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Interim Report **R&D Project 0295**

Geochemical Process Modelling

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Geochemical process modelling

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CONTENTS

EXECUTIVE SUMMARY

This is the first interim report of the *Geochemical Process Modelling* project, which is concerned with the modelling of the transport of contaminants in the subsurface. The main aim of this document is to help direct work on that project by describing the general approach being taken by the British Geological Survey (BGS). In particular, the report attempt to make clear what range of topics BGS intend to covered during the project. It is hoped that the report will attract constructive criticism from both NRA and BGS staff.

It is explained that the project formulation is based on the fact that modelling must involve: a set of models, parameters to use in those models and a methodology for applying the models. An outline is given of the literature review, which is being undertaken as the first phase of the project; this makes clear the range of subsurface processes involved in pollution migration that will be covered. Also to be included in the review are topics which relate to the successful application of models, these will form the basis for the methodology.

Databasing needs of the project are only discussed briefly as it is too early to assess those needs in detail. It is, however, obvious that a centralized collection of hydrogeological data for UK aquifers would be of great value in pollution modelling (as well as for other purposes). A recommendation is made that consideration should be given to establishing a database of such information.

1. AIMS OF THIS REPORT

This report is an important working document as it provides a relatively early opportunity for critical discussion of the philosophy of the programme of work being undertaken by BGS within the project. The goals of the project can only be attained with coordinated inputs from both NRA and BGS and this report is very much part of that coordinating process.

Thus far, the majority of work carried out by BGS has been concerned with collecting information, in the form of papers, books (especially conference proceedings) and lists of computer codes, that relate to the problems of transport modelling. The volume of information available is immense, so it is important to filter that information to extract only directly relevant items. This task will continue for a further period of about six months and it is premature to give even a preliminary critical review while many, possibly key, sources are as yet unseen. This report does not therefore attempt a detailed technical review of any topic but instead provides a tentative outline of the review document, replacing the review material with general comments that: (i) indicate the relevance and importance of the various topics, and (ii) serve as a guide for the review process. Also, the review structure makes it easy for readers of this report (both from NRA and BGS) to identify missing topics they consider important and included topics they consider insignificant.

Some of the sections, particularly that on *The application of models* (Section 3.4), deal with non-technical issues; the ideas presented in such sections are important in establishing a sensible methodology for model use, although they will eventually need to be presented in a more structured manner for that purpose.

Of particular interest to those readers who wish to help by making a critical review of the work programme outlined in this report are: (i) the structure of the review topics (see the table of contents), (ii) the tentative list of pollution scenarios of interest to the NRA listed in Table 1, and (iii) the tentative list of topic not to be covered, given in Table 2.

For the benefit of readers not familiar with the project the report starts with an outline of the project. That is followed by the review outline, a brief discussion of databasing, a section on progress and future work, and, finally, recommendations.

2. OUTLINE OF THE PROJECT

2.1 Objective

As stated in the PIA, the overall objective of the project is:

> *To review, assess and develop modelling techniques for representing subsurface contaminant transport arising from typical pollution problems which occur in England and Wales.*

The concern of the project is not simply with computer codes but, more fundamentally, with the subsurface processes affecting pollutant migration, the mathematical description (if available) of those processes, and the problem of choosing suitable parameter values to use in those equations. Both the saturated and unsaturated zones are to be considered, but the soil zone is excluded.

2.2 Basic philosophy

Fundamental to the approach being taken by BGS to this project is the idea that the modelling process must be based on the existence of:-

(1) SUITABLE MODELS,
(2) PARAMETER VALUES APPROPRIATE TO THOSE MODELS, and
(3) A METHODOLOGY FOR USING MODELS.

These three elements, which represent the intended tangible product of the project, are discussed separately in the following sections.

Another important idea in the project formulation is that of identifying those scenarios most likely to concern the NRA. Taken in its broadest sense, the process of pollution model development is a task that will involve the efforts of a large proportion of hydrological scientists for the foreseeable future. Limitations must therefore be placed on the scope of the project, and particularly restrictive is the range of situations that could be of significant interest to the NRA. For example, there is no intention to cover the problem of radionuclide migration from potential radioactive waste repositories: this is a topic of great concern but not one of immediate importance to the NRA.

A problem pervading the application of models to subsurface transport is that of uncertainty. The recognition of the existence of many sources of uncertainty will be a constant feature of the project.

Since the task of pollution modelling is such an imposing and long-term one, it is important to identify where further effort should be placed to give the best benefits in both the medium and long term. These efforts must extend across many areas, including: numerical modelling, mathematical formulation, laboratory measurement, field testing and sampling. Throughout the project, obvious needs in these areas will be identified and reported to the NRA as potential areas in which future work should be encouraged and, perhaps, funded.

2.3 Suitable models

The rate of production of groundwater models is so high that it has given rise to the existence of an international organisation (The International Ground Water Modeling Center (IGWMC) which has offices both in the USA and Europe) to help list, evaluate and distribute those models. 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 appear 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. The problem of choosing between models is seen, in the context of this project, as being part of the *methodology*, but a separate problem is that of identifying a set of models from which to make that choice.

The effort that has been put into developing some of the better numerical transport models can be measured in several man-years. Within the current project there are insufficient resources to produce even one comparably sophisticated code. The intention is therefore to identify which of the existing codes are most suitable for application to the cases identified by the NRA, and to produce some more basic codes. Assessment of existing codes will include a clear indication of data needs and the cost of implementation.

The potential need for some new codes is based on several ideas. Firstly, in cases where the data are sparse, a sophisticated model is inappropriate and a simplified approach is justified. Also, there is a need for models which can take account of the very significant uncertainties that are normally involved in subsurface transport. It is envisaged that simple models which can include, in some form, that uncertainty will give better insight into the limitations of model results. Such models can be used alone or alongside more sophisticated models which, although more accurate, are not easily used to test the sensitivity of results to parameter uncertainty. The models to be developed will therefore tend to be based on simplifying assumptions and may be analytical and semi-analytical as well as numerical; numerical codes will at most be spatially two-dimensional.

No decision has yet been made to develop any specific model, that choice will be based on the review of models currently under way: the choice will be a joint decision between NRA and BGS.

2.4 Parameter values

The parameters of concern are those entering the transport equations on which the models are based. There is a very wide range of types of information that can enter a single model, including: aquifer porosity, dispersion coefficients, diffusion coefficients, and sorption coefficient, geochemical rate processes, and so on. Such information can be found in a variety of places. It is the intention of this project to identify such sources, identify gaps in the information, and to bring together into a compact database some of the more useful information for use in modelling.

Parameter values used in models come from a variety of sources, including: field measurements, laboratory measurements, 'expert' opinion, and model calibration (*inverse* modelling). The problem of choosing appropriate values will be dealt with in this work as an element of the *methodology*, but a related issue is that of databasing of parameter values.

2.5 Methodology

Subsurface modelling is widely viewed as being as much an art as a science. That view will be disputed by some but it must be agreed that very significant problems exist in the modelling process which are not purely technical ones. Those problems include: selection of a suitable code, choice of parameters, problems associated with uncertainty and risk, and the interpretation and presentation of model results in a form suitable for management decisions.

The intention is that this project should provide some aids to resolving these problems. These aids could take the form of flowcharts, tables and so on; they could perhaps form the basis of an *expert system* but there is no intention to produce such a system within this project.

This report presents, in the review section on model application, topics which will form a basis for development of the methodology.

3. REVIEW OUTLINE

3.1 Introduction

This section gives an outline of the scope of review work being undertaken by BGS. It is intended both to provide a structure within which to continue that work and to attract critical comment from the NRA. In the latter regard it may help to use the *Contents* of this report in order to get an overview of the topics that we aim to cover by the end of the review stage of the project. (A deep section hierarchy has been adopted in order to impose a clear structure on the review.)

We omit technical details and specific references at this stage, and prefer to give a broad indication of the importance of each topic and difficulties associated with it. The amount of discussion varies from section to section; this should not be interpreted as a measure of the relative importance of the topics covered, it is rather an indication of the extent to which the authors have considered those topics to date.

As with the rest of the report, constructive criticism of the structure and range of the review would be welcomed.

3.2 Transport processes

Within the context of this project the term *transport process* will be understood to represent any process affecting contaminant transport and will include advection, dispersion, diffusion, attenuation and persistence.

The review will describe all processes of any significance to contaminant transport, where possible giving a mathematical formulation of the process and emphasising the meaning of parameters in those equations (for example, in relation to field and laboratory measurements). Where different mathematical formulations are in use these will be critically compared.

3.2.1 Physical processes

3.2.1.1 Advection

Although the transport of potential pollutants is the focus of attention in this project, no transport model will be successful if it does not correctly describe the flow of water itself. Although it will not be appropriate to discuss codes which simply simulate groundwater flow (without any transport), the flow process in the more general transport models is important and therefore advection (also referred to as convection) must be considered.

3.2.1.1.1 The saturated zone

Groundwater flow in saturated porous media is almost invariably described by Darcy's law in which the flux divided by the head gradient is equal to a constant (the *hydraulic conductivity*). When flow rates are very high this law can break down but such situations are unlikely to occur in pollution migration problems (except very close to wells) and they can be ignored.

When only the gross volumetric flow through an aquifer is of interest it is normally appropriate, at least on an areal scale many times the aquifer thickness, to model the flow as being essentially horizontal. This proves to be a very good approximation. However, when considering solute transport it is important to recognize that flow rates at different depths vary considerably, and therefore travel times along paths descending to different depths can differ greatly (often by several orders of magnitude). Such travel-time variations are very important when there is a decay process at work. A related factor that must be considered is the variations with depth both of the rock type and other conditions such as the oxygen content of the water.

3.2.1.1.2 The unsaturated zone

The most popular description of water flow in the unsaturated (vadose) zone is the classical Richards equation, which essentially extrapolates Darcy's law for saturated flow to the unsaturated case. The value of that formulation for application at the field scale has however been questioned and several alternative formulations have been proposed. Those alternatives have specifically been aimed at overcoming problems associated with preferential flow and heterogeneity.

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.

3.2.1.1.3 Fractured media

Two types of models have been studied in relation to flow through fractured porous media. In *double porosity* models, flow is assume to take place only in the fractures (or fissures) with the matrix water being effectively immobile. However, when head changes occur in the fissure system water is assumed to move into and out of the matrix. In *double permeability* models, flow takes place in both the fissure and matrix systems.

The double porosity models are obviously of importance for transport in the Chalk, and several case studies exist.

Flow in fractured non-porous rocks have received much attention recently because of the investigations relating to subsurface radioactive waste repositories. Such systems do not appear to be particularly relevant to the work of the NRA.

3.2.1.2 Molecular diffusion

In laboratory and field investigations (especially tracer tests) it is often observed that when a pulse of solute passes through a subsurface system to a detector that the observed concentration/time *breakthrough curve* is asymmetrical, with a tail indicating significant delay of part of the solute. In very general terms such behaviour can be interpreted as being due to some local non-equilibrium effect. A physical mechanism that can give such effects is that where water is mobile in part of the system and (effectively) immobile in the rest of the medium. The exchange of solute between these parts of the system (*phases*) must be taking place by molecular diffusion.

A term often used to describe such systems is *double porosity*. Much work in recent years has been directed towards understanding the behaviour of such systems, which include a wide range of rock types from aggregated soils to fractured hard rocks. Amongst UK hydrogeologists, the main interest in such systems has focused on the problems of transport in the Chalk, although the same mechanism must be of importance in other aquifers.

Laboratory measurements of diffusion coefficients in saturated rocks have not been numerous. Some measurements on inorganic solutes in chalk have been made, and a few for sandstone (during studies of radioactive waste disposal). When diffusion coefficients in water are known, these results can be extrapolated to diffusion through porous media by multiplying by a factor which represents the effects of tortuosity and porosity: estimates to within about half an order of magnitude can often be made. Few measurements have been reported on the diffusion of organic compounds in porous rocks but studies have recently begun (including one in the BGS laboratories).

The appropriateness of a double-porosity model depends very much on the various time scales involved. If changes in the mobile phase (e.g. fissures) are very slow then the diffusion into the immobile phase (e.g. chalk matrix) may be sufficiently fast for an assumption of local equilibrium to be valid. In that case a single phase transport model will be appropriate provided the assumed porosity is the bulk porosity of the mobile and immobile phases. If, at the other extreme, the transport through the mobile zone brings about very sudden changes, the diffusion may have no significant effect and, once again, a single phase model can be used, but in this case a porosity equal to that of the mobile phase alone is appropriate. Between the two extreme cases indicated, a fully double porosity model is required.

When the rock matrix material is capable of significant adsorption, it must be recognized that the diffusion process can make much more surface area available for that process than exists at the boundary of the mobile phase. For example, the internal surface area per cubic centimetre of chalk is of the order of one square metre.

Recently, the double porosity concept has been extended and generalized to what are referred to as *hierarchical porous media*. Although such considerations are mostly theoretical, they do appear to have important potential for application to UK aquifers, particularly the Chalk.

3.2.1.3 Hydrodynamic dispersion

Hydrodynamic dispersion refers to the spreading of a solute during its passage through a porous medium due to spatial variations in the flow velocity and branching of the flow paths. The process takes effect at many scales, from the pore-scale upwards. It has attracted the attention of theoreticians in recent times because it has been found that the phenomenon cannot normally be characterized by a Fickian dispersion coefficient.

In pollution studies this spreading 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, 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.

3.2.1.4 Multiphase flow

Interest in the problems of non-aqueous phase liquid (NAPL) migration has grown rapidly in recent years because of the need to understand and predict the fate of organic pollutants in the immiscible phase.

Quantitative modelling of NAPL transport has long been undertaken in order to simulate and predict behaviour in petroleum reservoirs. However hydrogeologists have now begun to adopt and adapt those modelling techniques. Models have included sorption and reaction terms, and special cases (such as an immobile organic phase) have produced simplified models. A distinction is made between liquids which are more or less dense than water, since not all formulations of the transport equations are applicable to both cases.

Attempts to formulate and model multiphase transport have often pointed to the need for increased experimentation. Laboratory observations indicate some very complex behaviour, especially in fissured rock, which will not be easily modelled.

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. Relatively simple models might be developed to cover such situations (none is known to the writers at this time).

It has been found that the so-called *kinematic theory* models provide several advantages over more complex traditional methods for describing multiphase flow in unsaturated media

3.2.1.5 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 (of chloride) in water. The transport equation then takes the classical form of the convection-dispersion equation. That equation is difficult to solve accurately with numerical models. Also, 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.

Special problems arise in fissured aquifers because of the rapid movement through the fissures and damping effect of diffusion into the rock matrix. Double porosity models (discussed elsewhere in this report) are relevant to such situations.

3.2.1.6 Some other physical processes

The ability of subsurface rocks to filter particulate matter is particularly important in understanding the transport of bacteria and viruses.

Vapour movement through the unsaturated zone must be considered when predicting the long-term loss of volatile liquids and it is important for the interpretation of soil-gas survey results.

Osmosis and reverse osmosis have been inferred to explain anomalous heads and concentrations in deep aquifers, it is not clear whether the effects can be ignored in pollution studies.

Colloidal transport is discussed briefly in the later section on geochemical processes.

3.2.2 Geochemical processes

3.2.2.1 Role in solute (pollutant) transport

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 and in the case of organic chemicals, even whether they persist or not.

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 delay its movement in relation to 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. 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 in groundwater.

3.2.2.2 Principal geochemical processes

3.2.2.2.1 Classical solution processes

3.2.2.2.1.1 Chemical speciation

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 chemical species with each other. For example, in solutions containing Ca^{2+} and SO_4^{2-}, a proportion of these two ions combine 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 concept of activity coefficients, ion pairs and complexes which today is 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 these species, there is often rather good agreement and the chemical speciation of most natural waters is 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' (see below) 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 $Al(OH)_2^{3+}$ species are most toxic whereas organically bound (or precipitated) Al species are not so toxic.

3.2.2.2.1.2 Acidity/alkalinity

The pH of groundwater is one of its most important chemical properties. Fortunately it is usually well buffered in the range pH 6 to 8.5, and it is only when it gets outside this range that acidity or alkalinity tends to create problems. Although the bicarbonate present in most groundwaters buffers the pH quite well, the major buffer in most aquifers is the aquifer solid itself not the dissolved bicarbonate.

Low alkalinity groundwaters (alkalinity less than 1 meq/l) are quite rare in the UK and occur in carbonate-free aquifers such as parts of the Triassic sandstone and in minor aquifers such as the Lower Greensand.

By contrast, surface waters with less than 1 meq/l alkalinity are common in the UK. Soil waters with a pH of 3.1 have been found in the UK. Generally, as water percolates through the unsaturated zone, it loses its acidity due to reaction with the 'solid' bases contained within rock minerals (CaO, MgO, Na_2O etc.). However, acid (pH < 5.5) unsaturated zone waters have been found down to depths greater than below 5 m beneath the Triassic (Sherwood) Sandstone. These acid waters tend to contain high concentrations of dissolved Al and other trace elements.

Although widely measured, the pH of groundwater is difficult to measure precisely since the partial pressure of carbon dioxide in most groundwaters is above atmospheric (ultimately because it was derived from respiration in the soil zone) and so tends to lose carbon dioxide on exposure to the air. This can raise the pH by a unit or more and makes the measurement rather unstable if not done with care. This degassing does not change the measured alkalinity.

Therefore, wherever possible pH should be measured where carbon dioxide loss is prevented, e.g. in the field, by passing the pumped groundwater through a closed measurement cell, or by a downhole probe. It is even possible to calculate a pH value from measurement of alkalinity and total inorganic carbon content of a groundwater although this is not done very often.

3.2.2.2.1.3 Redox processes

Reduction-oxidation (redox) processes are some of the most important groundwater geochemical processes. For example, they control the dissolution and precipitation of iron and manganese. They determine whether sulphides can be produced or not and they are important for determining the extent of the degradation of nitrate to nitrogen gas (denitrification) as well as the transformation of many synthetic organic chemicals. As waters become more and more reducing so new reduction reactions become possible. The most highly reduced waters can contain methane for example.

Redox is normally measured by the Eh of the solution using a platinum electrode. However Eh is not parameter that has the same thermodynamic significance as pH since many redox reactions are slow to come to equilibrium and the Eh reflects the overall status of many reactions. Strictly speaking, the ratios of the redox couples Fe^{2+}/Fe^{3+}, Mn^{2+}/Mn^{4+}, NO_2^-/NO_3^- should all indicate the same Eh value but they rarely do. Therefore redox potential should be used in a qualitative manner only.

In reducing waters, it is even more sensitive to exposure to air than pH and the same precautions mentioned above apply with even greater necessity. It is one of the most difficult parameters to measure and obtaining precise and reproducible results is often a problem especially between different analysts. The Eh measurement is often slow to stabilize even under ideal conditions.

The redox potential is most useful in waters where the dissolved oxygen is less than 5% saturation (0.5 mg/l); it can help to differentiate between mildly reducing and strongly reducing waters.

Reduction reactions tend to produce alkalinity; oxidation reactions tend to produce acidity. The most important oxidation reaction is that of iron pyrites. This can produce extremely acid groundwaters (e.g. mine drainage). It is often difficult to predict the rate of this oxidation since it will be limited by the access of fresh air which itself is often difficult to quantify.

3.2.2.2.2 Precipitation/dissolution reactions

In principle, solids should precipitate when their solubility products are exceeded but many solids do not precipitate immediately this occurs and some may never do so. Therefore unlike most homogeneous solution reactions, heterogeneous (solid-solution) reactions can be slow.

Usually some supersaturation is required before precipitation (nucleation) begins. Simple minerals, such as carbonates and sulphates, tend to precipitate and dissolve quite readily and predictably. Metal oxides, such as those of aluminium and magnesium, are not so predictable and complex silicates such as most rock minerals and clay minerals far less so.

The solubility of minerals can be profoundly affected by the speciation of the solution. Any ligand which tends to form soluble complexes with a cation will tend to help minerals containing that cation to dissolve, e.g. organic acids which complex Al will tend to enhance the solubility of Al minerals.

Apart from the kinetic aspects mentioned above, one of the other major difficulties with predicting the behaviour of solids is their variable composition. All minerals contain impurities and sometimes there can be a complete range of compositions going from one mineral (end member) to another. These are known as 'solid solutions'. Therefore there can be an infinite number of minerals; the behaviour of these solid solutions cannot necessarily be related simply to the proportion of each of the end members.

3.2.2.2.3 Surface processes

Many solutes that cannot be precipitated are adsorbed on the surface of minerals. Even those solutes that can be precipitated from bulk solution often prefer to precipitate at surfaces. With charged solutes, special ion exchange reactions can occur.

3.2.2.2.3.1 Ion exchange reactions

Most, but not all, inorganic solutes are charged and some, but not most, organic solutes are also charged. Furthermore, many solids also bear a net electrical charge either because of the strong adsorption of certain 'potential determining' ions such as H^+ or because of an imbalance in the number of cations and anions within the mineral structure. The former gives rise to surfaces with a variable charge (and sorption capacity) whereas the latter gives rise to a more or less fixed sorption or exchange capacity. A fixed charge is found in some clay minerals where isomorphous substitution within the mineral structure, e.g. Mg^{2+} for Al^{3+}, leaves the mineral with a net negative charge and hence a fixed cation exchange capacity.

Ion exchange is now reasonably well understood in simple laboratory systems. It is an important process in some aquifers since it can release one ion in exchange for another. For example, after deposition from a saline environment, clays will have their exchange sites largely filled with sodium. As calcium-rich water passes through this, some of the Na from the clay will be exchanged for Ca. The whole process of flushing out the sodium could take millenia.

The major problem with applying ion exchange theory is two-fold: characterizing the aquifer (which will not be uniform) not only in terms of its cation exchange capacity but also in terms of its selectivity for the various ions; working in a complex mixture of solutes rather than the binary or ternary systems usually studied in the laboratory. Most natural waters usually contain at least four major cations.

3.2.2.2.3.2 Sorption isotherms

Very few solutes are not adsorbed at all. However, since the strength of sorption is determined by a combination of the solute of interest and the solid surface, the task of predicting the extent of sorption of a range of solutes is considerable. Furthermore the extent of sorption varies with the concentration of the solute in solution in a non-linear way. Therefore predicting sorption is usually difficult.

Again the theory is well-advanced; the problem in applying it to natural systems is that they tend to consist of complex mixtures of many minerals, mostly not pure and perhaps covered with coatings of iron and aluminium oxide or organic matter.

Unlike precipitation/dissolution reactions, sorption reactions tend to be quite fast usually within a few hours or a day or so. Sometimes surface rearrangements take place following sorption and these can lead to slow reactions, e.g. phosphate sorption by oxide minerals.

Much work has been done to try and predict sorption of pesticides by soils and aquifer materials. Sorption can often be related to the octanol/water partition coefficient. Many organic compounds are themselves most 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.

3.2.2.2.3.3 Ion exclusion

While oppositely charged ions are attracted to each other, similarly charged ions repel each other. For example, chloride ions are repelled from negatively charged clay surfaces. This is called ion exclusion. Chloride ions could be completely excluded from small pores. This could make chloride move faster than the bulk of the water since it will be confined to the large pores containing the faster flowing water. A somewhat similar effect can occur for large uncharged molecules which can be excluded from molecularly small pores on account of their large size. This would tend to make the excluded molecule move faster than the average water. This is the basis of the analytical procedure of exclusion chromatography.

3.2.2.2.4 Degradation and volatilization

Unlike most inorganic solutes, organic solvents and pesticides can be lost from groundwater by degradation and volatilization. Degradation is often microbiologically controlled but not necessarily. Abiotic degradation of many synthetic organic chemicals can occur. This is often redox-sensitive.

3.2.2.2.5 Colloid transport

Those involved in the safety of nuclear waste depositories have been aware that the migration of small amounts of colloidal material in groundwater could disperse significant amounts of strongly-bound nuclides further than otherwise anticipated. This is a case where strong binding can enhance mobility rather than retard it.

Very little is known about the concentration of colloids (mineral or organic) moving in British aquifers and it is quite difficult to see how this could determined (especially without changing conditions excessively by pumping).

A recent review of the subject pointed out that such colloid transport was unlikely to dramatically increase the rate of transport of solutes through aquifers. The reasoning behind this is that as the colloid with attached sorbed solute moved into a new part of the aquifer, the solute would desorb onto the fresh aquifer until it had come to equilibrium with it. This sorption would retard it.

The critical factor here is the extent of reversibility of sorption. If sorption were irreversible, then such retardation by continuous re-equilibration would not occur. Most surface reactions are at least somewhat reversible, but where occlusion in new phases such as precipitating oxides occurs, some irreversibility would be expected.

3.2.2.3 Chemical reaction versus mixing and dispersion

Often we can only infer the chemical processes taking place by observing what takes place in the field. However, most real world situations are far from perfect laboratories and we only get an imperfect and partial view of what is going on.

Perhaps the greatest problem is that of spatial variability. Changes in water chemistry may be seen from one place to another but it is often difficult to separate chemical reaction from the simple mixing of two waters from different sources.

If enough is known about the hydrogeology and geochemistry of the aquifer then it may be possible to resolve this by using one of the geochemical 'reaction path' models. Various examples exist mainly from the USA.

3.2.3 Biochemical processes

Microorganisms within groundwater systems obtain energy and nutrients from the passing water, they often become attached to solid surfaces and form biofilms as their numbers increase.

For an active microbial population to develop, certain conditions for the synthesis of protoplasmic constituents and the liberation of energy necessary for life processes must exist. The synthesis of protoplasm requires a carbon source (organic or inorganic), nitrogen, phosphorus, and sulphur, and energy source plus certain minerals (trace elements) and water. The biochemical liberation of energy in the absence of light requires:

1. The presence of an electron donor such as oxidizable organic compounds or, in the case of chemolithotrophs, oxidizable inorganic substances such as molecular hydrogen, ammonia, sulphide or ferrous ions.
2. The presences of an electron acceptor such as molecular oxygen, sulphate, nitrate, ferric compounds, carbon dioxide and simple organic compounds.

Quantitatively, by this approach most geological formations have a capacity to support at least a limited microbial population due to the presence of:

a. Carbon sources - dissolved organic matter, carbonates, dissolved CO_2.

b. Electron donors - dissolved H_2 and CH_4, and Fe_{2+}.

c. Electron acceptors - dissolved O_2, SO_4^{2-} and NO_3.

d. Moisture - conditions in the saturated zone are, generally, more favourable than those in the unsaturated zone.

If molecular oxygen is not available in deep groundwater, populations would be initially limited to anaerobic or facultatively anaerobic microorganisms. However, any activity will alter the chemical environment forming micro-environments where a wider range of organisms may exist. Although geological formations generally have all the prerequisites for the maintenance of microbial life, the extent of activity will be dependent on material fluxes and hence there will be a limiting growth factor. The integrity of petroleum and coal reserves would suggest that, in these cases the rate of replenishment of electron acceptors limits mircobial activity. Rates of biotransformation are also affected by factors such as temperature and pH.

Attempts to model such complex situations have been relatively few, they include particularly biofilm modelling and models which attempt to account for the rate limiting effect of oxygen on microbial growth.

Of particular interest is the use of nitrate when dissolved oxygen falls below a given threshold. Also important is the transformation of organic contaminants (due to carbon and hydrogen synthesis), and some current research is concerned with the potential to exploit such degradation for the in situ treatment of contamination.

3.3 Models

3.3.1 Introduction

The review of models will tabulate models with respect to their characteristics in such a way as to facilitate comparison and choice of model for any particular application. The characteristics of concern will include: which equations are solved (the equations will be included in the *process* section of the review), the dimension of the flow system (1, 2 or 3), whether source code is available (to allow modification), and so on. Also included will be references to publications describing applications of the various models.

Not every model can be mentioned, some initial sieving will be required to eliminate models of no potential value to NRA. The selection process will be based on: user-friendliness, level of support, width of use, reliability, and related factors. Codes will not be eliminated simply because they are big or slow to run since the pace of increase of computing power available, for example by the use of workstations, is so great as to render most mainframe and some supercomputer applications amenable to desktop work within the next few years.

Until very recently most groundwater models fell into one of two very broad classes: hydraulic (or hydrologic) transport models and geochemical models. It is widely recognized that a major challenge facing groundwater modellers is the combination of these into *hydrochemical* models which couple physical flow and transport processes with chemical reactions. It is that relatively new class of models which is a major concern of this project although simpler models cannot be ignored.

It has not been established whether or not the geochemical models (with no transport) are of significant interest to NRA in their own right.

Much effort in groundwater modelling is directed towards the development of efficient numerical formulations. Such work will only be described in the context of this project insofar as it determines whether or not a particular model can be run sufficiently fast that it is a practical tool.

Analytical, semi-analytical and numerical models will all be considered in the study, although the latter class is of dominant importance.

3.3.2 Simple transport models

For many applications (for example, protection zone delineation) 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 convection-dispersion equation. These models normally include linear source and loss (decay) terms and are based on an assumption of local chemical equilibrium.

3.3.3 Chemical mixing models

The flow system in these models is represented by a relatively small number of cells (sometimes only one or two). The models focus on the accurate description of chemical interactions. The cell size should if possible be matched to the dispersive characteristics of the aquifer.

3.3.4 Modularized chemical models

These models essentially use transport and chemical reaction models that have been developed separately. An iterative procedure is necessary to ensure that the results are accurate and consistent with the governing equations.

3.3.5 Integrated transport and chemistry models

The chemical reaction equations and transport equations are directly coupled in these models, leading to a set of non-linear partial differential equations (or sometimes integro-partial differential equations). The numerical formulation of the equations can then take specific account of the structure of those equations to help ensure that the resulting code is stable and efficient.

3.4 The application of models

3.4.1 Introduction

Modelling is not an end in itself, it is part of a wider process of decision making. It is therefore intended that brief reviews will be undertaken on those topics that interface modelling to that decision-making process.

The actual process of applying a model (or models) to solving a field problem is normally a complex multi-disciplinary process in which there is a continual (usually iterative) interaction between model results, field measurements, and various management options. While each field situation tends to present new challenges, this application process can be outlined in a fairly systematic way to guide a modelling project.

A systematic approach to model application can help to avoid problems such as a failure to conceptualize the system or that of insufficient data. It can also be an aid to project management by defining a series of goals. This direction can extend beyond the modelling activity itself since the modelling requirements will often help to ensure a balanced field programme.

3.4.2 Model selection

The problem of model selection is an important component of model application. In some cases the problem may be amenable to treatment by means other than a computer code; for example, a suitable 'model' for pumping test analysis is often takes the form of a set of standard graphs (*type curves*). However, for groundwater contamination problems model selection will normally be synonymous with code selection.

The task is not simply one of choosing the best model that can handle the problem, since many extraneous factors such as cost and time constraints must be taken into consideration. Also it may not always be the case that a single model is the best way to handle the problem.

Code selection can be aided by listing the many factors that need to be taken into consideration, but it is not obvious that these can be organized in a systematic format such as a decision tree. It seems that *expert systems* have a role to play in this area of the modelling activity.

3.4.3 Model validation

Whenever a model is used to make a management decision of importance, confidence that the model is providing sound results is essential. The process involved in establishing the validity of a model involves a number of elements, some of which can be carried out in a fairly systematic and objective manner but others of which will remain subjective. Broadly speaking, it is necessary to establish that: the conceptual model correctly represents reality, that the mathematical formulation represents the conceptual model, and that the code is consistent with that mathematical formulation (code verification).

In the past code verification was simply a matter of comparing code results with those from other sources such as analytical solutions of the transport equations. The verification procedure can, adopting procedures developed by software engineers, be carried out in a far more formal and quantitative manner. It might be judged that, by such standards of testing, many widely used groundwater codes are very poorly verified.

In order to test the validity of a model with respect to a given groundwater system a number of techniques can be applied, depending on the type, quantity and accuracy of data available.

3.4.4 Quality assurance

The rapid growth in the use of models for groundwater management have led to adversary legal procedures in which model application or even the model's theoretical framework have been contested. Quality assurance (QA) procedures provide a framework for avoiding (but not eliminating) such situations, and QA is therefore of particular value to regulatory agencies such as the NRA.

Quality assurance must pervade all aspects of an investigation, and cover procedures from problem formulation and code development through to the interpretation of model results. Quite detailed suggestions have been made for the implementation of QA in model development and application by the International Groundwater Modelling Center (IGWMC), although experience of applying such procedures is not yet great. Those suggestions could be adopted and developed by the NRA.

3.4.5 Risk analysis

Risk analysis appears to have relevance to the project from two points of view. Firstly, if the output of a model is to be used as input to a formal risk-analysis procedure then that output must take a suitable form. Secondly, modelling carries with it the (internal) risk of producing incorrect results; the possible sources of such error include: field uncertainty, bad coding, and errors in data input. These problems are related to *quality assurance.*

3.4.6 Expert systems

As mentioned elsewhere, *expert systems* appear to have a role to play in the problem of identifying a suitable model. Some consideration will be given to other possible uses in contaminant modelling.

3.4.7 Geostatistical techniques

Field data invariably carry an element of uncertainty both due to data errors and geological variability. Much effort in recent years has gone into developing probability-based techniques for dealing with such uncertainty. Those techniques apply in a variety of ways to the modelling process. The extent to which they are likely to be of value depends on the data density.

3.4.8 Site-specific versus generic modelling

If a particular site has been the subject of very intensive investigation (for example one where a major pollutant spill has occurred) then it is natural to develop a model which is capable of representing all of the known complexity of that site. Either a model needs to be specially constructed or an existing model needs to be adapted. In the latter case the source code must be available and well-documented and it is preferable if the code was designed in a modular fashion to facilitate modification.

When environmental analysis of many sites has to be undertaken (as, for example, in protection-zone delineation) site specific models are not appropriate and generic models must be applied. Generic models will normally be simpler than site-specific models and analytical models may often be adequate. The Environmental Protection Agency (EPA) in the USA has encountered legal problems with the application of generic models.

Both type of model would seem of interest to the NRA, although in relation to site specific models this project will only attempt to indicate which models are readily adapted to complex situations

3.4.9 Distance and time scales in modelling

When choosing an appropriate model consideration must be given to spatial and temporal time scales of interest. In the interest of model efficiency it is normal to exploit the possibility of averaging whenever possible. So, for example, rock permeability variations at a scale of a few metres will not be important in a model of grid size hundreds of metres. Similarly, daily fluctuations in aquifer stresses (such as pumping or rainfall) will not be important when modelling average behaviour over a period of several years. In particular, it is important to decide whether a transient or steady-state (or perhaps quasi steady-state) model is required.

When any kind of averaging process is carried out care must be taken to use appropriate parameters. There is a strong relationship between the problem of heterogeneity and that of parameter selection; geostatistical methods have a role to play in this context.

3.4.10 Models in data collection and analysis

Models serve to direct field and laboratory investigations in a rational, balanced and targeted manner; they also provide for a methodical interpretation of data.

Care must be taken to ensure that models used in the analysis of data, to produce characteristic parameters, are consistent with any other models in which those parameters might be used.

4. DATABASING

4.1 Introduction

The project will aim to identify various sources of parameter values that appear in the transport equations (and hence the transport models), and to bring together in a compact database some of the more useful information for use in modelling. That information may range from geological information to chemical reaction parameters. One of the aims of this report was intended to be to advise on databasing. On reflection it seems rather early to make such recommendations since databasing depends on too many as yet unanswered questions. In particular, the nature and volume of data of interest cannot be decided until model recommendations are made (at least in terms of broad functionality) and sources of useful numbers identified.

It must be recognized that the range and quantity of parameter values is so great that a significant amount of selectivity will need to be imposed. Possibly the task is so great that all that can reasonably be achieved is to produce a kernel database to which information can be added over an extended period of time.

Since one primary aim of the project is to emphasize the problems of uncertainty, it is important that any source of parameter values should indicate variability as well as most likely values.

It seems likely that any database resulting from this project will be either rather small or rather expensive to develop. The reason for this is that in order to produce a large database much of the information would have to be extracted from existing databases. Most owners of databases, including BGS, regard them as a significant asset which can be accessed at a moderate charge but only copied at a considerable cost. However, where information is collected together into published (paper) tables, and only a few numbers from any such table are required at any one time, those tables represent a very efficient and cost-effective form of database.

4.2 Software and hardware systems

We have decided to work with the dBase IV software package because of its wide use and compatibility with many other systems. We would not foresee any difficulty in transporting any database produced to another software package. It might, for example, be convenient to transfer some data to a system which can be accessed by a geographical information system (GIS).

It is not envisaged that the databases produced during this project will be either very complex or large. Therefore personal computers will be more than adequate.

4.3 Geochemical and biochemical data

Large quantities of geochemical and biochemical data are to be found both in the form of computer databases and handbooks. We have yet to attempt to make any systematic investigation of these.

4.4 Geological data

A recent review of databasing in BGS has revealed that there exist almost as many databases as people in the organisation. Significant funds are to be put into rationalizing and centralizing the information. Those efforts will make it possible, before the end of this project, to identify information that may be of relevant to pollutant modelling.

4.5 Hydrogeological data

Within the Hydrogeology Group of BGS we hold several databases of potential relevance to this project. In particular, a geochemical database and an aquifer properties database.

At present the aquifer-properties database only contains porosity and permeability values: about 20,000 of each, taken from about 1,450 different locations, and depths ranging from outcrop to about 2 km (although most samples are from depths of a few tens of metres). This information is currently being transferred from a card index to a (dBase IV) computer format. The main shortcoming of the database is that the information is not spread evenly, either over the country as a whole or over particular aquifers. It may be possible to broaden the coverage by using further core information (mostly only porosities) held at BGS Keyworth.

Core permeability values are useful but in formations such as the Chalk, aquifer hydraulic conductivity and transmissivity values would be of greater value. Unfortunately, pumping-test data has not been gathered in any systematic way within BGS, although a significant volume of data has been found to exist in paper form. Internal funds are not currently available to undertake the formation of a database of such information and a recommendation is made at the end of this report for the NRA to consider the possibility of funding the construction of a database using their own information, that from BGS and from other sources.

Where models have already been applied, the calibration process will have revealed parameter values that may be even more relevant to this study than parameters from core measurements or field tests.

4.6 Water quality data

Time-dependent modelling of changes in water quality will require historical information on the chemistry of the water (for calibration). The establishment of a groundwater-quality archive for the UK aquifers is widely recognized as an important but expensive need. Within this relatively modest project, it seems unlikely that much can be achieved in this direction other to point to the most useful types of information that could be included in such an archive.

5. MODELLING SCENARIOS

As mentioned near the beginning of this report, it is important to impose some reasonable constraints on the variety of cases for which models are to be recommended. The decision on which cases to consider explicitly is very much one to be made by the NRA rather than BGS. However, as an aid to identifying these scenarios, a tentative list of scenarios is given in Table 1. The NRA will probably wish to add to this list but may be reluctant to reduce it; in either case it would help if some priorities could be set. Also it would help if the purpose(s) to which models might be put in each case would be helpful.

A closely related problem is that of restricting the list of potential contaminant to consider (explicitly).

TABLE 1. A tentative list of modelling scenarios to be covered.

Main Group:	Sub-groups.
Agricultural pollution:	chemicals (fertilizers, herbicides, pesticides), manure, irrigation.
Accidents:	leakage (storage tanks and drums, pipelines, sewers), spills.
Waste disposal:	landfills, uncontrolled dumps, sludge, mine tailings.
Miscellaneous:	sea water intrusion, highway drainage (especially salts), heavy metals (especially mobilized by acid rain), surface water infiltration (polluted lakes, rivers and canals).

6. PROGRESS AND FUTURE WORK

Much of the effort on the project so far has been concerned with the process and model review which has included: the identification of key references, purchase of some books, and computer-based literature searches. (It had originally been intended to form a PC database of the references, however copyright issues prevent us from doing that for references obtained from existing databases.) Requests to purchase or borrow a substantial number of reports and books (mainly conference proceedings) have been made. We have obtained much useful information but are aware of the existence of much more. As the work progresses, this review process will have to become more structured and specific goals and deadlines set with respect to the topics to be covered (one purpose of this report is to aid that structuring).

Work has begun on the production of a database of models relevant to the project. This has been implemented using the dBase IV personal computer package. This process is still in its early stages. It has been found necessary to work flexibly with the database since different types of models require different ranges of fields in order to characterize them.

Related work has been carried out by BGS on other NRA projects; in particular, a review of models for protection-zone delineation has been produced and a review of denitrification in the unsaturated zone is nearing completion.

Over the next three months work will continue on reviewing. The review topics in the section on *the application of models* will initiate the development of the methodology. Some obviously important models will be identified for purchase (in order that they can be properly assessed).

7. RECOMMENDATIONS

1. This report should be distributed to appropriate staff to attract constructive criticism.
2. BGS and NRA should agree on a list of scenarios for which models would be of value to the NRA. Table 1 provides a tentative list, but the final list will depend on the interpretation by NRA of their remit. An agreed list of the most important contaminants should also be established.
3. Consideration should be given to the establishment of a database of aquifer field data, particularly information from pumping tests (held in paper form by BGS, NRA, and water companies). (This project could play a useful part in such an undertaking, but could not support a significant proportion of the effort that would be needed.)
4. Consideration should be given to establishing a list of existing site (or region) specific models, both for use in their own right, for transfer to other areas, and for their ability to indicate parameter values, as a result of their calibration.
5. A decision should be taken on whether or not to provide a review and assessment of geochemical models in their own right, in addition to their use in combination with flow models.

6. NRA should inform BGS of any databasing activities within NRA which may be relevant to this project.

7. It is recommended that the topics listed in Table 2 should not be considered explicitly in the study. In order to keep this project to manageable proportions it will be necessary to restrict its scope in several ways. The intention through most of this report has been to indicate what will be covered by the study: the appearance of a topic as a section title should be taken to indicate an intention to include it. But in Table 2 an indication is given of topics that, although often important in their own right, are considered rather peripheral if not irrelevant to this study.

TABLE 2. A tentative list of modelling issues not to be covered.

Non-Darcian flow models.
Radioactive waste.
Plant processes.
Non-isothermal systems (except insofar as temperature affects biochemical transformations).
Hydrochemical reactions that tend to be important at only elevated temperatures, such as in geothermal investigations.
Fractured non-porous rocks.
Review of the details of numerical techniques.
Databasing of groundwater quality (except to indicate what information would be most useful).

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