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Numerical Model Parameters for Simulation of Contaminant Transport

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ABSTRACT

The use of models to assess the risk to the subsurface environment from contaminants is becoming increasingly popular and a wide range of modelling software is readily available. Inconsistent and inappropriate approaches to modelling can make the assessment difficult and may render the results invalid. The development of a conceptual model involves a number of assumptions regarding system behaviour. The assessment must take these assumptions and uncertainties into account and understand how they could influence the predicted results. This paper outlines the fate and transport processes, numerical models, and the model parameters required for simulation of contaminant transport. It will provide guidance on good practice in the development of conceptual models and application of mathematical models to contaminant transport problems.

KEY WORDS: Contaminant transport; Conceptual model; Parameters; Numerical model

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INTRODUCTION

Fate and transport models provide a tool in the assessment of contamination problems. However, the danger in the use of all models is their inappropriate application to hydrogeological situations such that the results may be misleading. A model should be used only when it is clear why and how it is to be used. The modelling approach must be determined by the objectives of the study, the availability of data and the complexity of the system and transport processes. A model should not just be used for the sake of it.

The next step is to formulate and document our understanding of how the system operates and to test these ideas quantitatively. This conceptual model should identify which elements of the system are important and how these could be represented using a mathematical model. The conceptual model will involve a number of hypotheses, simplifications and assumptions which should be challenged continually throughout the modelling project by quantitative testing and comparison with field observations. This quantitative testing is one of the main purposes of any mathematical modelling.

The development of a conceptual model and mathematical modelling approach must be iterative and linked. Typically the modelling approach will start with relatively simple calculations or models moving through to more complicated analytical or numerical models if these are required to meet the objectives of the study. In some cases, it may be appropriate to use simple calculations only, if this can be justified in the context of the project. A brief description of the different types of mathematical models is given below:

Analytical models use exact solutions to the equations which describe the migration of contaminants. In order to produce these exact solutions the flow/transport equations have to be considerably simplified such that they are typically only applicable to simple flow and contaminant transport systems. Analytical models can be simple formulae, spreadsheets or even sequences of calculations packaged up in a piece of software. The advantages of these models are that they are simple and quick and have limited data requirements. They are particularly useful as an initial modelling tool in understanding the system behaviour. Analytical models can also be easily combined with probabilistic analysis (Monte Carlo) techniques to provide a powerful modelling tool. Monte Carlo methods are a class of computational algorithms that rely on repeated random sampling to compute their results. Monte Carlo methods are often used in computer simulations of physical and mathematical systems.

Semi-analytical models are used to refer to a range of modelling approaches. Examples include:

- Models that require numerical solutions to solve equations;
- Models that combine an analytical and numerical approach, e.g. numerical particle tracking on an analytical flow field;
- Models that allow superimposition of a number of analytical equations.

Numerical models use approximate numerical solutions to the governing equations of groundwater flow and/or contaminant transport. Parameter values are specified at certain points in space and time, and provide for a more realistic representation of the variation of parameters than analytical models. The use of a numerical model will require technical expertise in groundwater and contaminant movement, together with specialist and detailed investigations to define the flow regime and contaminant transport processes. Numerical models can range from relatively simple one dimensional steady-state transport models to three dimensional time-variant models and may consider any or all of advection, dispersion and retardation, biodegradation, multiphase flow and density driven flow. The data requirements are significantly greater than for analytical models, and can include spatial variation in aquifer properties plus time variation of inflows (recharge) and outflows (abstraction).

Deterministic models: Deterministic models require a single value to be defined for each model parameter at any point, and the result is a single value. Commonly a range of input parameters are used to determine the range in possible model results.

Probabilistic models**:** For probabilistic models, the parameter values are defined by a distribution (log normal for example) usually referred to as a probability distribution or probability density function, and the model result will be described by a range of values. Probabilistic models are used to take account of the uncertainty in defining or measuring parameter values (e.g. due to sampling or analytical errors), or represent the intrinsic variability of a parameter (for example the variation of hydraulic conductivity in a heterogeneous aquifer). Probabilistic models do not allow for uncertainty in the definition of the system behaviour. For example, there may be uncertainty as to whether biodegradation could be described by a first order reaction or as a rate limited reaction (availability of oxygen). A probabilistic model cannot be used to deal with this type of uncertainty, but could be used

to evaluate uncertainty in oxygen availability. Monte Carlo simulation is the most widely used stochastic technique. In general the method involves:

1. Definition of a probability distribution for each model parameter;
2. Repeated solution of the model with parameter sets chosen from the probability distributions;
3. Analysis of the model results to describe the likelihood of a certain result being obtained.

***Steady state models or time variant models*:** Mathematical models can be described as steady state or time variant. Groundwater flow models describe their capabilities as either steady state and/or transient. Steady state flow occurs when the magnitude and direction of flow is constant with time throughout the entire domain. Conversely, transient flow occurs when the magnitude and direction of the flow changes with time. In other words, the hydraulic head doesn't change with time in a steady state flow system, but does change during transient flow. This does not mean that in a steady state system there is no movement of groundwater, it simply means that the amount of water within the domain remains the same, and that the amount of water that flows into the system, is the same amount as flows out. In a steady state model, the input parameters and solution are independent of time. For a time variant model, input parameter values can be specified as a function of time, and the solution is dependent on this.

FATE AND TRANSPORT PROCESSES

The conceptual model should describe the processes that control the movement of contaminants in the soil, unsaturated and saturated zones. These processes include advection, dilution, dispersion, diffusion, sorption, degradation (biotic and abiotic), volatilisation, and multiphase flow. A brief description of these processes and how they are typically represented in a mathematical model is given below.

Advection

- Movement of solute by bulk groundwater movement.
- Dependent on aquifer properties, mainly hydraulic conductivity and effective porosity, and hydraulic gradient. Independent of contaminant properties.
- Main mechanism driving contaminant movement in the subsurface.

Dispersion

- Fluid mixing due to groundwater movement and aquifer heterogeneities.
- Dependent on aquifer properties and scale of observation. Independent of contaminant properties.
- Causes longitudinal, transverse, and vertical spreading of the plume. Reduces solute concentration at any point, but not overall solute mass.

Diffusion

- Spreading and dilution of contaminant due to molecular diffusion.
- Dependent on contaminant properties and concentration gradients. Described by Fick's Laws.
- Diffusion of contaminant from areas of relatively high concentration to areas of relatively low concentration. Generally unimportant relative to dispersion at most groundwater flow velocities.

Sorption

- Reaction between aquifer matrix and solute whereby contaminants become sorbed on organic carbon or clay minerals.
- Dependent on aquifer matrix properties (organic carbon and clay mineral content, bulk density, specific surface area, and porosity) and contaminant properties (solubility, hydrophobicity).
- Tends to reduce apparent solute transport velocity and remove solutes from the groundwater via sorption to the aquifer matrix. May reduce mobile contaminant mass, but reversible process.

Dilution

- Mixing of contamination with groundwater or surface water (driven by dispersion).
- Dependent on aquifer matrix properties, depth to groundwater, surface water interactions, and climate.
- Causes reduction in contaminant concentrations but not total mass.

Volatilisation

- Volatilisation of contaminants dissolved in groundwater into the vapour phase (soil gas).
- Dependent on the chemicals vapour pressure and Henry's Law constant.
- Removes contaminants from groundwater and transfers them to soil gas.

Biodegradation

- Microbially mediated oxidation-reduction reactions that degrade contaminants.
- Dependent on groundwater geochemistry, microbial population and contaminant properties. Biodegradation can occur under aerobic and/or anaerobic conditions.
- May ultimately result in complete degradation of contaminants. Typically the most important process acting to reduce contaminant mass. May produce new contaminants in the ground.

Abiotic Degradation

- Chemical transformations that degrade contaminants without microbial facilitation, e.g. hydrolysis.
- Dependent on contaminant properties and groundwater geochemistry.
- Can result in partial or complete degradation of contaminants. Rates typically much slower than for biodegradation. May produce new contaminants in the ground.

Partitioning from NAPL (Non-Aqueous Phase Liquids)

- Non-Aqueous Phase Liquids (NAPL) are liquids that, like oil, do not dissolve readily in water.
- Partitioning from NAPL phase into groundwater. NAPL plumes, whether mobile or residual, tend to act as a continuing source of groundwater contamination.
- Dependent on aquifer matrix and contaminant properties, as well as groundwater mass flux through or past NAPL plume Raoult's Law for mixtures.
- Raoult's Law is used to determine the vapor pressure of a solution when a solute has been added to it. The law states that this change in vapor pressure of a substance can be determined by the product of the mole fraction of the substance and the vapor pressure of the pure substance.
- Dissolution of contaminants from NAPL represents the primary source of dissolved contamination in groundwater.

NUMERICAL MODELS

Numerical models allow more complex systems to be represented than can analytical models, providing approximate solutions to the equations governing contaminant transport. Numerical models still require simplifications to be made about system behaviour.

The development of a numerical model should represent the last stage in a contaminant problem, i.e. only when an understanding of the system behaviour has been developed through the use of analytical models and where it can be demonstrated that the use of a numerical model will be beneficial. The application of a numerical model should also be dependent on a robust conceptual understanding of the problem and the availability of adequate data. Numerical models are relatively time consuming and costly to construct and should not be used as an alternative to data collection. For this reason, the application of a numerical model should be undertaken only in a limited number of cases.

In distributed numerical models, space and time are divided into discrete intervals where for each model grid cell, parameter values are defined including hydraulic conductivity, porosity, aquifer thickness, initial contaminant concentration etc. The main advantage of numerical models is that different parameter values can be assigned to each cell, such that lateral and vertical variations in property values can be taken into account. The geometry of the model can also be designed to reflect the geometry of the system to be represented. In addition, models can be constructed as more than one layer to allow multi-layered aquifers to be represented. For time variant models, model inflows (e.g. recharge and its contaminant concentration) and outflows (e.g. groundwater abstractions) can be specified for each model time step. Numerical models will generally be applicable where:

- Previous modelling studies using simple analytical models have shown that a more sophisticated approach such as incorporating spatial variability is required;
- The groundwater regime is too complex to be robustly represented by an analytical model;
- Processes affecting contaminant transport cannot be readily represented by simple equations;
- An analytical model is inadequate for the design of mitigation measures, e.g. in determining the optimal location and pumping rate for boreholes in a pump and treat scheme.

Numerical models should be considered where the scale and importance of the problem warrants the use of a more sophisticated approach. For such sites the scale of the problem should demand detailed investigations which should provide sufficient information to allow the construction of a numerical model. The use of a numerical model will require technical expertise in groundwater and contaminant movement, together with specialist and detailed investigations to define the flow regime and contaminant transport processes.

Types of Numerical Model and Numerical Techniques

There is a wide range of numerical codes and solution techniques available to solve the equations describing contaminant transport. The numerical solution methods for contaminant transport require a solution of the flow field, which can be obtained using finite element, finite difference, or the less used integrated finite difference and boundary integral equation methods. The contaminant transport solution can be used for either steady state or time variant flow fields.

Finite Difference is the most commonly used approach in numerical modelling. For most finite different models, the space and time co-ordinates are divided on a rectangular grid and model parameters (hydraulic conductivity, aquifer thickness) are specified for each model grid cell. Wang and Anderson[1] and Zheng and Bennett[2] provide a description of this method. The flow and transport equations are solved by direct approximation. The grid spacing represents the degree of accuracy of the model in representing lateral or vertical changes in the property values that describe the system. Finite difference methods have the advantage in being relatively simple to use, but have the disadvantage of not accurately representing irregular boundaries and it is also difficult to change the grid spacing to provide greater precision in areas of interest.

Finite Element Method: The spatial domain is divided into a mesh of elements, generally of triangular or quadrilateral shape. The variation in a model parameter across the model element is normally approximated by a polynomial function. This technique provides greater flexibility than finite difference methods in representing the model domain, particularly complex geological boundaries. The model mesh can be easily modified to provide greater precision in areas of interest although complex meshes require software tools for their management. Finite element models are less susceptible to numerical dispersion than finite difference models (Zheng and Bennett[2]), but for the same number of elements/cells the computing cost is higher.

Other methods include the integrated finite difference method and the boundary integral equation method (Zheng and Bennett[2]). A number of solution methods have also been developed to solve the contaminant transport equations. The choice of whether to use a finite difference or finite element model will generally be a matter of personal preference.

The method of transport calculation depends on the approach to the co-ordinate system i.e. Lagrangian (the particle is fixed in relation to a moving co-ordinate system) or Eulerian (the particle moves in a fixed co-ordinate system) or a hybrid (i.e. a combination). The choice of solution technique

(Method of Characteristics, random walk etc.) is important and depends upon whether we have an advection-dominated system or dispersion dominated (i.e. low permeability) system.

BOUNDARY CONDITIONS

There are a number of different types of boundary condition that can be specified in a model in terms of flow and/or contaminant flux, including constant head, constant concentration, specified contaminant flux, and no flow, ASTM[3] and ASTM[4], Zheng and Bennett[2]. Examples of boundaries include a river fed by the aquifer, solution of contaminants into groundwater from a NAPL source. Boundaries may be specified at the edge of the model (external boundary) and within the model area (internal boundary).

Flow boundary conditions

1. Constant head: The head within a cell is specified and remains fixed during the model simulation. The cell acts as either a sink in removing water from the model or as a source in adding water to the model depending on the water levels within the model relative to the fixed head. The main problem in specifying fixed head cells is that an unrealistic volume of water could be added to or lost from the model. Inflow or outflow from the constant head cell to the adjacent model cells is usually controlled via a hydraulic resistance.

2. Specified flow: The flow into or out of the model is specified at this boundary.

3. No flow: No component of groundwater flow across them and they are used to represent impermeable boundaries, groundwater catchment divides, or groundwater flow lines.

Mass transport boundary conditions

1. Constant concentration (referred to as the Dirichlet condition): The contaminant concentration of a cell on the boundary or within the model remains fixed during the model simulation. The cell may act as a sink in removing solute mass from the model or as a source in adding solute mass to the model. The dispersive flux is calculated based on the difference in concentration between the boundary cell and the adjacent internal cell and is directly analogous to the flow of water from a constant head cell. There may also be an advective component, if flow occurs at that boundary in the flow model. An illustration of this boundary condition is that the dissolution of contaminants from a NAPL plume could be specified as a constant concentration boundary. The main problem in specifying fixed concentration cells is that an unrealistic mass of contaminant may be added to the model (which may far exceed the actual contaminant source). The mass balance for the model should be reviewed to check

on contaminant fluxes into and out of the model. The assumption of a continuous contaminant source in an analytical model is analogous to a constant concentration boundary.

2. Specified concentration gradient (referred to as the Neumann condition): This boundary considers the dispersive flux only and is dependent on the specified concentration gradient and dispersion coefficient. Typically the dispersive flux at a model boundary is small and this condition is rarely used.

3. Specified concentration and concentration gradient (referred to as the Cauchy Condition): The dispersive and advective fluxes are specified. The advective flux is calculated based on a specified concentration and flow rate.

4. Impermeable boundaries (no flow boundaries in groundwater flow models) are special cases of the Neumann or Cauchy boundary condition where the advective and dispersive flux is zero.

Boundary conditions can have a significant effect on the model results, and consequently the location and type of boundary condition needs to be selected with care. The influence of the boundary condition on the model results should be evaluated including:

- Examining the influence of moving the boundary location;
- Examining the influence of different contaminant release histories on model output;
- Checking modelled inflows or contaminant fluxes from constant concentration or specified flux boundaries.

Grid Spacing and Time Step

Distributed numerical models require the model area or domain to be divided into a polygonal grid. For each model grid cell, parameter values (e.g. hydraulic conductivity, porosity need to be defined). This allows the lateral and vertical variation in parameter values to be taken into account. However, dependent on the grid spacing, an individual model node can represent an area of hundreds to thousands of square metres. Since the variation in a parameter value is likely to be at a smaller scale, then an average value will need to be determined for the grid cell area. The grid and time discretisation will determine:

- The ability of the model to describe variations in system behaviour (e.g. variation in hydraulic conductivity);
- The data requirements for the model; these increase the finer the model grid and time discretisation;

- Computer memory and model run time requirements; these increase with the fineness of the model grid and time discretisation;
- Numerical dispersion; the coarser the discretisation of space and time, the greater the likelihood of model instability.

The model grid and time step will always be a balance between the above factors. In an ideal study, the effect of grid spacing will be subjected to sensitivity analysis, but because of the considerable effort to do this, the test is seldom made, relying instead on an assessment of the likely effects of grid spacing by other means, such as calculation of the maximum grid Peclet number. A common problem in setting up and running a numerical model is in preventing or minimising numerical dispersion. Numerical dispersion can be minimized by a number of methods:

- Decreasing the model grid spacing and time step to minimise dispersion particularly for models that are solved by Eulerian methods, although this will increase model run times;
- Choice of the solution method; for example, Lagrangian methods are less susceptible to numerical dispersion;
- Choice of initial or starting conditions;
- Choice of convergence criteria for the model.

The change in grid spacing and time step will also need to be designed carefully as changes in the grid spacing can result in model instability. In general, the change in grid spacing from one row or column to another should be less than a factor of 2 (a multiplier of 1.5 is typically recommended in the supporting documentation to codes). Changes in the model time step can also result in model instability. Most codes will provide guidance on the appropriate time step. A key part in reviewing the results from numerical models is to check the:

1. Mass balance: Errors in the mass balance provide evidence of numerical instability;
2. Time series: Oscillations in predicted contaminant concentrations with time may indicate instability;
3. Contaminant distribution: Anomalies in contaminant distributions may also indicate instability.

Selection of Numerical Model

Numerical models can range from relatively simple one-dimensional to three-dimensional codes and can consider advection, dispersion, retardation, biodegradation, multiphase flow and density. In selecting a numerical model, the following factors need to be considered:

- What processes need to be represented, e.g. advection, dispersion, linear and non-linear sorption, first order decay, variable density;
- How are these processes simulated, e.g. linear or non-linear sorption, first order decay and reaction limited biodegradation (usually oxygen, but possibly nutrient supply);
- Solution technique (e.g. Eulerian, Lagrangian) and is this appropriate to the flow field;
- Number of model layers;
- Steady state or time variant conditions;
- Pre/post processors.

For details of numerical models the following references can be referred: Zheng and Bennett[2], National Rivers Authority[5], International Groundwater Modelling Centre[6], van der Heijde[7], Anderson and Woessner[8], Spitz and Moreno[9] and Bear and Verruijt[10].

FIELD OBSERVATIONS USED IN MODEL REFINEMENT

Few examples of errors in field measurements and problems associated with the model (that may give rise to anomalous results) are given below.

Groundwater levels (spot water levels, groundwater level contours or distribution plots, horizontal hydraulic gradients, vertical hydraulic gradients, groundwater level variation, groundwater level recession):

- Error in measurement of water level or borehole datum; borehole construction (more than one aquifer or layer penetrated).
- Initial conditions; boundary conditions; coarse grid spacing; coarse time step; model parameters; simplification of flow system e.g. multi-layered aquifer represented as single layer; observation borehole not in centre of model grid.

Spring or baseflow (spot flows, flow recession, flow variation, gains or losses in stream flow):

- Error in flow measurement; separation of baseflow and surface water runoff.
- River/aquifer interaction coefficients.

Contaminant concentrations (spot measurements, contaminant contours or distribution plots, vertical sections, variation in time, travel or breakthrough times):

- Laboratory error; sampling or handling error; borehole construction (short circuiting, long borehole screen section may result in mixing of groundwater from different horizons).

- Initial conditions; boundary conditions; coarse grid spacing; coarse time step; simplification of physico-chemical processes; numerical precision or instability.

MODEL PARAMETERS

Brief description of physical and chemical model parameters (McMahon et al.[11]) required and their relevance in contaminant transport simulations are presented below.

1. Source term

- Mass of contaminant entering the system;
- Contaminant concentrations in groundwater;
- Source term often represented as continuous source term (conservative assumption). In this case it is possible that the modelled contaminant mass may exceed actual contaminant release;
- Source term can alternatively be described as a declining source, usually represented as first order reaction (exponential reduction), but in this case important to check that modelled contaminant mass equates to the measured or estimated total contaminant release mass.

2. Recharge

- Dilution;
- Contaminant loading (leaching);
- Seasonal variation in effective rainfall and leaching of contaminants;
- Indirect recharge (leaking drains, rivers, soakaways etc.);
- Influence of cover (hardstanding, impermeable liners) on infiltration (run-off may flow to leaking drains or soakaway).

3. Horizontal hydraulic conductivity

- Rate of contaminant transport (advection) and arrival time at receptor;
- Calculated groundwater dilution. If value increased, will reduce concentrations due to dilution, but will decrease arrival times at receptor;
- Contaminant transport sensitive to this parameter;
- Field measurements can often vary by more than an order of magnitude (due to the natural heterogeneity of most aquifers);
- Important parameter to determine by field measurement - literature values unlikely to be sufficiently precise.

4. *Vertical hydraulic conductivity*

- Rate of contaminant transport;
- Leakage rates through low permeability layers;
- Usually considered in terms of contaminant migration through the unsaturated zone, mainly in terms of calculation of leakage rates based on vertical hydraulic gradient;
- If no hydraulic head measurements are available, a hydraulic gradient of 1 is often assumed;
- Unsaturated zone travel times are typically calculated as function of unsaturated zone thickness, infiltration and moisture content;
- Heterogeneity in vertical hydraulic conductivity may limit vertical dispersion (mixing zone in aquifer).

5. *Hydraulic gradient (i)*

- Rate and direction of groundwater flow;
- Calculated groundwater dilution. If value increased, will reduce concentrations due to dilution, but will decrease arrival times at receptor;

- Hydraulic gradient is dependent on hydraulic conductivity, steep gradients unlikely to occur in zones of high permeability;
- Important to determine by field measurements (minimum of three boreholes required);
- Hydraulic gradient and direction of flow can vary with time (seasonality).

6. *Transport Porosity (n)*

- Rate of contaminant movement and arrival time at receptor;
- Important to determine if fissure or intergranular flow;
- Fissure-pore water diffusion may be important in some systems;
- Transport in fissured aquifers is often represented by using a low value for porosity (equivalent to fissure porosity or kinematic porosity) in a homogenous medium.

7. *Dispersivity*

- Spreading of contaminant;
- Arrival time at receptor reduced if longitudinal dispersion occurs;
- Reduction in contaminant concentrations;

- Scale dependent;
- Important to consider when calculating arrival times as results in faster breakthrough than from plug flow calculations;
- In more complex models relating to biodegradation, dispersion may be important in reducing contaminant concentrations and in introducing electron acceptors (e.g. dissolved oxygen, nitrate).

8. Longitudinal dispersion

- Longitudinal dispersion typically assumed as 0.1 times pathway length (Domenico and Schwartz[12]).

9. Transverse and vertical dispersion

- Transverse dispersion often assumed as 0.01 to 0.03 times pathway length;
- Vertical dispersion often assumed as 0.001 times pathway length (because of layering of strata);
- Different analytical solutions are available depending on whether vertical dispersion can occur (in one or two directions);
- For a contaminant entering at the water table, the analytical expression should only consider dispersion in one direction.

10. Diffusion

- Spreading of contaminant due to concentration gradient;
- Usually only significant where rates of groundwater flow are low, e.g. strata characterised by values of hydraulic conductivity of less than $1 * 10^{-9}$ m/s;
- Can be important in controlling contaminant movement in dual porosity systems (fissure- porewater diffusion), such as the Chalk.

11. Mixing depth/aquifer thickness

- Dilution by groundwater flow Significance of vertical dispersion (for thin aquifers vertical dispersion should be negligible);
- Mixing depth will typically be less than the aquifer thickness;
- Influenced by groundwater level variation (e.g. smearing of contaminant);
- Typically estimated based on experience, theoretical calculation, hydrographs (variation), borehole logs (high k zones);

- Large mixing depths, greater than 20 m, should be treated with caution.

12. Bulk density

- Used in calculation of contaminant retardation;
- Measurement is straight forward and relatively cheap, once samples have been obtained;
- Literature values typically fall in narrow range and can reasonably be used - depends on grain mineralogy and porosity - check for consistency (1.2 to 1.6 for soils, 1.6 to 2.0 g/cm^3 for rocks) and consequently calculations of retardation rates are relatively insensitive to this parameter.

13. Sorption/retardation

- Rate of contaminant migration;
- Will indirectly increase time for degradation;
- Typically represented as a linear reversible reaction;
- For some situations sorption may be more accurately represented by a non-linear isotherm;
- Be wary of models relying on sorption at high concentrations (where linear sorption has been shown to be inappropriate);
- If contaminants are strongly sorbed to aquifer material they may not be bioavailable (and therefore degradable).

14. Partition coefficient (K_D)

- Used in calculation of retardation of contaminant or in soil water partitioning;
- Rate of contaminant migration;
- Partition coefficients can be sensitive to soil or groundwater pH, pK_a, H, K_{oc}, foc and values can range by more than an order of magnitude;
- Typically based on literature values, although range of different values may be given in literature sources.

15. Organic partition coefficient (K_{OC})

- Used in calculation of retardation of contaminant or in soil water partitioning;
- Rate of contaminant migration;
- Partition coefficient typically calculated as: $KD = f_{OC} * KOC$ (for non-ionised organic contaminants);
- Literature values for organic species can vary.

16. Fraction of organic carbon (f_{OC})

- Calculation of partition coefficient;
- For low f_{OC} values (less than 0.001), sorption/retardation of pollutants to the substrate may be dependent on mineral surface area and mineralogy.

17. Cation Exchange Capacity (CEC)

- Delay for breakthrough of cations (e.g. potassium, ammonium);
- Sensitive to pH, Eh, solute concentration and aquifer mineralogy;
- Aquifers have a finite capacity for cation exchange;
- Cations will compete for available exchange sites and this is typically handled by specifying a reaction efficiency as a measure of available sites;
- Cation exchange is a reversible process;
- Laboratory determination of CEC is normally performed on crushed samples, (Environment Agency[13]) which will increase the surface area, when compared to in-situ samples.

18. Biodegradation

- Reduction of contaminant mass and concentration;
- Contraction of contaminant plume (where the rate of degradation exceeds the contaminant advective and disperse flux), ultimate plume size;
- Calculation of contaminant transport and remedial targets very sensitive to degradation rate;
- Check contaminant is biodegradable (e.g. metals and chloride are not).

Typically represented as first order reaction but degradation:

- can be inhibited at high concentrations of contaminant;
- is sensitive to environmental conditions (pH, temperature, redox); optimal pH is typically between 6.5 and 8;
- is reaction-dependent (i.e. availability of dissolved oxygen or electron acceptors such as nitrate, sulphate, iron);
- often requires other nutrients especially N and P, or cometabolites (e.g. a carbon source for the reductive dechlorination of chlorinated solvents).

Assessors should be expected to demonstrate degradation (Environment Agency[14]) by observable mass loss and geochemical indicators, and should not rely solely on literature data.

Degradation rates derived from literature values:

- may not be appropriate to Indian conditions;
- may relate to different conditions from that observed at site (e.g. anaerobic conditions may occur at site, whereas the literature value may be for aerobic conditions);
- may be derived from laboratory studies which do not reflect field conditions.

The breakdown products may be more mobile and toxic than the parent compound. Build up of degradation products can cause inhibition. The determination of field rates of degradation will often be dependent on detailed site investigation and monitoring, supported by modelling and statistical analysis of the data (Environment Agency[14]).

CONCLUDING REMARKS

A phased approach in using mathematical models is recommended, moving from simple calculations, to analytical models, and finally to numerical models (if appropriate). In each case, the selection of the modelling approach should be justified and appropriate to the available data and understanding of the system behaviour. A model should not be used as an alternative to obtaining site-specific data. Data collection should be an iterative process and linked to the development and refinement of the conceptual model and the mathematical model. Site-specific data should be obtained wherever possible and for certain parameters, site-specific data are essential. Literature values may need to be used for some parameters, and will need to be justified.

The results of the mathematical model will need to be checked against historic data to provide assurance that the model provides a credible and acceptable representation of system behaviour. If this cannot be achieved, the conceptual model and adopted mathematical model should be re-assessed and additional site-specific information collected. Reporting of modelling studies must be clear and concise but also include information and justification for all assumptions and decisions made and parameters used. All stages of the process should be reported and be auditable.

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