Laplace-transform solutions for solute transport in a set of parallel fractures was given by Barker (1982). A more comprehensive set of solutions were given by Lever et al. (1983), who provided a careful account of the various definitions of the diffusion coefficient and the parameters determining retardation. The FRACSOL package contains a number of analytical solutions.

Numerical codes

There does not appear to be any user-friendly, well-supported numerical model for fractured media. Leading double-porosity codes include SWIFTII, FRACFLOW and TRAFRAP-WP.

2.6 Transport in the unsaturated zone

2.6.1 Introduction

The soil and unsaturated zones above an aquifer were until a few decades ago regarded as filter both retaining and degrading applied wastes, not without reason. The zone delays transport and provides an environment in which chemical processes can reduce the contaminant loading at the water table. The top few metres is often characterized by high microbial activity, which promotes biodegradation. The presence of organic matter and clays enhances sorption, biodegradation and other processes. However, the limited capacity of these zones to delay pollutants is now well recognized. Further it is appreciated that there often exist preferential-flow pathways through which pollutants can pass rapidly to the saturated aquifer.

Under some circumstances the unsaturated zone can be regarded as a persistent pollution source. Pollutants such as organic solvents and oil can become trapped in the pores or diffuse into immobile water (particularly in the Chalk aquifer). Then the release of these chemicals can be very slow so the unsaturated zone can become a particularly long-lived source. This can have serious implications when attempting remediation of an aquifer and when anticipating long term treatment of polluted water.

Transport in the unsaturated zone involves the same processes as in the saturated zone. Additionally, vapour phase transport of both water and volatile pollutants must take place.

Much of the earlier work by soil scientist concentrated on studying flow and transport in well controlled laboratory and small-scale field experiments. The need for 'field-scale' studies has now been appreciated and, particularly in the USA, study areas have been established where site characterization data can be collected for model validation. Jury and Sposito (1985) examined the interrelationships between sampling methodology and parameter estimation in relation to model validation at the field-scale.

Unsaturated soils and rocks are heterogeneous. Since measurements of properties are only possible down to some scale, variations at a smaller scale must always be considered spatially random. Average properties obtained at the measurement scale give transport parameters which may or may not provide an adequate basis for modelling unsaturated flow and transport. This also points to the need for detailed field investigation.

A very general stochastic theory of three-dimensional transient flow and transport at the field scale was provided by Mantoglou and Gelhar (1985); the analysis is based on a local Richards equation and a dispersion-convection equation.

2.6.2 Classification of models

Such a variety of different types of model have been applied to the unsaturated zone it is useful to attempt to introduce order by classifying models. Addiscott and Wagenet (1985) proposed the classification given in Table 2.3. Although this table is intended for leaching models, it appears to have wider application, at least as far as most unsaturated zone models.

Addiscott and Wagenet described deterministic models as those which presume that a system or process operates such that the occurrence of a given set of events leads to a uniquely-definable outcome. Stochastic models presuppose the outcome to be uncertain and are structured to account for this uncertainty. However, stochastic models often utilize a deterministic representation of processes but take on a stochastic character from uncertainty in inputs and rock characteristics: these are the 'stochastic-mechanistic' models in Table 2.3.

Mechanistic models (Table 2.3) have a more fundamental representation of processes (e.g. Richards equation) than non-mechanistic models. The stochastic non-mechanistic models must rely on calibration for evaluation of some parameters.

Table 2.3 A Classification of leaching models. (After Addiscott and Wagenet 1982.)

I. DETERMINISTIC MODELS

A. Mechanistic (usually based on rate parameters)

1. Analytical

2. Numerical

B. Functional (usually based on capacity parameters)

1. Partly analytical

2. Layer and other simple

II. STOCHASTIC MODELS

A. Mechanistic

B. Non-mechanistic (transfer function)

2.6.3 Transfer function models

For solute transport, stochastic-convective ('transfer-function') models have been found superior to the more traditional (deterministic) convection-dispersion model which do not reveal the wide range of travel times observed at the field scale (e.g. Butters and Jury 1989). For an up-to-date treatise on the transfer function method see Jury and Roth (1990) and for case studies see Roth et al. (1990).

The transfer-function model does not make direct use of known or computed water velocity variations, instead it requires calibration to concentration measurements at some depth. (By contrast the model of Jaynes et al. (1988) does use computed velocities.)

It should be appreciated that solutions of the convection-dispersion equation (CDE) (possibly also including sorption and reaction) are equivalent to transfer-function models in which the moments of the travel time (or distance) distribution are functions of the parameters in the transport equation. For example, the CDE gives a mean travel time of z/V and travel time variance of $2Dz/V$, where z is distance travelled, V is the mean velocity, and D is the dispersion coefficient. This shows that the transfer-function model is consistent with the less general classical transport equations.

Much recent research has been concerned with transfer-function formulations for heterogeneous systems. However, the results obtained are usually limited to cases with uniform velocity and constant dispersion coefficients.

2.6.4 Structured soils

While the soil zone is strictly speaking outside the remit of this project, it is worth making a few comments about structured soil modelling since structured soils are similar in some respects to weathered rocks and even to fissured Chalk.

Structured soils contain large voids which are quite continuous; these are often referred to as macropores. One definition of a macropores is that it is sufficiently large that capillary forces are unimportant: a size limit of 3 mm has been suggested. The flow through the system takes place preferentially through the macropores, by-passing much of the soil volume (matrix). Slow infiltration and diffusion into the matrix can occur.

Transient flow and transport in structured soils have been modelled (Germann 1989) using three approaches: (a) macroscopic averaging of flow and transport based on the 'mobile-immobile' zone concept; (b) routing procedures along presumed stream lines; and (c) 'transfer function' models based on a continuous velocity distribution. As with fissured systems, the main hurdle to successful modelling of such systems is the limited characterization of the geometry.

2.6.5 Codes

Models relating to transport in the unsaturated zone appear to be fairly specialized, some are mentioned in the geochemical and biochemical sections of this report. No general-purpose transfer-function code appears to be available - other than those listed in the book by Jury and Roth (1990).

3. GEOCHEMICAL MODELS

'Far better an approximate answer to the right question, which is often vague, than an exact answer to the wrong question, which can always be made precise'

Tukey's Principle.

3.1 Types of geochemical model

Geochemical models apply the principles of chemical thermodynamics to geochemical systems. Two approaches have evolved: *forward modelling* in which an aqueous speciation model is used to predict the result of various hypothetical reactions forward in time. The calculation begins with the composition of an initial water and various minerals, gases etc are added to it or subtracted from it and the new equilibrium assemblage is calculated.

The other approach is called *inverse modelling* and combines information on mineral saturation indices with mass balance modelling to identify and quantify mineral reactions which may have taken place in the system backward in time. It is a useful approach where there are two waters, perhaps from along a groundwater flow path, one of which is known to have been derived from the other by a series of geochemical reactions (mineral dissolution or precipitation, gas evolution etc). Inverse modelling attempts to identify and quantify these reactions. It is most useful where a series of groundwaters have been obtained from a regional aquifer which is close to a steady state. For a good account of the scope and current capabilities of geochemical modelling, see the review by Plummer (1992).

3.2 Chemical speciation

3.2.1 Historical perspective

Early physical chemists showed that the behaviour (e.g. freezing point and electrical conductivity) of solutions often did not depend in a simple way on the chemical composition of the solutions. Rather it was necessary to take into account the interactions of the various ions with each other. For example, in solutions containing Ca^{2+} and SO_4^{2-} , a proportion of these two ions combines to form a neutral ion pair, CaSO_4 , which behaves quite differently from the two separate ions (it is not charged for a start). This led to the concepts of activity coefficients, ion pairs and complexes which today are encompassed in the broad concept of the chemical speciation of solutions.

We now know that a great number of these ion pairs and complexes exist and compilations of the stability of these are available. Although there is doubt about the stability of many of the less common species, there is often rather good agreement and the chemical speciation of most natural waters is now quite well understood. The major limitations are where dissolved organic matter or other organic acids are present and where trace elements are involved.

The major use of chemical speciation for groundwater geochemistry is to understand when minerals should or should not precipitate or dissolve. It is also important from the point of view of toxicity - for example, it is usually considered that only the inorganic Al^{3+} , AlOH^{2+} and $\text{Al}(\text{OH})_2^+$ species are toxic whereas organically bound (or precipitated) Al species are not nearly so toxic. The toxicity of different redox states of an element may also be important. For example, arsenite ($\text{As}(\text{III})\text{O}_3^{3-}$) is 60 times more toxic to humans than arsenate ($\text{As}(\text{V})\text{O}_4^{3-}$). If ion exchange and sorption reactions are included, then chemical speciation also describes the distribution of elements between sorbed and solution phases. This is critical in determining element mobility and therefore some sort of chemical speciation is an integral part of all solute transport models. Solute transport models will only be as good as the speciation submodels that they contain.

3.2.2 Approaches to aqueous chemical speciation modelling

Two approaches have been followed. The *ion association approach* accounts for the nonideality of aqueous solutions by individual activity coefficients and the formation of aqueous complexes. The *specific interaction approach* uses a sophisticated model to account for the electrical interactions between ions in solution. The Pitzer model has been most widely used in the latter category; this accounts for specific interactions between every pair and triplet combination of aqueous species. Most of the weaker ion pairs and complexes included in the ion association model are no longer necessary with this approach.

The ion association approach is more flexible in that new elements and species can be added relatively easily but it breaks down in concentrated solutions such as seawater and brine. The specific interaction approach works well in these systems but the current database is restricted to the major salt systems. There is no data for aluminosilicate or redox reactions, for example.

3.2.3 Mass transfer and reaction path models

Chemical speciation programs use field measurements of temperature, pH, Eh, dissolved oxygen and alkalinity, and the full chemical analysis of a water sample as input, and calculate the distribution of aqueous species, ion activities and mineral saturation indices. These programs do not attempt to dissolve or precipitate minerals - this is the purpose of a more sophisticated type of geochemical program called a *mass transfer* program. These programs quantify the masses of substances changing phase, i.e. going from solid to solution or from gas phase to solution. *Reaction path* programs attempt to follow in detail the entire course of such a reaction. Plummer et al. (1983) give a good account of the use of such models.

A major difference between speciation and reaction path programs is the way that they treat pH. In speciation codes the pH is given by the user whereas in the reaction path codes the initial pH of the solution is given but the final pH is determined by the reactions that occur. Hence if you want to determine the solubility of calcite as a function of pCO_2 at a fixed pH say, you must use a speciation model. If you want to calculate the pH of a groundwater after it has lost some of its CO_2 , you must use a reaction path model. Similar comments apply to pe.

3.2.4 Equilibrium versus kinetic-based models

There is a choice between two types of geochemical model for simulating groundwater transport: one in which local equilibrium is assumed and one in which it is not. The question of kinetics is a relative one not an absolute one: the rate of reaction compared with the rate of groundwater flow, for example. The *local equilibrium assumption* (LEA) assumes that transport processes are so slow that all chemical reactions are at equilibrium. This obviously simplifies calculations and is usually adequate for groundwater where the timescales are relatively long. Often the slowest reactions are those involving a phase change, e.g. mineral dissolution, and a pragmatic approach is usually adopted here. The modeller only allows those minerals that are known to dissolve or precipitate relatively rapidly to be selected by the geochemical speciation calculations. This prevents thermodynamically stable but kinetically unfavoured minerals from influencing the reaction.

Reaction kinetics can often be described as belonging to one of three categories: (i) very fast; (ii) very slow or (iii) intermediate. All of these are relative terms. (i) is no problem, the LEA is assumed. (ii) is also no problem, the reaction is ignored. (iii) is where kinetics-based models are required. A distinction between homogeneous (solution phase) reactions and heterogeneous (solid-solution phase) reactions is useful (Rubin, 1983; Kirkner and Reeves, 1988). Bahr and Rubin (1987) discuss the implications of the LEA in detail.

Most of the recent kinetics-based modelling has been concerned with the transport of solutes undergoing microbial reactions since these reactions tend to occur at an intermediate rate and so the kinetics must be incorporated into a time-dependent model. These models have centered around denitrification and pesticide degradation. If sorption or precipitation reactions are slow then a solute will move further than otherwise anticipated.

3.2.5 Model use and validation

Tukey's Principle which is cited at the beginning of this Section is particularly relevant to geochemical modelling since important matters of judgement have to be made at an early stage - the 'correct' formulation of the problem is critical. What are the most important factors to consider and are there any existing models that consider all of these factors? Inevitably simplifications will be required and choices have to be made about exactly what to simplify and what to omit. There is often a balance between using a program with which you are familiar but which accounts for most but not all of the important processes and using a new program with all the effort that this entails. If no existing model is suitable then a new program may have to be developed. This is usually a major effort.

There are two broad uses of groundwater geochemical models: (i) to understand the factors controlling the concentration of a solute of a chemical in the groundwater and its sensitivity to a change in some other system parameters; and (ii) to predict in some detail the evolution of a particular geochemical environment which may be groundwater within an aquifer or groundwater beneath agricultural land or a landfill. (i) only requires generalizations about the aquifer while (ii) requires specific detailed characterization of an aquifer and its heterogeneity. (i) can be useful in planning and in providing guidelines for legislation whereas (ii) is much more ambitious and challenging and only likely to be successful in

special cases.

Before embarking on a modelling exercise, the following need to be determined (Mangold, and Tsang, 1991):

- (i) the observable quantities of interest;
- (ii) the accuracy required for the prediction of these quantities;
- (iii) the range of conditions for which the model to be used has been validated.

In their review of hydrogeological and hydrogeochemical transport models, Mangold and Tsang (1991) differentiate between processes (e.g. redox, ion exchange, flow, diffusion etc) and geometric structures (geology, fractures, heterogeneity etc). Processes can be studied in the laboratory whereas geometric structures are peculiar to the site. A successful model requires both of these to be described adequately. Geometric structures are usually difficult to determine independently and are often derived by optimizing model fit. Hence it is not possible to 'validate' a model for all situations rather it is often only possible to validate it for a given process or for a given site.

Chemical speciation models can be relatively easily validated because they do not involve the geometric structures defined above. Several attempts to validate chemical speciation codes have been carried out using the 'round robin' approach: different modellers are given a problem to solve (e.g. speciate a water) and the results compared. Nordstrom et al. (1979) carried out an early study of this kind in which they attempted to speciate a seawater and a river water using a variety of the then current programs - EQUIL, EQ3, GEOCHEM, IONPAIR, MINEQL2, MIRE, MINEQL/REDEQL2, REDEQL2, SEAWAT, SOLMNEQ, WATEQF, WATEQ2, WATSPEC, SIAS/COMIC.

Read and Brøyd (1989) have carried out a much more comprehensive validation of speciation models in use today (WHATIF, EQ3, CEQSY, MINEQL, MEQTP, and PHREEQE). A number of test cases were computed for four hypothetical aquifer materials (clay, sandstone, granite, and limestone) as well as a cement-containing material of interest in nuclear waste disposal. This study showed that not only were the results dependent on the thermodynamic database used, as expected, but that subjective decisions on the part of the users about how a particular problem should be tackled, for example the choice of activity coefficient correction, the definition of alkalinity and pH and Eh control, were important. Very few of the discrepancies could be attributed to errors in the programs or by the operators which is perhaps not surprising since the exercise was carried out using popular programs by experienced modellers.

3.3 Recent developments in geochemical programs

3.3.1 Capabilities

Improvements in geochemical speciation models only become available to a wide audience when they are incorporated into generally available computer programs. An important aspect of this is the reviewing and compilation of a reliable thermodynamic database. The US Geological Survey has a long and distinguished history of doing this which is reviewed

below. Other recent developments in geochemical speciation programs have included:

- (i) Improvement of the user interfaces or development of preprocessors for simplifying preparation of input files, e.g. MINTEQA2 (USEPA) has a relatively simple preprocessor program PRODEFA2 which has a menu-type user interface, ECOSAT (a promising speciation program under development at the University of Wageningen) has a more sophisticated user interface with menu bars and drop down menus, and PHREEQE (USGS) has a separate preprocessor program called PHRQINPT for preparing input files. Nowadays most of these programs can be run on a PC;
- (ii) Incorporation of more sophisticated sorption and surface chemistry models, e.g. MINTEQA2 and ECOSAT, including the ability to model organic-metal interactions (an important limitation of most speciation programs);
- (iii) Linkage of comprehensive speciation and mass transfer models to transport models, e.g. EQ3/EQ6 (Wolery, 1983, 1989; Wolery et al., 1990), P H R E E Q M (PHREEQE in a mixing cell flow tube), MST1D (1-dimension analytical solution for saturated flow);
- (iv) Inclusion of kinetics (EQ6);
- (v) Extension to high ionic strengths, e.g. the use of Pitzer's equations (EQ6, PHRQPTZ and others).

The report by Ashton et al. (1991) provides a recent tabulation of geochemical speciation codes and their capabilities. It provides the most comprehensive reviews for EQ3/6, MINEQL and PHREEQE. Although there has been a great proliferation of codes, it seems likely that there will be some 'shake-out' in the future. Ease of use, reliability and the user interface are likely to be important factors in this.

3.3.2 Thermodynamic and environmental fate databases

Inorganics

All geochemical models require chemical thermodynamic data and a great deal of effort has gone into measuring and tabulating such data. However there is at present no single 'best' source of data to which to refer.

There are a number of important sources of published compilations of thermodynamic data. These are listed in Table 3.1. Many textbooks also contain tables, e.g. Baes and Mesmer (1976), Stumm and Morgan (1981), Drever (1988). Nordstrom and Munoz (1986) contains a listing of more than 200 sources of thermodynamic data and a guide to the major compilations for particular classes, e.g. acid-base dissociation, aqueous solutes, elements, gases, minerals, organic compounds etc.

An important part of geochemical modelling is obtaining a comprehensive and self-consistent

Table 3.1 Important collections of chemical thermodynamic data

| Source | Year | Comments |
|----------------------|--------------------------------------|--|
| Sillen and Martell | 1964 | Comprehensive but uncritical (up to 1963) |
| Sillen and Martell | 1971 | First Supplement (up to 1968) |
| Perrin | 1979 | Organic Ligands (up to 1973) |
| Högfeldt | 1982 | Inorganic Ligands (up to 1974) |
| Baes and Mesmer | 1976 | Cation hydrolysis constants |
| Garvin et al. | 1987 | CODATA Recommended Key Values for standard enthalpies and entropies of Ca compounds and related mixtures. Includes standard deviation. Prototype set of tables. |
| Cox et al. | 1989 | CODATA Recommended Key Values for standard free energies of formation and entropies for a wide range of chemical species. Includes standard deviation. |
| Serjeant and Dempsey | 1979 | Ionization constants of organic acids in aqueous solutions (up to 1970) |
| Perrin | 1982 | Ionization constants of inorganic acids and bases in aqueous solution (up to 1980) |
| Martell and Smith | 1974 1975 1976 1977 1982 | <i>Critical</i> stability constants A collection of 5 volumes (see references for details) |
| Read and Broyd | 1989 | CHEMVAL Stage 1 database in PHREEQE format Comprehensive. Includes transuranics. |
| Nordstrom et al. | 1990 | Critical tabulation of equilibrium constants and enthalpies for major geochemical reactions. Contains a useful guide to other important sources of thermodynamic data, e.g. NBS and USGS |
| Waters et al. | 1991 | CHEMVAL Project. Update to Stage 1 database |

set of thermodynamic data particularly for the minerals. For example, 'thermo' data for a mineral such as calcite (CaCO_3) could be derived from solubility measurements but in interpreting such measurements, the complete speciation in solution would have to be calculated in order to be able to estimate the true activities of Ca^{2+} and CO_3^{2-} correctly. This model should include all the significant calcium and carbonate species including species such as $\text{CaHCO}_3^+(\text{aq})$; a different value for the solubility product would be obtained depending on whether this species was included or not. Since the thermo data for aqueous species is

constantly being refined, this means that the solubility measurements must also be refined at the same time in order to be consistent with the new aqueous model. For an example of this process of refinement, see Apps and Neil (1990) who discuss the case of aluminium hydroxide minerals, one of the more important suite of minerals for geochemists. This is a major undertaking recently but a similar exercise has been undertaken for all of the major aqueous and mineral species of geochemical interest (Nordstrom et al., 1990). Baes and Mesmer (1981) review the important area of cation hydrolysis.

The User's Manual for WATEQ4F Version 2.0 (Ball and Nordstrom, 1991) contains a fairly comprehensive listing of chemical thermodynamic data (log K's and enthalpies) for the major species and minerals and documents their source and 1 σ uncertainties. Several other projects and organizations are involved in similar database collection and verification exercises, e.g. the CHEMVAL project (Read and Broyd, 1989; Waters et al., 1991), CODATA (Garvin et al., 1987; Cox et al., 1989), the US National Bureau of Standards and the OECD Nuclear Energy Agency (NEA). Wolery et al. (1990) give a review of the extensive databasing activities at the Lawrence Livermore National Laboratory, California. They have set up a thermodynamic database using the INGRES relational database system which documents the source of data and is able to output databases in different formats, e.g. EQ3/EQ6 or PHREEQE. It is periodically updated and is available to the public. Johnson et al. (1992) have recently released the SUPCRT92 software package which calculates the thermodynamic properties for geologically important minerals, gases, aqueous species and their chemical reactions from 1 to 5 kb and 0 to 1000°C. It includes data for 294 aqueous species including 86 organic species, and 179 minerals. Much of this databasing activity is prompted by the need to model the reactions and transport of radionuclides during the underground storage of nuclear waste but it obviously has wider applicability.

A problem area is for some of the rarer trace elements where much of the thermodynamic data is either not known at all or is subject to large errors. Also thermodynamic data for adsorbed species is generally not tabulated since it varies with mineral type and model assumptions. Great care has to be taken in using surface complexation 'constants' from the literature since these will depend on many factors such as the double layer model used and the importance placed on the binding of background electrolyte ions.

There has been a considerable effort recently to reinterpret experimental data for the binding of metal ions by amorphous iron oxide ('ferrihydrite'), perhaps the most studied and most reproducible of minerals (Dzombak and Morel, 1990; Smith and Jenne, 1991 and also the lively discussion of this paper in Dzombak and Hayes, 1992 and Smith and Jenne, 1992). Ferrihydrite is abundant in nature and adsorbs a wide range of metals quite strongly and is sometimes used in modelling studies to represent the behaviour of hydrous metal oxides in soils and sediments more generally. MINTEQA2 (Version 3.11) contains a database for 42 surface species on iron oxide using a double layer model. Dzombak and Morel (1990) include data for the proton (H⁺) plus Ag, AsO₃, AsO₄, BO₃, Ba, Be, Ca, Cd, Co, Cr(III), Cu, Hg, Ni, PO₄, Pb, SO₄, SeO₃, SeO₄, Sr, VO₄ and Zn.

Databases for intrinsically heterogeneous materials such as organic matter are only just beginning to be compiled and it is usually up to the user to select the most appropriate data. Similar comments apply to soils and aquifers.

Table 3.2 Summary of the main features of the thermodynamic databases associated with various geochemical models

| Model | Ease of extension | Form of storage | Comments | Author |
|------------------------|---------------------------------------|-----------------|--|-------------------------|
| EQ3NR | Moderate | Binary | 8 gases, 29 elements, 285 aq. species, 255 reactions. No sorption. Separate database processor. 0-300°C temp. range | Wolery (LLNL) |
| WATEQ4 | Difficult because need to change code | ASCII | 2 gases and about 30 elements and 650 species including aq. and minerals. Simple humic complexation but no sorption. | Ball et al. (USGS) |
| PHREEQE | Easy for a small number of additions | ASCII | 6 gases, 19 elements, 31 minerals, about 160 aq species. Not many toxics but up to 11 could be quite easily added. | Parkhurst et al. (USGS) |
| MINEQL | Easy | ASCII | User defined database | Westall (Univ. Oregon) |
| GEOCHEM (now SOILCHEM) | Easy because uses matrix approach | ASCII | 2 gases, 44 elements, about 2000 aq species and 185 minerals. Extensive organic (EDTA etc) database. | Sposito (Univ. Calif.) |
| MINTEQA2 | Easy; added by menu selection | Binary + ASCII | 34 elements, 3 gases (+ HG vapours), about 930 aq species and 500 minerals. Extensive metal-organic database (EDTA, Cit etc) Includes 7 sorption models (triple layer) and data for sorption on iron oxide | Allison et al. (USEPA) |

Most geochemical programs contain substantial geochemical databases although the degree to which the data have been scrutinized for reliability and internal consistency varies greatly. Table 3.2 lists some of the more important models and comments on their internal databases. It is possible to change the thermodynamic data in all of these models but the ease with which new components and new species can be added depends on whether the species are 'hard coded' into the program or not. It is easiest when the data are stored in a matrix notation in a separate database file. In some cases the data are stored in a file in binary format for fast retrieval and so need a special program to update the database (e.g. EQ3NR). The EQ3NR database file is generated from a larger thermochemical database. Other models have their data in ASCII files and so can be updated with an ordinary text editor.

The databases vary in the way in which they store their thermo data, e.g. as free energies or as formation constants. The models also vary in the way in which they store the temperature dependence of the free energies or formation constants. This can either be as

enthalpies or more precisely as empirical functions of temperature (e.g. $\log K = A + BT + CT^2 + DT^3$) over the temperature range of interest. Some models (e.g. WATEQ4) use a mixture of both of these methods while others (e.g. GEOCHEM) cannot deal with temperature changes (by default the databases usually refer to 25°C although the user can change the values to some other temperature if necessary). The usual warning of 'buyer beware' has to be attached to all of these. All of these databases are stored in a different format although automatic conversion would be possible. Some of the newer models are adopting existing formats, e.g. the PHREEQE format.

Organics

The movement of persistent, man-made organics into groundwater is of increasing concern. This is a broad area and an excellent introduction can be found in the review by Jones and Wild (1991). This reviews methods of screening organic chemicals for their ability to transfer to crop plants and livestock via the land disposal of contaminated sewage sludges. Much of this review is relevant to the allied threat to groundwater, e.g. the description of sorption, leaching, degradation and volatilization. More comprehensive sources of data on the environmental fate of specific classes of organics can be found in Mackay et al. (1991, 1992). Canter et al. (1987) give a broad discussion of the environmental fate of a wide range of pollutants, including organics, but the discussion is largely from an American perspective.

Much work has been done to try and predict the sorption of pesticides by soils and aquifer materials. Sorption can often be related to the octanol/water partition coefficient. Many organic compounds are themselves strongly sorbed by solid organic matter. This tends to be present at low concentrations in most aquifer materials and is usually poorly quantified and characterized. There has been very little work done on the sorption of pesticides and solvents on the major UK aquifers even though this could be important in retarding their mobility.

A comprehensive 7-volume series of reference books is going to be published (beginning in Autumn 1992) by the Royal Society of Chemistry that will contain critical data for more than 5000 chemical substances. It is being marketed as **DOSE**, Dictionary of Substances and their Effects (Richardson, 1992). It contains information on: Identifiers (Chemical names, synonyms, formulae etc.), Uses and Occurrences, Physical Properties (including $\log K_{ow}$), Occupational Exposure, Ecotoxicity, Environmental Fate (including degradation rates), Mammalian Toxicity, and Legislation. It has extensive references to primary data. Substances to be included were selected from the EC Black and Grey lists, the UK Department of Environment Red List, and the USA and Canadian Priority Pollutants.

The Royal Society of Chemistry also publishes 'The Agrochemicals Handbook' (Royal Society of Chemistry, 1992) that contains data on pesticides, notably their half-lives in soils, degradation pathways, and their plant and animal metabolism. The price of purchase includes periodic updates (about every 6 months). Several other extensive handbooks on pesticides are also available.

Before a new pesticide is used, basic data such as its persistence, toxicity and octanol-water

partition coefficient are usually known. There is a good correlation between the octanol-water partition coefficient and other properties such as water solubility and sorption. For example, the octanol-water partition coefficient, K_{ow} was found to be given by the equation

$$\log K_{ow} = 5.00 - 0.670 \log S \quad (3.1)$$

for a wide range of organic compounds where S is the aqueous solubility in $\mu\text{mol l}^{-1}$ (Canter et al., 1987). Substances with a low K_{ow} are the more polar, water-loving substances whereas substances with a high K_{ow} are highly non-polar, water-insoluble and prefer to associate with other non-polar organic substances. $\log K_{ow}$ can also be correlated with the adsorption affinity of a substance; Jones and Wild (1991) make the following classification

| | |
|------------------------------|---------------------------------|
| Low adsorption affinity | $\log K_{ow} < 2.5$ |
| Moderate adsorption affinity | $\log K_{ow} > 2.5$ and < 4.0 |
| High adsorption affinity | $\log K_{ow} > 4.0$ |

This classification reflects the fact that most organic substances tend to sorb onto the organic fraction of soils and sediments which will favour the non-polar substances. If the surfaces were purely inorganic this relationship would not hold. Even small amounts (c. 0.1%) of organic matter can be important. For example, Larsen et al. (1989) found a significant correlation between $\log K_d$ and $\log K_{ow}$ for the adsorption of 11 organics on three low organic matter Danish sands even though the carbon content averaged only 0.016% C. the K_d is sometimes called the organic carbon-water distribution coefficient, K_{oc} . There is often a good correlation between K_{oc} and K_{ow} (Table 3.3).

Other key parameters are the volatility of the substance and its degradation potential. Volatility depends on its Henry's Law constant, H_c (the ratio of concentration in the air to that in solution) and also on the potential of the vapour to be sorbed by the soil or sediment. Jones and Wild (1991) suggest that the air-octanol partition coefficient is a more useful measure of volatilization potential than the air-water partition coefficient since it takes into account the tendency of the substance to be adsorbed by the soil (since this is correlated with K_{ow}). K_{ao} is given by the ratio of K_{aw} and K_{ow} which are better known. They propose the following cut-off values

| | |
|-----------------------------------|---|
| High volatilization potential | $H_c > 10^{-4}$ and $K_{aw}/K_{ow} > 10^{-9}$ |
| Possible volatilization potential | $H_c > 10^{-4}$ and $K_{aw}/K_{ow} < 10^{-9}$ |
| No volatilization potential | $H_c < 10^{-4}$ and $K_{aw}/K_{ow} < 10^{-9}$ |

There has been a good deal of research to try and predict the properties and reactivities of organic compounds from a few basic properties; the correlation between water solubility and the octanol-water partition coefficient has been mentioned. Another set of correlations that is widely used is that between reaction rate constants and equilibrium constants for related reactions; these are often known as *linear free energy relationships* or LFER's (usually displayed by a plot of the log of a rate constant and the log of the equilibrium constant). This has developed further into more general relationships known as *property-activity relationships* (PARs) and *structure-activity relationships* (SAR's) which seek to predict

Table 3.3 A summary of the octanol-water and organic carbon-water partition coefficients for a range of organic compounds and a summary of some useful regression equations describing their correlation (from Appelo and Postma, 1992)

Partition coefficients for octanol-water (K_{ow}) and organic carbon-water (K_{oc})

| Compound | $\log K_{ow}$ | $\log K_{oc}$ | compound | $\log K_{ow}$ | $\log K_{oc}$ |
|--|---------------|---------------|--------------------------------|---------------|---------------|
| <u>Hydrocarbons and Chlorinated Hydrocarbons</u> | | | <u>Carbamates</u> | | |
| 3-methyl cholanthrene | 6.42 | 6.09 | carbaryl | 2.81 | 2.36 |
| dibenz[a,h]anthracene | 6.50 | 6.22 | carbوتران | 2.07 | 1.46 |
| 7,12-dimethylbenz[a]anthracene | 5.98 | 5.35 | chlorpropham | 3.06 | 2.77 |
| tetracene | 5.90 | 5.81 | | | |
| 9-methylanthracene | 5.07 | 4.71 | <u>Organophosphates</u> | | |
| pyrene | 5.18 | 4.83 | malathion | 2.89 | 3.25 |
| phenanthrene | 4.57 | 4.08 | parathion | 3.81 | 3.68 |
| anthracene | 4.54 | 4.20 | methyparathion | 3.32 | 3.71 |
| naphthalene | 3.36 | 2.94 | chlorpyrifos | 3.31 | 4.13 |
| benzene ^a | 2.11 | 1.78 | | | |
| 1,2-dichloroethane ^b | 1.45 | 1.51 | <u>Phenyl ureas</u> | | |
| 1,1,2,2-tetrachloroethane ^b | 2.39 | 1.90 | diuron | 1.97 | 2.50 |
| 1,1,1-trichloroethane ^b | 2.47 | 2.25 | fenuron | 1.00 | 1.43 |
| tetrachloroethylene ^b | 2.53 | 2.56 | linuron | 2.19 | 2.91 |
| γ HHC (lindane) | 3.72 | 3.30 | monolinuron | 1.60 | 2.30 |
| α HHC | 3.81 | 3.30 | monuron | 1.46 | 2.00 |
| β HHC | 3.80 | 3.30 | fluometuron | 1.34 | 2.24 |
| 1,2-dichlorobenzene ^a | 3.39 | 2.54 | | | |
| pp' DDT | 6.19 | 5.38 | <u>Miscellaneous compounds</u> | | |
| methoxychlor | 5.08 | 4.90 | 13Hdibenzo[a,i]carbazole | 6.40 | 6.02 |
| 22',44',66'PCB | 6.34 | 6.08 | 2,2' biquinoline | 4.31 | 4.02 |
| 22',44',55'PCB | 6.72 | 5.62 | dibenzothiophene | 4.29 | 4.05 |
| | | | acetophenone | 1.59 | 1.54 |
| <u>Chloro-s-triazines</u> | | | terbacil | 1.89 | 1.71 |
| atrazine | 2.33 | 2.33 | bromacil | 2.02 | 1.86 |
| propazine | 2.94 | 2.56 | | | |
| simazine | 2.16 | 2.13 | | | |
| trietazine | 3.35 | 2.74 | | | |
| ipazine | 3.94 | 3.22 | | | |
| cyanazine | 2.24 | 2.26 | | | |

Estimation of K_{oc} from K_{ow} by the expression $\log K_{oc} = a \cdot \log K_{ow} + b$.

| Regression coefficient | | Correlation coefficient | number of compounds | Type of chemical |
|------------------------|--------|-------------------------|---------------------|--|
| a | b | | | |
| 0.544 | 1.337 | 0.74 | 45 | Agricultural chemicals |
| 1.00 | -0.21 | 1.00 | 10 | Polycyclic aromatic hydrocarbons |
| 0.937 | -0.006 | 0.95 | 19 | Triazines, nitrotriazines |
| 1.029 | -0.18 | 0.91 | 13 | Herbicides, insecticides |
| 1.00 | -0.317 | 0.98 | 13 | Heterocyclic aromatic compounds |
| 0.72 | 0.49 | 0.95 | 13 | Chlorinated hydrocarbons alkylbenzenes |
| 0.52 | 0.64 | 0.84 | 30 | Substituted phenyl ureas and alkyl-N-phenyl carbamates |

environmental fate of related compounds or their bioactivity based on correlations with physicochemical properties (Brezonik, 1990). These provide a useful bridge between empiricism and theory and enable the generalization of results from observations on a few compounds to a much larger number of compounds. Such relationships are important not only for organics but also for inorganic reactions especially where measurements are difficult, e.g. surface reactions.

3.3.3 Pesticide leaching models

The fate of man-made pesticides, solvents and other organics in the environment is receiving a lot of attention at present. Since most of these enter the hydrological cycle at the soil surface, much of the work on pesticides has centered around their uptake by crops, their volatilization, and their degradation and attenuation in the soil (see Jones and Wild (1991) for a review). Solvents, particularly the water-immiscible and denser-than-water solvents, pose a particular threat to groundwater since they rapidly find their way down fissures.

Pesticide leaching models must consider pesticide metabolites whose behaviour may be quite different from the parent compound. The latest Groundwater Loading Effects of Agricultural Management Systems, GLEAMS) model attempts to do this (Leonard et al., 1990). The GLEAMS model now considers hydrology, erosion and pesticide sorption and metabolism and is aimed at predicting the movement of pesticides through soils and in run-off. The organic matter content of the soil is used to estimate the soil-water partition coefficients for the pesticides and metabolites of interest.

Since the behaviour of pesticides is markedly different from that of natural organics and inorganics, pesticide leaching and fate models tend to have been developed independently of the more traditional geochemical models. However, there are important common principles particularly understanding the subsurface redox-pH environment. Kinetic aspects and sorption (adsorption and desorption) are often important for pesticides as well as dispersion (Figure 3.1).

We have not evaluated the existing pesticide leaching models in detail but the front-runners appear to be the two USEPA models, the Pesticide Root Zone Model (PRZM) for pesticide leaching through soils and RUSTIC, the pesticide groundwater leaching model.

3.3.4 Mass transfer and reaction path programs

Geochemical speciation programs increase their usefulness greatly when they can calculate the mass transfer, i.e. the amount of a substance dissolved or precipitated (in kg or mol) or the weight of gas taken up or released by a reaction or series of reactions. Speciation programs such as WATEQ4 will report when a solution is oversaturated with respect to a mineral but will not actually precipitate it to achieve complete equilibrium. At their simplest, they do not consider transport but they can be linked with a flow model to give a solute transport model (see Solute Transport).

Amongst the popular geochemical mass transfer programs in order of increasing complexity are MINTEQ, PHREEQE, and EQ6 (Wolery, 1983 and 1989; Wolery et al., 1990). EQ6

is much larger than the previous two and is used by a more restricted clientele. It is usually run on workstations (under UNIX) and mainframes rather than PC's. It is useful for calculations with brines and crystallization of simple salts since it can use Pitzer's equations for calculating activities; it also keeps a proper mass balance on the water (this is important when considering precipitation of hydrated minerals). Although it is large it is quite straightforward to set up input files for it. It is more powerful than PHREEQE since it will automatically trace along a reaction path boundary as the reaction proceeds whereas to do this with PHREEQE would require a lot of separate runs.

There are many variants of MINEQL, PHREEQE and MINTEQA2 in existence. A recent version of PHREEQE called PHRQPITZ uses Pitzer's equations (Plummer and Parkhurst, 1990); another, PHRQXL, models non-ideal solid-solutions. Many of the most important geochemical programs including source code are in the public domain and this has led to the proliferation of customized variants.

EQ3/EQ6 has the unique ability to incorporate reaction kinetics and to track the reaction path taken while a system goes from one equilibrium state to another. For example, if feldspar is placed in water, the system is not at equilibrium and will dissolve until it is. During this dissolution, various secondary minerals may be precipitated (e.g. gibbsite, $\text{Al}(\text{OH})_3$ or kaolinite, $\text{Si}_4\text{Al}_4\text{O}_{10}(\text{OH})_4$) and dissolved. Some such as gibbsite may be transitory products, redissolving before the end of the reaction. EQ6 can track such a reaction either using an arbitrary time frame (extent of reaction) or using a real time frame if the appropriate rate laws are known. Following a reaction path is like carrying out a titration - the extent of reaction is like the amount of titrant added.

3.3.5 'Open' versus 'closed' systems for gases

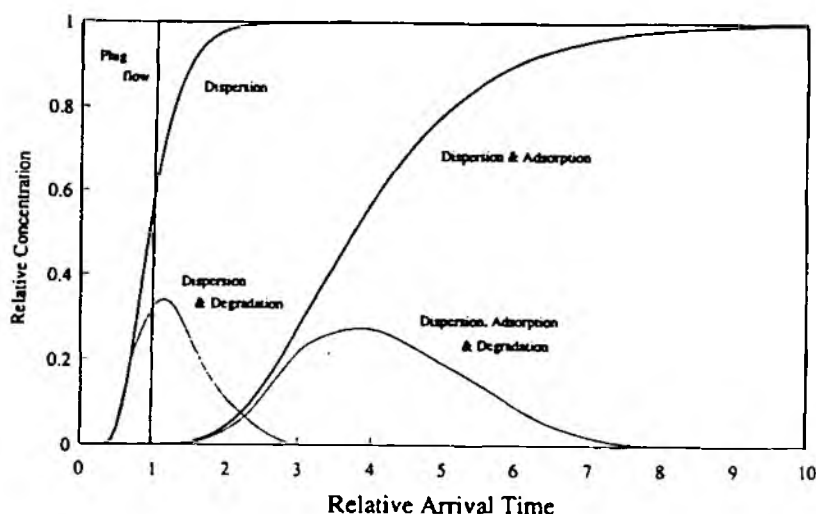


Figure 3.1 Processes taking place during transport of a pesticide

The partial pressures ('concentrations') of certain gases are critical in geochemical calculations. CO₂ and O₂ are the most obvious but H₂S and CH₄ may be important in reducing environments. CO₂ is particularly important since it affects the pH of the water and therefore has repercussions for a very wide range of reactions.

Most models assume either an 'open' system in which the pCO₂ is fixed by some large external reservoir or a 'closed' system in which the amount of CO₂ is fixed although it can be transformed into other forms such as CaCO₃. In practice, reality often lies somewhere between these two extremes: near to the surface, the open option is more realistic whereas deeper in the aquifer the closed option is more realistic. Until the behaviour of gases is well understood and well characterized, the application of geochemical models will have to make these somewhat arbitrary assumptions. Some of the programs that can maintain a fixed partial pressure of a gas also keep a mass balance on that gas so that the amount transferred is known.

3.3.6 Compartmental models

The compartmental models are based on the partitioning of solutes between different environmental compartments or 'boxes', e.g. air, water, soil and sediment. The aim is then to define the reactions within each compartment and the transfers between them. This approach has been popular for understanding global geochemical cycles (e.g. the carbon cycle in the oceans, sediments, atmosphere) and has recently been developed for predicting the fate of organics in the environment (Mackay and Paterson, 1991). The layer model of PHREEQM is also a type of compartmental model with the different compartments being different layers of the soil or aquifer.

Essential differences are whether the reactions are transient or steady state, the scope of the reactions considered and the transfer functions used. It is relatively straightforward to include first order kinetics for the reaction rates.

3.3.7 Recommended programs

The geochemical programs discussed above represent a major effort and one or more deserves to be on every geochemist's PC. The programs can best be thought of as 'geochemical calculators' - they take the drudgery out of solving geochemical problems rather like *Mathematica* takes the drudgery out of solving mathematical problems. This allows the effort to be applied to formulating the geochemical problem and in interpreting the results.

The formulation process involves making important assumptions about what processes can safely be ignored, what may be important but cannot be included and in how the model is going to be calibrated including choosing an appropriate set of thermodynamic data. The interpretation of the data will include checking for obvious errors in formulation or input, comparing with observed data and with previous experience and identifying the sensitivity of the output in relation to the choice of parameters input.

There are many potential pitfalls in geochemical modelling. Most of the programs are still

not sophisticated enough to make helpful comments when the problem has been incorrectly formulated and can sometimes be made to 'crash'. However in the longer term the situation is likely to improve as more user-friendly front ends become available. These may be linked with expert systems to guide judgement and to detect incompatibilities (Pearson et al., 1990). An important application of geochemical programs is in determining the sensitivity of groundwater chemistry to various changes in external factors such as aeration, the input of pollutants, pumping regime and the mixing of different waters. Providing they are carefully used, geochemical programs can provide a sound foundation for groundwater protection policy. Often rather simple simulations can provide useful insights. As more processes are included, the problems tend to increase (Table 3.4).

We have selected a group of programs (Table 3.5) which we recommend as being useful a useful set for solving general purpose geochemical problems. They have been chosen for their reliability, good documentation and ease of use. All are free although the documentation may need to be bought (you are asked to send a blank, formatted 1.4 Mb 3.5" disc to the USEPA and USGS if you want to receive copies of the programs). For other options or for more specialized applications, consult one of the existing directories or recent reviews (Grove and Stollenwerk, 1987; Mangold and Tsang, 1991; IGWMC, 1991; Ashton et al., 1991). Each of these programs has its own thermodynamic database. MINTEQA2 (Allison et al., 1991) is a good general purpose speciation program; NETPATH (Plummer et al., 1991) is one of the only inverse modelling programs available and PHREEQE/PHREEQM (Parkhurst et al., 1990 and Appelo and Postma, 1992) is a relatively simple and reliable reaction path program with 1D transport capabilities.

In order to see how sensitive the results are to the program used, we have made a simple calculation with both MINTEQA2 and PHREEQE using the databases unamended. For this we calculated the pH in pure water, pure water plus calcite, and pure water plus calcite plus dolomite, all at various partial pressures of CO_2 . The results are shown in Table 3.6. The pH's calculated by PHREEQE were consistently about 0.02 pH unit higher than those calculated with MINTEQA2. This reflects the different thermodynamic databases used (we used the databases released with the programs).

At the atmospheric partial pressure of CO_2 (0.00035 atm), the pH of pure water is 5.6. Rain substantially more acid than this is generally called 'acid rain' as it must contain a stronger acid than CO_2 . At the $p\text{CO}_2$ found in soils (0.1-0.01 atm), the pH of pure water would be in the range 4.3-4.9, i.e. quite acid. In the presence of calcite, we would expect a pH of 8.3 for systems open to the atmosphere and as low as 6.6-7.3 in soils. The presence of dolomite raises the pH by about 0.13 unit. Even a simple example like this helps to explain reasons for possible variations in groundwater pH.

3.3.8 Volatile substances

Unlike most inorganic solutes, organic solvents and pesticides can be lost from groundwater by degradation and volatilization. Jury et al. (1990) discuss a screening model to evaluate the relative volatilization losses of a number of organic compounds under standard soil conditions. The model is an analytic solution to the problem which assumes that the organic chemical is located at time zero at uniform concentration in a finite layer of soil covered by

a layer of soil devoid of chemical. The compound is assumed to move by mass flow under the influence of steady upward or zero water flow while undergoing first order degradation and following a linear adsorption isotherm. Somewhat surprisingly their model calculations showed that certain compounds may volatilize from deep subsurface locations or even groundwater. This is the basis for gas 'sniffing' to locate contaminated groundwater.

Table 3.5 Geochemical modelling programs recommended for general use

| PROGRAM | USE | SOURCE |
|---------------------|---|---|
| MINTEQA2 | Chemical speciation and mineral solubility. Sorption modelling including the Triple Layer Model. Some organic complexation capability. Fairly extensive database especially for USEPA priority pollutants. Includes many organic ligands. Easy to use. A companion preprocessor program PRODEFA2 builds the input file. | Dr J. D. Allison USEPA Environmental Research Laboratory, Athens, Georgia GA 30613 USA |
| NETPATH | Given a series of chemical analyses of waters sampled along a flow path, calculates plausible mineral dissolution/precipitation reactions that account for the variation in composition (inverse modelling). | U.S. Geological Survey Water Resources Division 437 National Center 12201 Sunrise Valley Drive Reston Virginia VA 22092 USA |
| PHREEQE/ PHREEQM | Mixing of waters, reaction of minerals with water, calculates pH and Eh after reaction. No sorption modelling or ion exchange reactions (forward modelling). Has a preprocessor program PHRQINPT to aid input. PHREEQM is an extended version of PHREEQE - it has all PHREEQE'S capabilities plus an improved treatment of cation exchange and a simple solute transport model to simulate reaction, diffusion and dispersion in 1 dimension. | PHREEQE:- USGS (See above) PHREEQM:- Dr. C.A.J. Appelo, Institute of Earth Sciences Free Univ. of Amsterdam Amsterdam The Netherlands |

Table 3.6 Estimated pH of solutions in equilibrium with calcite and dolomite at various p_{CO_2} 's calculated using both MINTEQA2 and PHREEQE

| p_{CO_2} (atm) | Pure water | | Pure water + Calcite | | Pure water + Calcite + Dolomite | |
|---------------------|------------|---------|----------------------|---------|---------------------------------|---------|
| | MINTEQA2 | PHREEQE | MINTEQA2 | PHREEQE | MINTEQA2 | PHREEQE |
| 0.1 | 4.346 | 4.366 | 6.645 | 6.668 | 6.779 | 6.793 |
| 0.01 | 4.846 | 4.865 | 7.293 | 7.318 | 7.425 | 7.440 |
| 0.001 | 5.346 | 5.363 | 7.947 | 7.972 | 8.076 | 8.093 |
| 0.0035 | 5.574 | 5.588 | 8.246 | 8.271 | 8.400 | 8.390 |
| 0.0001 | 5.846 | 5.855 | 8.602 | 8.627 | 8.728 | 8.746 |

Some models consider the mass transfer between aqueous-gaseous phases. Nair et al. (1990) found that neglecting the gas-phase diffusion in the unsaturated zone could result in an underestimation of the leach rate of volatiles such as benzene to the underlying groundwater.

Degradation is often microbiologically controlled but not necessarily so. Abiotic degradation of many synthetic organic chemicals can occur. This is often redox-sensitive and so there can be an important interaction between organic and inorganic processes.

3.3.9 Immiscible liquids

The contamination of aquifers with toxic immiscible liquids is currently of great concern. These liquids are usually known as non-aqueous phase liquids (NAPL's) and can be either denser-than-water (DNAPL's) or lighter-than-water (LNAPL's), sinkers and floaters, respectively. Lawrence et al. (1992) have recently reviewed the situation for DNAPL'S in the UK Chalk and Triassic Sandstone. The DNAPL's, which are mostly halogenated solvents, are persistent and highly toxic so that even great dilutions in an aquifer may not be sufficient to render the water of drinking water quality standard. Models for the movement of DNAPL's are complicated because flow is invariably preferential, vertical movement can be extremely rapid and can even go against the direction of flow of groundwater. Dissolved DNAPL will obviously follow the groundwater flow. LNAPL's, which include petrol, are not such a serious long term hazard since they will tend to be confined close to the surface. Again modelling is complicated by density differences and often by the need to consider volatilization. Figure 3.2 shows the processes affecting the fate and transport of chlorinated solvents at Picatinny Arsenal, New Jersey.

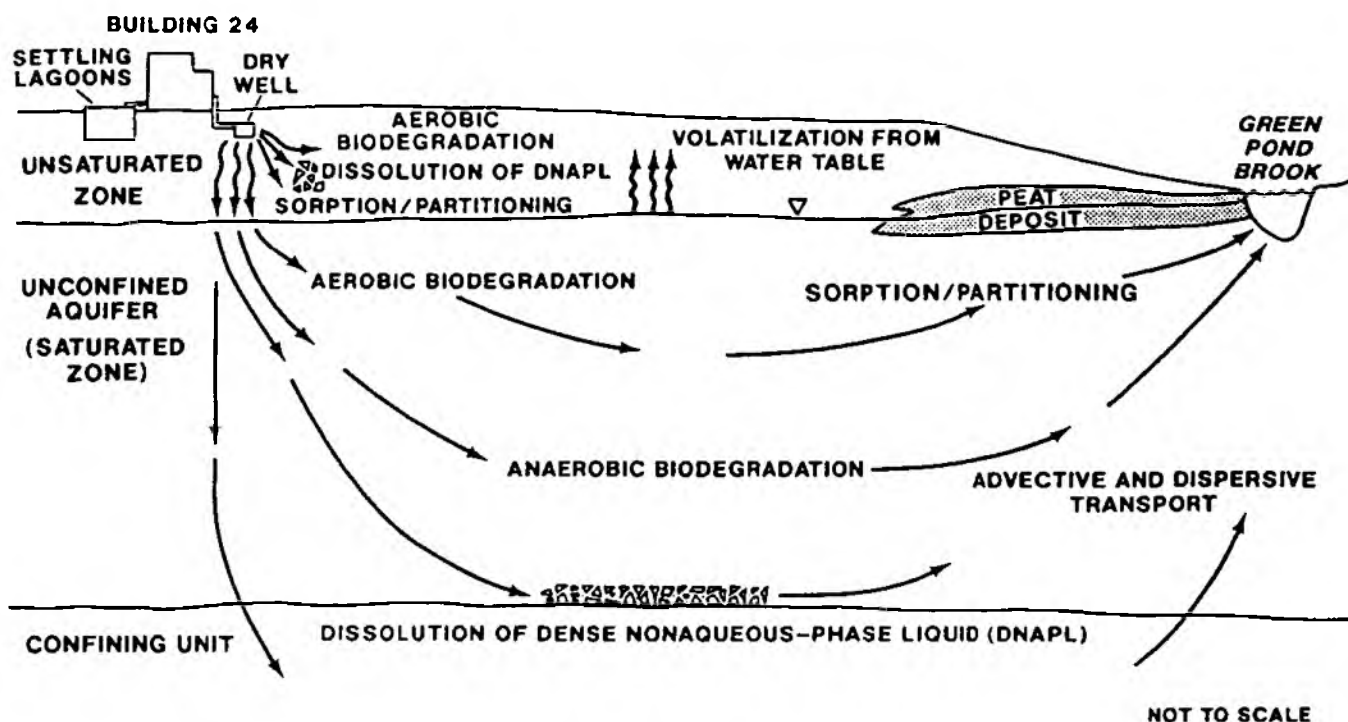


Figure 3.2 Processes affecting the fate of chlorocarbons in the groundwater at Picatinny Arsenal, New Jersey (from Mallard and Aronson, 1991)

3.3.10 Exposure and risk assessment models

Canter et al. (1987) discuss many of the earlier approaches to risk assessment, for example various point scoring systems for assessing the pollution potential of various practices, e.g. use of pesticides, brine disposal, siting of waste disposal (Superfund) sites. The **DRASTIC** index attempts to rank sites according to their pollution potential. It is a seven factor index based on Depth to groundwater, Recharge rate, Aquifer media, Soil media, Topography, Impact of unsaturated zone and hydraulic Conductivity of the aquifer. A potential site is rated 1-10 on each of these seven factors and then a weighted sum formed which is then used to classify the site. Various programs are now available from the USEPA which do this.

Specialized models are available for pesticide leaching. Quantitative efforts to classify the leaching potential of pesticides are based on a combination of their mobility and their transformation properties (Jury et al., 1987). Jury et al. based their early screening model on a linear sorption isotherm and a depth-dependent transformation rate. They assumed a constant sorption coefficient with depth and constant liquid fluxes and ignored plant uptake and diffusion/dispersion and preferential flow pathways.

There are now a number of more realistic pesticide leaching models available (see Boesten and van den Linden, 1991 for a review). For example, PRZM is a management model but uses the convection/dispersion equation for solute transport, reversible linear sorption,

first-order transformation rates and passive plant uptake. These models do not consider non-linear sorption or temperature effects but a recent model by Boetsen and van den Linden (1991) does. These authors found that changing the sorption coefficient by a factor of two changed the leaching by a factor of ten. The Freundlich isotherm is probably the most appropriate isotherm for pesticide sorption - the linear isotherm is a special case (Singh et al., 1990). The time of application (e.g. Spring or Autumn) was also very important. Autumn application gives rise to much higher leaching.

3.3.11 Solute transport and predicting breakthrough curves

The great majority of solutes, natural and man-made, interact with each other and with the natural solid surfaces around them. This affects the rate at which they move through the environment. Geochemists often talk about 'conservative' solutes meaning solutes that do not react to any great extent with the surrounding rock and so remain essentially all in the aqueous phase. Such substances obviously make useful water tracers.

The most commonly quoted 'conservative' tracers are the halogens particularly the chloride ion. Chloride is sometimes used as a water tracer. However, although chloride does not interact with most solids very strongly and does not form common insoluble salts, it is an important component in the cell sap of plants, animals and microbes and therefore does get involved in biogeochemical cycles which can move at a different rate from the bulk of the water.

The other halogens tend to be more reactive: fluoride reacts strongly with many silicate and oxide minerals, and bromide and iodide are sorbed quite strongly by solid organic matter.

Most other inorganic solutes and most organic solutes interact more strongly with their surroundings. This usually has the effect of slowing down their movement maybe by an order of magnitude or more. A simple formula for estimating the magnitude of this retardation is given by the retardation factor, R_d , which is given by

$$R_d = 1 + \rho K_d / \epsilon \quad (3.2)$$

where K_d is the solid/solution distribution coefficient (the slope of the adsorption isotherm which is assumed to be linear), ρ is the bulk density of the medium and ϵ is its fractional porosity. The mean rate of movement of the solute, v_i , will then be given by

$$v_i = \frac{v_{H_2O}}{R_d} \quad (3.3)$$

where v_i and v_{H_2O} are the rates of movement of the solute and water, respectively. A K_d of 1 ml/g means that the solute will move only about 1/5 th of the speed of the groundwater. Therefore a detailed understanding of the geochemical (and biochemical) reactions taking place in groundwater is an important prerequisite to understanding the movement and fate of chemicals.

Much work has been carried out in recent years in trying to predict the breakthrough curves of various contaminants particularly pesticides. The usual approach is to carry out a column experiment in which a pulse of contaminant is put in at the top of the column and the output at the bottom is measured as a function of time. Various 1-d solute transport models have been developed to explain such data but the more sophisticated include non-equilibrium sorption, biotransformation and 'immobile' water. Physical non-equilibrium is often more important than chemical non-equilibrium (see the review by Sabatini and Austin, 1990), i.e. it is often the rate of transport of a solute rather than the rate of chemical reactions that controls the rate of sorption and solute transport.

Brusseau et al. (1992) present an example using their multiprocess non-equilibrium with transformation (MPNET) model. The transformations are formulated as first-order processes and slow sorption is modelled by assuming sorption at two types of 'site', one in which equilibrium is instantaneous and the other in which the sorption kinetics are first-order. Water only moves through the 'mobile' regions but there is a constant interchange of solutes with the 'immobile' region. The sorption isotherm is assumed to be linear. Clearly even with these simplifications, the model is already complicated and there are a large number of parameters to estimate. However the model successfully predicted the sorption, degradation and transport of 2,4,5-T in a column packed with aggregated soil (Figure 3.3). The main use of such a model is in the simulation of solute transport for sensitivity analyses and for interpreting laboratory column experiments.

3.3.12 Linking geochemical speciation code to transport models

There are now a great number of computer programs that link chemical speciation and transport so that they can in principle simulate solute transport. However, they vary greatly in size, complexity and capability and there is no single program that will solve all problems (it is debateable whether there ever should be one). Ashton et al. (1991) give an up-to-date and comprehensive summary of a wide variety of computer programs dealing with problems associated with radioactive waste disposal but also relevant to more general problems. They cover corrosion, leaching, geochemistry, geomechanics, heat transfer, groundwater flow, gas transport (Volume 1), radionuclide migration, biosphere, and safety assessment (Volume 2). Altogether over 300 programs are reviewed. Special problems dealt with include simultaneous heat transfer, brines, and finite element groundwater transport.

Speciation codes that have been linked with transport models are PHREEQE (in PHREEQM, CRACKER, CHEQMATE), MINTEQ (in HYTEQ) (MINTEQ was itself a derivative of MINEQL) and MICROQL, a scaled-down version of MINEQL (TRANQL) (Cederberg et al., 1985). Westall, the originator of MINEQL, has recently produced a model STEADYQL for simulating quasi-steady state chemical changes of a water while flowing through a soil or similar column (Furrer et al., 1989). It has been used to analyze the sensitivity of the pH changes that occur in acid soils as a result of various processes such as slow weathering reactions and the presence of organic acids (Furrer et al., 1990).

Recent reviews of solute transport models are by Grove and Stollenwerk (1987), Engesgaard and Christensen (1988), Yeh and Tripathi (1989), Mangold and Tsang (1991) and Engesgaard (1991).

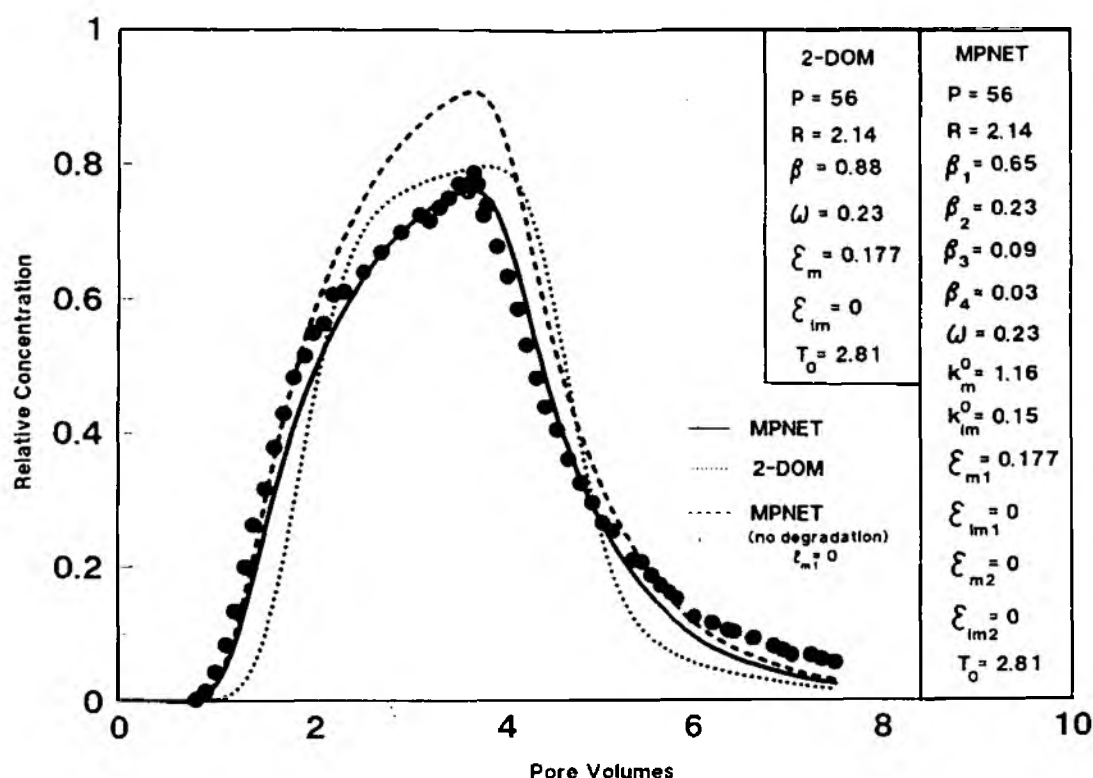
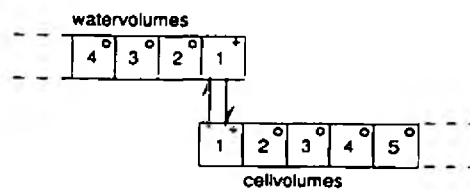


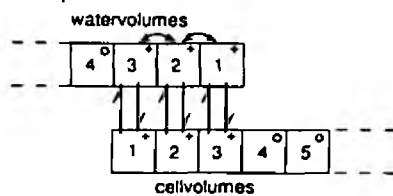
Figure 3.3 Comparison of observed (points) and predicted (smooth curves) results for the breakthrough of 2,4,5-T through a column packed with an aggregated soil. The model used was MPNET. Inclusion of degradation kinetics substantially improved model fit (from Brusseau et al., 1992)

PHREEQM is a relatively simple but powerful 1D solute transport program; it is strong on its chemistry, weaker on the transport part. However, it is able to make useful predictions and can simulate dispersion and diffusion which when combined with the facilities of PHREEQE such as precipitation and dissolution, and an improved treatment of ion exchange makes it a versatile program. It simulates transport by using a 'mixing cells' approach (Figure 3.4). It works in a simple way by making use of cells and timesteps. After each timestep, the water is shifted along or down one cell, and all the cells before or above thoroughly mixed and reacted. Providing the timestep is sufficiently small, the model performs well numerically. PHREEQM keeps the transport and chemistry separate which makes it easy to program on small computers and is able to model transport situations with complex initial conditions (which are normal). Quite complex profiles can be set up by dividing the cells into different layers. Radial flow can be simulated by systematically varying the cell volumes. Figure 3.5 gives an example of the use of PHREEQM for predicting the breakthrough of various ions after eluting a column of soil with SrCl_2 . The results look very encouraging.

After 1 timestep :



After 3 timesteps :



o original composition

+ composition after combination
of water- and cellvolumes

mixing
(geo)chemical model

Figure 3.4 The 'mixing cell' approach to simulating solute transport used by the PHREEQM program (from Appelo and Postma, 1992)

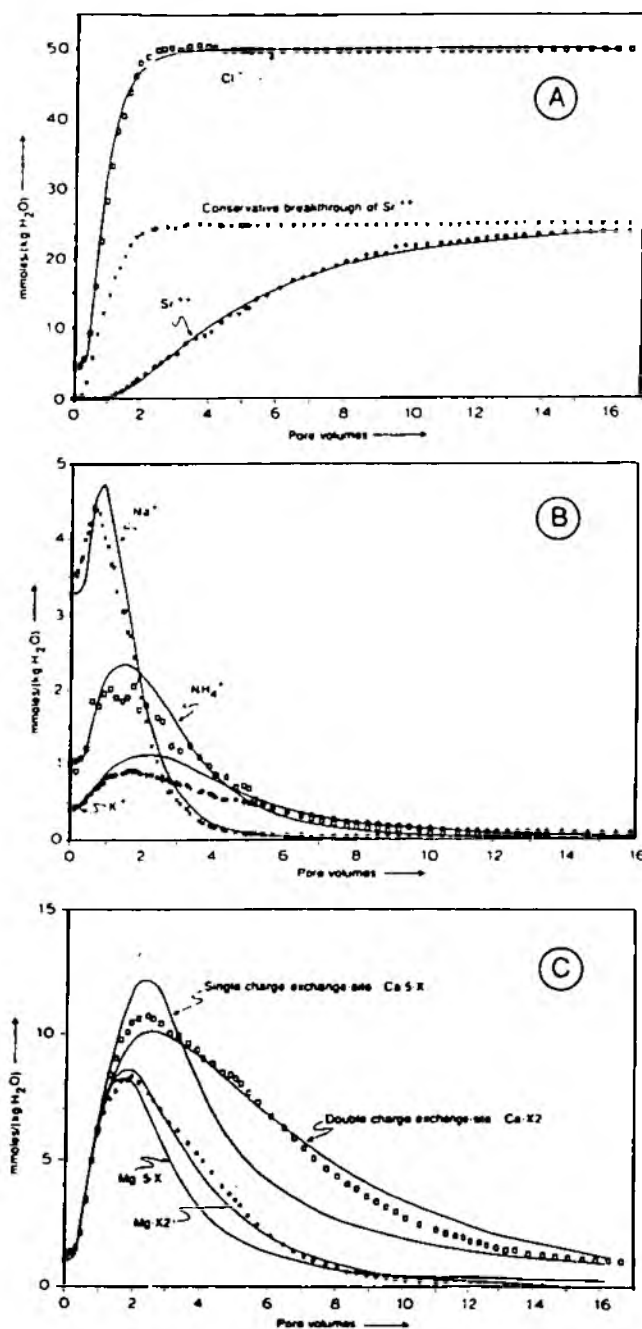


Figure 3.5 Elution of exchangeable cations from a column of soil using SrCl_2 . Theoretical breakthrough curves were calculated using PHREEQM with two different conventions for formulating the ion exchange reactions (from Appelo and Postma, 1992)

4. BIOCHEMICAL MODELS

4.1 Biofilm modelling

An idealised biofilm can be envisaged as being made up of a homogeneous mixture of bacteria and binding extracellular polymers. McCarty et al., (1984) describe an idealised biofilm (Figure 4.1) having a uniform cell density of $X_f (M_x L^{-3})$ and a locally uniform thickness of L_f . Groundwater flows in x direction and substrates are taken into the biofilm in z direction. The distance L represents the thickness of a mass transport diffusion layer through which the substrate must pass before it is utilised. Within the biofilm the substrate is utilised by the bacteria following a Monod-type relation with diffusion of the substrate through the biofilm according to Fick's Law. Equation (4.1) (McCarty et al., 1984) is the differential equation with steady-state substrate utilisation (the right hand side) equating with molecular diffusion (the left hand side) at all points in the biofilm.

$$D_f \frac{d^2 S_f}{dz^2} = \frac{k X_f S_f}{K_s + S_f} \quad (4.1)$$

where

S_f = concentration of rate-limiting substrate at a point within the biofilm (M, L^{-3})

D_f = molecular diffusivity of the substrate within the biofilm ($L^2 T^{-1}$)

k = maximum specific rate of substrate utilisation by the bacteria ($M, M_x^{-1} T^{-1}$)

K_s = Monod half-maximum rate concentration (M, L^{-3})

z = distance normal to the surface of the biofilm (L)

The substrate reaches the biofilm surface via mass transport across the diffusion layer, Equation (4.2) from McCarty et al., 1984

$$J = -D \frac{dS}{dz} = D \frac{S - S_s}{L} \quad (4.2)$$

where

L = thickness of diffusion layer (L)

J = flux of rate-limiting substrate across the diffusion layer and into the biofilm ($M, L^{-2} T^{-1}$)

D = molecular diffusivity of the rate-limiting substrate in water and

S and S_s = substrate concentrations in the bulk liquid and at the biofilm surface, respectively

Further details on biofilm modelling are given in McCarty et al. (1984) and much work on both steady-state/non steady-state biofilm models plus utilisation of very low substrate levels in biofilms is detailed by them.

4.2 The significance of microbial activity to contaminant transport modelling

Most contaminant transport models have four main components (Mackay et al., 1985; Newsom, 1985): decay; advection, dispersion (diffusion and mechanical mixing) and adsorption. Detailed discussion on the mathematics describing these processes can be found in Dickinson (1991).

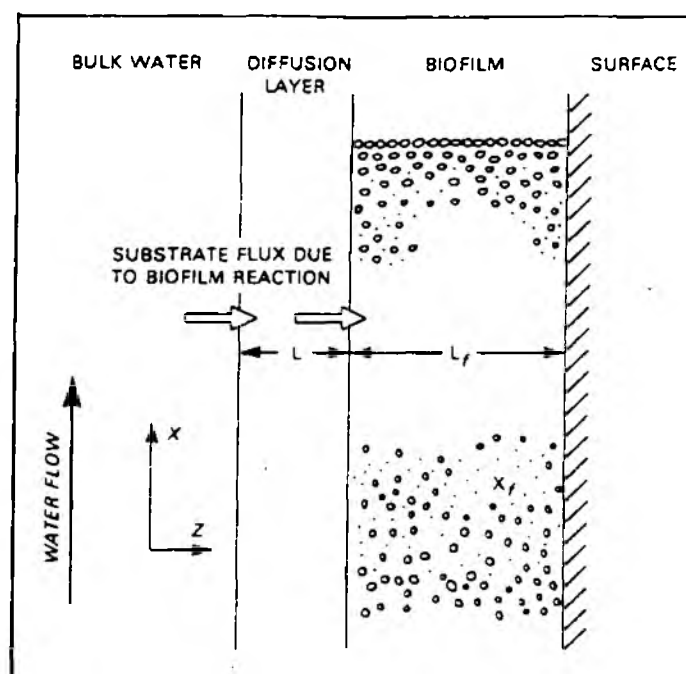


Figure 4.1 Idealised biofilm showing uniform cell density (X_f), thickness (L_f), water flow, and substrate flux into biofilm (from McCarty et al., 1984)

Yates and Yates (1990) discuss the role of microbiological presence on each of these components. Decay rates are often taken as a constant but many decay rates are known for microbes which vary with species and growth conditions. Thus it may be prudent to take the most conservative value or calculate the effects of individual decay rates and then combine their effect. In advection and dispersion the velocity of microbes may be faster than that indicated by conservative tracers (see also Section 4.3). This may be explained by the fact that larger microbes may only be able to travel through large pores where their velocity is larger than when the medium is taken as a whole. Tracer test with microbes are thus suggested.

Adsorption of microbes onto surfaces varies greatly and is site-specific, activities of sorbed and non-sorbed microbes also vary (see Section 3.4.5). Yates and Yates (1990) illustrate these microbial effects on model predictions (Figure 4.2). Microbes are added to water for 12 hours with the water moving 10 m day^{-1} . If advection only is occurring (A) then the first microbes will travel 10m in 24 hours whereas those added after 12 hours will travel 5 m. The concentration of microbes from 5 to 10m from the source is constant and equal to the applied concentration ($c/c_o = 1$). The concentration will remain constant for 12 hours after which the microbial concentration at 10m drops to zero because they have all travelled at the same velocity. If advection and dispersion influence transport (B) the area is the same as A. However, the microbes are travelling at different rates although the average velocity is the

same as A. When adsorption is added (C) to advection and dispersion the area under the curve is reduced because some microbes are sorbed, decreasing numbers and slowing movement. Decay removes microbes permanently from the system (D) and the area under the curve is reduced further although movement is not changed. Thus D is probably the most realistic curve.

Dickinson (1991) details a number of existing transport models which have been developed to describe microbial movement in, for example, saturated and unsaturated porous media. Examples of these include Sumatra-1 and WORM (Van Genuchten, 1978; 1986) both of which are finite element model of one dimensional contaminant transport in the vadose zone. Another more complex model is BIOPLUME II (Rifai et al., 1987) which is a two dimensional contaminant transport model designed to simulate transport of dissolved hydrocarbons in groundwater under the effect of oxygen limited biodegradation. The theoretical background to this code is given in Konikow and Bredehoeft (1978) and Borden and Bedient (1986). A decision support system for groundwater contaminant problems termed OASIS has been developed for BIOPLUME II which helps to assess and analyse groundwater contamination problems.

These models are, however, based on the advection-dispersion equation for solute transport (Corapcioglu and Haridas, 1984) and most of these studies have generated insufficient data

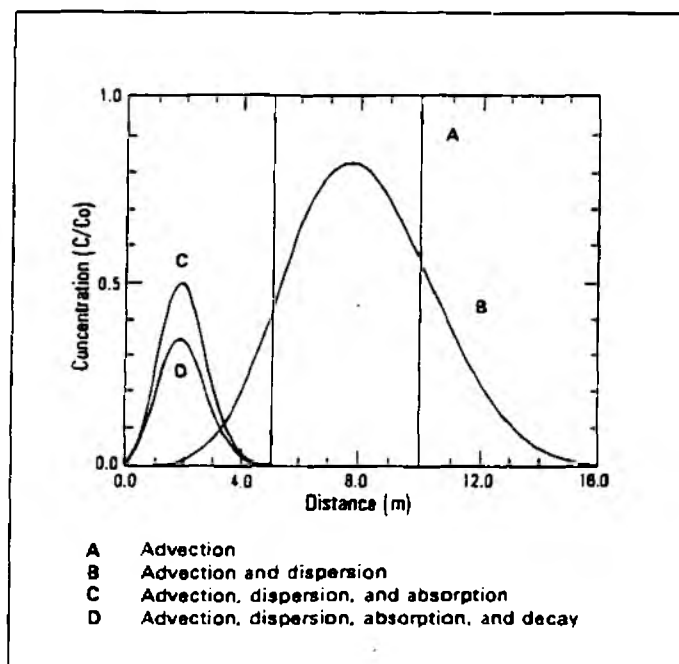


Figure 4.2 Effects of various processes on contaminant transport (after Yates and Yates (1990))

to establish a predictive model (Dickinson, 1991). Many important parameters are not directly measurable or are variable (e.g. microbial source population). Many microbial studies do not report aquifer hydraulic properties necessary for the models. Microbes tend to be transported as colloids and not as contaminants in solution and their physiological behaviour such as the formation of biofilms is not considered. The ideal model for microbial transport would take into account these shortcomings. Models also exist to calculate microbial growth rates in subsurface environments, e.g. MGSE (Rochelle et al., 1992) but these are not linked to contaminant transport codes.

We have not found models which describe the relationships between contaminant movement, microbial movement and biodegradation although there has been a considerable effort in recent years to model denitrification in aquifers and these contaminant transport models are beginning to include microbial growth and the utilization of biomass (Frind et al., 1990; Kinzelbach et al., 1991).

5. RESEARCH NEEDS

5.1 General

Research sites would greatly benefit the whole community of groundwater researchers by providing laboratories in which to undertake many of the investigations suggested below. More generally, they would provide a body of field data against which models could be validated. It needs to be recognized that such efforts are long-term.

5.2 Dispersion

Tracer tests need to be far more routinely performed on the Chalk and sandstone aquifers to build up a body of information on dispersive characteristics.

5.3 Unsaturated zone

Unsaturated zone field experiments need to be performed on a variety of scales. Possibly, tracer tests using lysimeters would be convenient and controllable.

Hysteresis is not well represented by existing models.

5.4 Multiphase flow

Qualitative observations - especially of dense organic liquids - must be carried out to establish a better conceptual understanding of the flow mechanisms. Large and small-scale experiments of multiphase flow are also required to provide model validation data.

In a recent report to the NRA, Lawrence et al. (1992) describe the particular problems of understanding the behaviour of halogenated solvents in the Chalk. In that aquifer the complexity of the fissure system precludes any attempt to even formulate the transport equations. Significant effort will be required in order to adequately characterize the Chalk fissure geometry.

Laboratory work is required to establish: specific retention, relative permeabilities, and hysteresis curves.

Dense non-aqueous phase liquids (DNAPLs) do not spread very far from the point of origin at the surface. Since these sink quickly, they must assume a static geometry in a time that will be short compared, for example, to the time taken for mobilization of a clean-up effort. Therefore the DNAPL can be regarded as a near-static source (via dissolution and advection) of solute, the behaviour of which can be modelled with the conventional convection-dispersion models. It would seem that effort in characterizing such 'secondary sources' would be very cost effective and relevant in comparison to effort on modelling the fast DNAPL migration.

Gas phase transport modelling needs to be developed further to aid clean-up design and soil-gas surveying techniques.

5.5 Fractured rocks

A complete characterization of a fractured rock system includes the dimensions of the system - the fracture positions, lengths, widths and apertures (and spatial variations of those apertures) - and the porosity and permeability of the matrix. The collection of such information is neither feasible nor economic within the context of most groundwater investigations. Even within the context of feasibility studies of radioactive waste disposal, where financial resources are relatively large, only limited success can be claimed. Without detailed characterization of fractured-rock systems, uncertainty in predictions is a fact that will have to be endured for the foreseeable future. Further effort must be made to develop geophysical, tracer and pumping-test techniques, both individually and as combined tools, to obtain a reasonable body of information for model formulation and calibration. But even then predictions of behaviour of the system must be formulated and presented in a probabilistic manner.

5.6 Chemical processes

Particular areas for further work include:-

- Denitrification.
- Sorption of pollutants by aquifer material, including the kinetics.
- Geochemistry of toxic metals, including cadmium and arsenic.
- Groundwater quality measurements.
- Degradation of organics in redox-sensitive aquifers.

5.7 Coupling of geochemical and transport models

The coupling of geochemical and transport models, each of which may be well proven individually, is a far from mechanical task. Firstly, the resulting codes tend to be very costly to run. Increasing computing power and (on-going) efforts to make the solution techniques more efficient will presumably pay off in the long term. However, another important issue is that of field data.

As always, adequate field data (water chemistry data) must be collected to permit model calibration and validation. For time dependent problems, this includes the need to know the original ('baseline') chemistry of the water prior to the change of interest (e.g. Pollution event); such surveying of groundwaters is almost totally lacking.

Another problem is that of the stratigraphic complexity of aquifers. In many cases of interest, the variations in mineralogy along a flow path will not have been studied in sufficient detail, even if their presence has been appreciated.

5.8 Numerical model development

By and large, mathematical and numerical techniques have gone ahead of the rest of the work needed to provide a foundation for reliable modelling. However, development of a generic double-porosity model specifically designed for flow and transport in the Chalk aquifer could be a worthwhile enterprise.

6. CONCLUSIONS

Groundwater contaminant modelling is a relatively immature field of study (about 20 years old) and, while much has been written on the subject (especially on the computational methods), model validation for anything but the simplest scenarios is lacking. Taking a highly sceptical view, it might be argued that transport models have only been successful when either: (i) they have been calibrated against all of the field data, and thus tell us little more than we already know, or (ii) they have been used to make long-term predictions (such as with radioactive waste disposal simulation) where it is not possible to compare with reality.

The positive attitude to this situation is to: (i) identify research that needs to be undertaken to enhance the abilities of our models, and (ii) adopt a sensible attitude to model use.

Groundwater modelling publications, naturally, tend to emphasize what can be done rather than what cannot be done or what cannot always be done well. They seem to offer the kind of results the manager desperately needs. However, models are no more than management tools which can be of use in many but not all circumstances. Models must be used in conjunction with field work, not instead of it. Also, modellers should provide and managers should expect a clear indication of the possibility of model error: both conceptualization and implementation errors.

Models of saturated groundwater flow (used, for example, in resource evaluation) have become reasonably reliable decision tools, given adequate data. However, problems of heterogeneity (e.g. depth variation of hydraulic conductivity) restrict the ability of these models to give accurate predictions of travel times, which are important for contaminant transport.

Models of unsaturated flow are far less reliable, even the correct formulation of the flow equations at the field scale remains open to debate. Partly, this problem arises from the fact that the standard theory based on the Richards equation has been developed and validated in the laboratory rather than the field scale. The acquisition of adequate field data on the relationships between conductivity, saturation and suction (head) remains a formidable task at the field scale, as does the problem of accurate numerical simulation given that data. There even remains disagreement on whether there can be significant horizontal movement in the unsaturated zone.

The understanding of flow and transport in fractured rocks has advanced greatly in recent years but much remains to be done. It is often assumed that the rock can be represented by an average 'equivalent homogeneous medium', but it is not easy to specify conditions under which such an assumption would be valid. For example, fissures represent pathways along which contaminants may pass very quickly relative to the bulk of the water, with serious risk implications. Double porosity models offer a reasonable balance between the equivalent homogeneous medium models and the highly complex discrete fracture models developed for the simulation of radioactive waste disposal. (The latter set of models must still be regarded by the general hydrogeological community as expensive research tools

rather than as practical tools for decision makers.) However, even for the double porosity models a very significant problems exist with regard to establishing the 'statistical geometry' of the system, and the transport characteristics of the rock are highly sensitive to that geometry. Channelling of flow deserves particular consideration. The calibration and validation of all but the simplest of these fractured-rock models poses a formidable task, with great demands on hydrogeologists and geophysicists to provide adequate data. So, although the models often have the potential to provide useful predictions, they can only be used to investigate a variety of possible scenarios with parameters being specified in the form of distributions of values.

Multiphase flow is a significantly more complex process than single phase flow since, as with unsaturated flow, it is necessary to establish complex (functional) relationships between conductivities, saturations and heads. And that needs to be done at the field rather than the laboratory scale. Models can and have been constructed, but validation is difficult. In some multiphase systems, for example where solvents are involved, observed laboratory behaviour is very complex and adequate formulation of transport equations remains a challenging task. Much further work is needed to obtain transport parameters appropriate to the wide variety of potential contaminants, particularly solvents. For multiphase flow in fractured porous media, models are beginning to appear but fundamental work is still required on the displacement processes. Some optimism can however be expressed given multiphase models are being successfully used by the petroleum industry, albeit at significant cost and for relatively restricted scenarios.

The processes governing the behaviour of a single nonreactive contaminant in the saturated zone of a consolidated aquifer are relatively well understood, and the corresponding 'simple' transport models can often be used with some confidence. As further processes are introduced the reliability of models falls off rapidly due to a lack of confidence in the underlying models of the processes combined with the complexity (especially, the heterogeneity) of natural systems. Models that include such processes as oxidation/reduction, precipitation, and biological processes have been developed but these need further development and testing before being regarded as practical tools.

When these reaction processes are included in models, significant problems arise due to numerical problems and data constraints. Data restrictions apply especially to reaction rates affected by mineralogy. Few successful applications of models have been reported for cases which involve complex chemical reactions.

Most microbial activity occurs on surfaces in biofilms and simple models exist to describe substrate utilisation in these structures. Microbial movement in the subsurface can also be described using modified contaminant transport codes. However, the link between biodegradation of pollutants and transport does not appear to exist.

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APPENDIX A - SOME GENERAL MODEL FEATURES.

A.1 Management, prediction and identification models

Possibly the broadest classification that can be applied to groundwater models is in terms of the general purpose for their use. It is normal to consider three categories: prediction, management and identification (or inverse) models.

Most models are prediction models, which simulate the behaviour of a system according to specified stresses (normally mass inputs) given a set of initial conditions. Prediction models aim to answer the question: "What would happen if ...?" and they are therefore best regarded as thinking tools. These models normally form the basis of management and identification models.

Management models are usually used to indicate which policies are consistent with management objectives and constraints. They will generally combine a prediction model with other quantifiable aspects of a problem. They will often incorporate some decision criterion - such as minimum cost or risk - with a set of quantifiable constraints such as minimum supply or maximum capital cost. Essentially, one of two methodologies is applied in management modelling. The simplest of these involves choosing the 'best' (according to the decision criteria) of a given set of proposed policies. The other method involves automatic identification of an optimum policy using the techniques of operational research (such as linear programming). This latter method is particularly appropriate when continuous design variables are involved.

An identification model is one which, roughly speaking, uses a prediction model in reverse (the term 'inverse model' is often used). Given observed responses of a groundwater system to various stresses, and identification model might be used to determine: unknown transport parameters, stresses (e.g. recharge), or boundary conditions. A simple and very common hydrogeological example arises in the analysis of pumping-test data, where observed water levels in boreholes are used to determine the hydraulic properties of an aquifer such as transmissivity and storage coefficient.

Various techniques are used to turn a prediction model into an identification model. Most simply, a trial-and-error variation of parameters is conducted until predicted system behaviour matches field data. Automatic computational procedures are now being developed to replace this technique. A problem that often arises in the use of identification models (and in model calibration) is that various sets of derived parameters give equally good predictions of the aquifer behaviour. Expert judgement must then be applied in order to choose the most appropriate parameter set. The usual cause of this problem is inadequacy of the data, either in terms of quality, quantity or range of measurement.

A.2 Methods used for solving the flow and transport equations

It is not appropriate to give full mathematical details of the various methods that might be used to solve the groundwater flow and transport equations, however it is of value to have some indication of the range of methods and their relative strengths and weaknesses.

A.3.1 Analytical methods

With analytical methods, solutions of the flow and transport equations are expressed in terms of standard mathematical functions. Rarely can solutions be found for: heterogeneous media (spatially dependent transport parameters); transport parameters that vary with either the head or concentrations; nonlinear sorption isotherms; boundaries that are other than linear, circular or spherical; or time-dependent boundary conditions.

Analytical solutions provide far more insight into the behaviour of systems than other methods, particularly the influence of controlling parameters. It is therefore often worthwhile to simplify the real problem down to a level where an analytical solution can be obtained. Such work should be considered in the initial phases of any modelling project.

Laboratory and field experiments are often devised in such a way that the conditions are (or are assumed to be) simple, and then it is appropriate to analyse the data obtained using analytical models.

Analytical solutions also provide a basis for verifying numerical solutions, which are potentially subject to far more errors.

Most groundwater textbooks provide sets of analytical solutions to a variety of simple flow and transport problems, but they vary greatly in the number of solutions presented and the extent to which they provide instruction in the derivation of those solutions. The reader interested in learning the techniques of solution derivation would be well advised to use texts concerned with teaching the methods of mathematical physics and the solution of partial differential equations. Texts and reports which are particularly rich in analytical solutions include: Cleary (1978), Hunt (1983), Strack (1985), van Genuchten and Alves (1982), Walton (1984), Bear (1979).

The transport equations are often linear: the sum of two solutions is also a solution. Under these conditions the solution for a homogeneous system with simple boundary conditions can be found in the form of a Laplace transform (of the time-dependent head, concentration, or temperature). Inversion of the transforms to reveal a solution in terms of time rather than a transform parameter, is often very difficult (in many cases impractical), and the results very complex (several erroneous results have appeared in the literature). Also, these results normally involve singular integrals which are numerically difficult and expensive to evaluate. An alternative technique advocated by Barker (1982, 1985a) is to evaluate the time-dependent solution directly from the transform by numerical inversion. The inversion algorithm described by Talbot (1979), was found to be particularly efficient

and accurate. This approach has been fairly widely adopted; for example, it provides the basis of the NAM1D program (Hodgkinson et al. 1984) for one-dimensional transport in fractured rock which includes radioactive chain decays.

Analytical solutions play an important role in that they permit a better understanding of the effects of uncertainties both in parameter values and the form of governing equations. When Monte-Carlo methods are necessary, many thousands of realizations are readily computed for analytical solutions (e.g. Chilton et al. 1989).

To emphasize the point that simple analytical models should not be ignored, mention is given here of the Vertical-Horizontal Spread (VHS) model used by the U.S. Environmental Protection Agency (EPA). In determining whether a particular solid waste is non-hazardous, the primary criterion is whether the leachable chemicals from the waste would result in unacceptable groundwater quality 500 ft down-gradient of the disposal location. It is EPA policy to use the VHS model of Domenico and Palciauskas (1982), which is described by the following equation for concentration:

$$c = c_0 \operatorname{erf}(z/\sqrt{4\alpha_z}) \operatorname{erf}(L/\sqrt{16\alpha_L x}) \quad (\text{A.1})$$

where c_0 is leachate concentration, z is penetration depth, x is distance from disposal site, L is the length of the disposal site, α_z is the vertical dispersivity, and α_L is the longitudinal dispersivity. The uncertainties in parameters are overcome by the EPA through the use of reasonable worst case values.

A.3.2 Semianalytical methods

Analytical solutions often take the form of very complex expressions involving the functions of mathematical physics and integral transforms. Evaluation of such expressions often requires computational assistance. With some models part of the problem can be solved analytically (e.g. the head distribution) while another part must be solved numerically (e.g. the construction of pathlines).

Such models and others that fall into neither the analytical or numerical categories are termed semianalytical models.

A.3.3 Numerical methods

Numerical methods are basically techniques which transform the partial differential equations of flow and transport into sets of algebraic equations (involving only arithmetic operators) which can be solved by computational means. This normally involves dividing the time and space coordinates into discrete intervals over which conditions are assumed to remain constant.

For readers unfamiliar with these methods a very brief outline of the techniques is given so that their relative merits can be appreciated.

Finite difference (FD) methods

For most finite difference methods the space and time coordinates are divided on a rectangular grid basis with the values of the independent variables (e.g. head and concentration) being specified on the grid nodes. The derivatives in the differential equations describing flow and transport are approximated by differences between the values of the independent variables on the grid nodes divided by the distance between the nodes. For example, the rate of change of head, $\partial h / \partial t$, would normally be replaced by $(h_i - h_{i-1}) / (t_i - t_{i-1})$ where h_i and t_i are the head and time for node i .

This technique, which has been in wide use since the 1960s, is easy to understand and relatively easily coded. The resulting numerical equations are usually well structured (e.g. a banded set of linear equations often results) which facilitates the use of very efficient solving algorithms. The main problem is in dealing with irregular boundaries and in varying the grid size, so that attention to be focused on regions of special interest such as wells and pollution centres.

An excellent introduction to this and other methods is given by Wang and Anderson (1982), although there are numerous other textbooks on the subject (see Cave and van der Heijde 1988).

Integrated finite difference (IFDM) method

The IFDM method generalizes the finite difference method by permitting an irregular mesh of polyhedrons rather than a rectangular mesh. Spatial derivatives are expressed in terms of the polyhedron volumes and face areas, and the normal distances from the nodes to the faces. The obviously greater flexibility of the method compared to the FD method is paid for by increased data requirement, code complexity, and computational cost.

This technique has been applied in the models: TRUMP, TRUST, TERZAGI, CCC and SHAFT79. Also, the important USGS model SUTRA combines the IFDM with the FE method. Narasimhan (1982), emphasizes the potential use of the method for modelling fractured porous media.

Finite element (FE) method

In the finite element method the spatial domain is divided into a mesh of elements of almost any convenient shape. The numerical formulation is normally based on a variational principle, rather than a direct approximation of the transport equation.

Variation of the independent variable (e.g. concentration) across elements is normally approximated by a polynomial function. When this function is linear and the elements are rectangles, the method is essentially equivalent to the finite difference method.

The ability to apply a variety of element shapes enables complex geological units to be accurately represented, and this has made the FE method very popular.

Standard texts are Huyakorn and Pinder (1983) and Pinder and Gray (1977)

Boundary integral equation (or boundary element, BEM) method (BIEM)

When geological units can be assumed homogeneous over large volumes, the flow and transport equations can often be discretized in terms of nodes on the boundaries of those regions: this is possible because the behaviour within a boundary is governed by the conditions on that boundary. This results in fewer nodes and algebraic equations than the FD and FE methods; however, the equations are more difficult to construct and the resulting solution matrices contain more non-zero terms.

Liggett and Liu (1983) provide the standard text on the subject.

Method of characteristics (MOC)

The method of characteristics (Konikow and Bredehoeft 1978) is applied to solute transport equations. The rate of change of concentration in the convection-dispersion equation is divided into separate advective, dispersive and loss components. The advective component is solved first, using a previously known or computed velocity field. This essentially gives paths ('characteristic curves') along which molecules flow. Marked points are moved along these paths, each of them representing the centre of gravity of a specified mass of solute. The dispersive and loss parts of the transport equation can usually be solved by very efficient (explicit) numerical methods. The MOC method is usually very fast but the codes tend to be long and complicated.

A set of methods, similar in philosophy to the MOC, are known as Eulerian-Lagrangian methods (e.g. Neuman and Sorek 1982).

Random walk methods

The method of random walk (RWM or MORW) (e.g. Prickett et al. 1981) can be regarded as a stochastic (refinement) of the deterministic MOC. The main differences are that in the RWM the walking points are regarded as expected values in a statistical sense, and the dispersive part of the transport equation is not solved but replaced by a random generator. This approach is much faster than that of the MOC and can allow for a growth of dispersivity with distance covered. The method allows great control on computational effort via the number of walking points (particles) followed but a large number of particles may be needed to obtain smooth results.

Equation solvers

Most numerical formulations of flow and transport equations results in a set of simultaneous linear equations to be solved; there will be as many equations as there are unknowns in

the system. Normally, most of the computational effort is involved in solving these equations. There are in broad terms two types of equation solvers in use: direct and iterative methods.

Direct methods provide solutions that should be exact if it were not for machine round-off errors. Such methods would be an obvious first choice if it were not for the fact that: (i) they are often computationally slow, and (ii) large (sometimes impossibly large) amounts of computer storage may be required.

Iterative methods aim to produce a sequence of approximate solutions - starting from an initial estimate - which converge towards the exact solution. Computer storage problems are far less than for direct methods, but errors are introduced by the termination of the iteration (truncation error). Errors tend to accumulate unless care is taken in formulating the iteration process.

Numerical groundwater models normally give rise to large sparse matrices. The Pre-conditioned Conjugate Gradient (PCG) solution approach has proved to be superior to most other iterative techniques under many conditions. In particular, it is applicable to both FD and FE approaches, it does not require iteration parameters, and it is better than other methods in dealing with 'stiff' matrices. A modified form of the PCG procedure used by Behie and Forsyth (1984) - known as ORTHOMIN - is becoming widely used.

Advection dominated transport equations are normally give rise to computational stability problems. Numerous attempts have been made to find alternative formulations. Particularly promising are the Laplace Transform Galerkin (LTG) method (e.g. Sudicky 1989) and the Taylor least-squares technique (Park and Liggett 1990). The LTG method is just one variant of technique first introduced for heat-conduction simulations, and subsequently adapted for the BIEM approach amongst others: it simply solves the Laplace transformed (with respect to time) transport equations and applies numerical inversion. It has potential for application to double porosity problems which would normally involve the solution of a partial integro-differential equation but where a general formulation in terms of the Laplace transform is very simple.

Some models provide two or more solvers which gives the user some control over the balance ('trade-off') between solution accuracy, mesh refinement and computational cost, given the memory and speed restrictions of the computer system in use.

APPENDIX B - TENTATIVE LIST OF TOPICS FOR THE REST OF THE PROJECT.

Because groundwater modelling is now such a vast enterprise it is important that work carried out within the limited resources of the current project (R&D 0295) is well targeted. The following list of topics is presented to encourage thought on what areas are of importance to the NRA and what priorities to put on those areas.

B.1 Follow-up to the model review and model directory improvement

Additions to the model features and descriptions tables (in R&D 0295/9/A).

Data needs of various models.

Database of references associate with models.

Inverse models - explanation and model descriptions.

List of suppliers - broaden.

Management models.

More categories tables in directory

Watershed models.

B.2 Topics to review under 'Modelling Methodology'

Calibration, verification, and validation.

Expert systems and decision support systems.

Geostatistical and Monte Carlo techniques.

Heterogeneity and uncertainty.

How to represent various features in models (e.g. boundaries and pollution sources).

Inverse (identification) models.

Legislative and legal use of models.

Management models.

Model selection process (including expert systems).

Models in data collection and analysis.

Quality assurance.

Risk analysis.

Scale effects in modelling.

Staffing of modelling projects and training.

APPENDIX C - RESULTS OF A RECENT SURVEY ON MODEL USE.

The US-based groundwater software distributors Geraghty & Miller recently conducted a survey of groundwater modellers. The results of that survey were briefly reported in a newsletter article (Geraghty & Miller 1992) and this appendix is based entirely on that article - a full report on the survey is in preparation.

The survey covered environmental researchers listed in the National Ground Water Association (NGWA) and International Ground Water Modeling Center (IGWMC) mailing lists. There were 876 responses, 67% from consultants, which identified 5564 modellers.

Table C.1 Top ten software packages identified by the Geraghty & Miller survey.

| | PACKAGES | HITS | DESCRIPTION |
|----|-------------|------|--|
| 1 | MODFLOW | 638 | 3-D transient, saturated flow model. |
| 2 | MOC | 267 | 2-D transient, saturated flow and transport model. |
| 3 | ModelCad | 187 | 'CAD-like' interface to: MODFLOW, MOC, PLASM, Random Walk, and other models. |
| 4 | SURFER | 177 | Surface contouring package. |
| 5 | PLASM | 118 | Quasi-3-D, transient flow model. |
| 5 | SUTRA | 118 | 2-D transient, saturated/unsaturated flow and transport model. |
| 7 | Random Walk | 111 | 2-D transient saturated flow and transport model. |
| 8 | AQTESOLV | 101 | Pumping-test analysis program. |
| 9 | MODPATH | 90 | 3-D particle tracking post-processor for MODFLOW. |
| 10 | FLOWPATH | 87 | 2-D steady-state flow and pathline model. |

The most used models identified are given in Table C.1, where a 'hit' indicates that the package is used by one modeller. The survey also identified the top three perceived benefits of models:-

- (1) The ability to make predictions.
- (2) Evaluation and design of remedial alternatives.
- (3) Development of a conceptual model.

The top three problems with groundwater modelling were identified as:-

- (1) Lack of adequate site-specific data.
- (2) Inadequate or complex modelling software.
- (3) Lack of trained and experienced modellers.