# ABSTRACT

National capital territory of Delhi is facing severe problems in management of groundwater quality and quantity. The quality of ground water within Delhi varies from the place to place along with the depth of the water table. Dissolved nitrate is most common contaminant in groundwater. Rising nitrate concentrations in rivers and groundwater in regions have been of concern for several decades. Diffuse pollution from agricultural activities and livestock are often the main sources of elevated nitrate concentrations in groundwater. These activities pollute superficial water courses as well as groundwater through percolation. The fertilizers deteriorate the water quality inducing economical and ecological problems. In the last century automation of agriculture and the introduction of high yield crops has raised the use of fertilizers, increasing nitrate concentration in groundwater. Initially, the main concern was about human health, reflected in the Drinking Water Directive. More recently, legislation, the Nitrates Directive, has included reference to nitrate's role in eutrophication.

Realizing the importance of groundwater quality in urban areas and its deterioration due to the various pollutants, leading by nitrate, study was carried out to determine the nitrate contamination of ground water in Delhi using the mathematical models. Groundwater models describe the groundwater flow and transport processes using mathematical equations based on certain simplifying assumptions. These assumptions typically involve the direction of flow, geometry of the aquifer, the heterogeneity or anisotropy of sediments or bedrock within the aquifer, the contaminant transport mechanisms and chemical reactions. Groundwater flow models are used to calculate the rate and direction of movement of groundwater through aquifers and confining units in the subsurface. These calculations are referred to as simulations. The finite difference method of mathematical modeling has been used for the solution of convective dispersion equation of transport of nitrogen in the sample.

Model with the least limitations and assumption have been selected for the calculation of the flow and transport of the nitrogen. The simulations using a uniform nitrogen to nitrate conversion ratio provides greater details of nitrate behavior. The results from the transport simulation are compared with the results of mass balance equation, which predict the average the nitrate concentration. Modeling errors are common in the simulations, due to the various assumptions taken in the modeling. For the reduction in the modeling errors, there is a need to apply best hydro-geological judgment. Hydro-geochemical data shows the great variation in the nitrate concentration. This data provide the basis for conversion of nitrogen to nitrate ratio in the simulation.

# CHAPTER 1

# INTRODUCTION

## 1.1 Introduction

The groundwater model is an important tool in the field of environmental engineering. Use of groundwater models is imperative for the study of groundwater flow and contaminant transport. Groundwater models have been applied to investigate a wide range of hydro-geologic conditions. Most recently, groundwater models are being used to predict the transport of contaminants for risk evaluation of groundwater quality.

In general, models are conceptual descriptions or approximations that evaluate physical systems using mathematical equations. Models are not exact descriptions of physical processes or systems. By numerical or mathematically representing a simplified version of a hydro-geological system, sustainable alternative scenarios can be predicted, tested, and evaluated. The usefulness or applicability of a model depends on how closely the equations approximate the physical system under investigation. In order to evaluate the usefulness or applicability of a model, it is essential to have a thorough understanding of the physical system and the assumptions undertaken for the derivation of the mathematical equations.

Groundwater models describe the groundwater flow and transport processes using mathematical equations depending upon on certain simplifying assumptions. These assumptions usually involve the direction of flow, or anisotropy of sediments, geometry of the aquifer, the heterogeneity or bedrock of the aquifer, the contaminant transport mechanisms and the chemical reactions. Due to the simplifying assumptions involved in the mathematical equations and the many

uncertainties in the values of data considered for the model, a model must be viewed as an approximation and not an exact duplication of physical conditions. Groundwater models, although an approximation, are a useful investigation means that groundwater hydrologists and researchers may apply for a number of applications.

Application of already existing groundwater models include water balance (in terms of water quantity), obtaining knowledge about the quantitative aspects of the unsaturated zone, simulating water flow and contaminant migration in the saturated zone including river-groundwater relations, assessing the impact of changes of the groundwater regime on the environment, setting up optimising monitoring networks, and setting up groundwater protection zones.

Groundwater flow models are used to monitor the rate and direction of movement of groundwater through aquifers and confining zones in the subsurface. These calculations are known as simulations. The simulation of groundwater flow needs a deep understanding of the hydro-geologic characteristics of the site to be modelled. The hydro-geologic investigation should include a complete characterization of the following:

- Subsurface conditions and thickness of aquifers and confining zones (hydro-geologic framework).
- Hydrologic boundaries or the boundary conditions, which control the rate and direction of movement of groundwater and contaminants.
- Hydraulic properties of the aquifers and confining zones.
- A study of the horizontal and vertical distribution of hydraulic head throughout the modelled area for initial conditions, equilibrium (steady-state conditions) and the transitional conditions when hydraulic head may or may not vary with time (transient conditions).

- Distribution and magnitude of groundwater recharge, pumping or injection of groundwater, leakage to or from surface-water bodies, etc. (sources or sinks, may be termed to as stresses). These stresses can be constant (not varying with time) or may change with time (transient) depending upon in-situ conditions.

The modelling studies in India have so far been confined to academic and research organisations. The professionals mostly still prefer to use lumped models for planning of groundwater recharge and development. These models completely ignore the distributed character of the groundwater regime and the subsurface explorations. Hence, they are based upon rather conservative concepts like safe yields and are incapable of accounting for the stream-aquifer interaction and the dependability of lateral recharge on the water table pattern only. Consequently, permissible pumping (withdrawals in excess of vertical recharge) and perennial yield cannot be obtained. The objectives of modelling studies in India have been mainly (i) the groundwater recharge, (ii) stream-aquifer interaction, (iii) dynamic nature of the water table and (iv) seawater intrusion etc. It is essential to understand general aspects of both groundwater flow and the transport models in order to evaluate application or usefulness of these models, may be performed correctly.

## 1.2 Groundwater Contamination

- **Nitrates**: Dissolved nitrate(in the form of $NO_3^-$) is most common contaminant in groundwater. High level may form carcinogens, can cause blue baby disease (Methamoglobinamia) in children & can promote eutrophication in surface water sources. Sources of nitrates include fertilizers, sewage, landfills, air pollution & industries.
- **Pathogens**: viruses and bacteria that cause water borne diseases such as typhoid, dysentery, cholera, polio, and hepatitis. Sources include sewage, septic tanks, landfills & livestock's.

- **Trace metals**: trace metals or heavy metals include Lead, Cadmium, Mercury, Copper, Chromium and Nickel. These heavy metals can be toxic and carcinogenic. Sources of trace metals include industrial & mine discharges, fly ash from thermal power plants either due to fall out or disposal in ash ponds. Industrial solid waste disposal and leaching into groundwater through rainwater;
- **Inorganic Compounds**: Inorganic dissolved salts contaminations such as $SO4^-$, Chloride, etc. along with Na, K, building up high dissolved solids and combination of Bicarbonates, Carbonates along with Ca and Mg building up high hardness of water and converting potable water in to hard water creating gastrointestinal problems in human being if they consume groundwater as drinking source;
- **Organic compounds**: these include volatile & semi-volatile organic compounds like petroleum derivatives, pesticides, PCBs. Sources of organic compounds includes agricultural activities, street drainages, sewage landfills, industrial discharges, spills, vehicular emissions fall out etc.

Water pollution is the most challenging environmental problem and nitrate is among the most common and widespread pollutants of groundwater. Dispersed pollution from agricultural activities and livestock are usually the main sources of increased nitrate concentrations in groundwater. These agricultural activities pollute superficial water courses as well as groundwater through seepage and percolation. The fertilizers affect the water quality enhancing economical and ecological problems. In the previous century automation of agriculture and the introduction of high yield crops has influenced the use of fertilizers, hence increasing nitrate concentration in groundwater.

High nitrate concentration in drinking water has been linked to human health issues like methemoglobinemia in infants and stomach cancer in adults, though the evidence for nitrates as a cause of these diseases remains controversial. Excess concentration of nitrates in ecosystems can cause serious environmental hazards, leading to eutrophication of connected surface water bodies that can eventually

accelerate algal blooms and fish killing. Although the control of point source emissions improved the quality of many water bodies across India, nitrate concentrations in rivers from diffuse sources have remained variable in India's rivers and groundwater, reflecting the large nitrogen surplus in agricultural soils and high livestock densities.

Realizing the importance of groundwater quality in urban areas and its deterioration due to the various pollutants, leading by nitrate, study was carried out to determine the nitrate contamination of ground water in Delhi.

## 1.3 Objective of the Study

- To study different types of Environmental models
- Development of models for Groundwater contaminations
- To develop model for nitrate contamination of Groundwater of Delhi.

# CHAPTER 2

# LITERATURE REVIEW

The word model has so many definitions and is so overused that it is sometimes difficult to derive the meaning of the word. A model is perhaps most simply defined as a representation of a real system or process (Konikow and Bredehoeft 1992).

The groundwater models may be applied as investigative and predictive tools with the objective of forecasting of future conditions or the impact of a proposed action on already existing conditions of a groundwater regime. They may also be applied as generic or screening tools in regulatory mode for the purpose of developing management standards and guideline (Bedient et al., 1994)

The flow and mass transport model to assess the migration of the contaminated plume for the Patancheru Industrial Development Area (Gurunadha et al., 2001) and the mass transport modeling to assess the migration of the contaminated plume for Treatment, Storage and Disposal Facility (TSDF) constructed for disposal of hazardous waste generated by industries in and around Hyderabad city (Gurunadha et al., 2004). Some of the groundwater modeling studies undertaken by various researchers in India are the flow and contamination transport model for the groundwater regime in upper Palar basin, Dindigul town, Tamil Nadu resulting from groundwater pollution by tanneries (Gurunadha and Thangarajan, 1999; Mondal and Singh, 2005),

Craner (2006) developed a steady-state mathematical groundwater flow model using MODFLOW with MODPATH to understand direction of groundwater flow, groundwater age, and nitrate transport pathways of the Southern Willamette

Valley, Oregon, USA. The study suggests it may take 10's of years to see measurable declines of groundwater nitrate in some locations.

Almasri and Kaluarachchi (2007) also developed a soil nitrogen dynamic model to estimate nitrate leaching to groundwater. These estimates were used in developing a groundwater nitrate fate and transport model. The framework considers both point and non-point sources of nitrogen across different land use classes. The methodology was applied for the Sumas–Blaine aquifer of Washington State, US, where heavy dairy industry and berry plantations are concentrated. Simulations were carried out using the developed framework to evaluate the overall impacts of current land use practices and the efficiency of proposed protection alternatives on nitrate pollution in the aquifer.

GIS offers data management and spatial analysis capabilities that can be useful in groundwater modeling. GIS is an important tool in development of conceptual model for any groundwater flow and contaminate transport problem. It provides automatic data collection, systematic model parameter assignment, spatial statistics generation, and the visual display of model results, all of which can improve and facilitate modeling (Watkins et al., 1996).

Gogu et al. (2001) designed a GIS database that offers facilities for groundwater vulnerability analysis and hydrogeological modeling for the Walloon region in Belgium. A "loose-coupling" tool was created between the spatial-database scheme and the groundwater numerical model interface GMS (Groundwater Modeling System). Following time and spatial queries, the hydrogeological data stored in the database can be easily used within different groundwater numerical models.

Remote sensing is another useful tool in the acquisition of spatially distributed data for groundwater modeling. Airborne geophysical surveys allow for the identification of faults and dikes, changes in lithology and the depth of magnetic

features (Doll et al., 2000; Danielsen et al., 2003; Jorgensen et al., 2003). This information is helpful in constructing realistic conceptual models of aquifers.

For unconfined aquifer (water-table) system, it must be assumed that flow is horizontal and equipotential lines are vertical, that means the horizontal hydraulic gradient equals the slope of the water table, and that the storage coefficient is equal to the specific yield (Sy) (Anderson and Woessner 1992).

When the water properties are heterogeneous and (or) transient, the relations among water levels, hydraulic heads, fluid pressures, and flow velocities are neither simple nor straightforward. In such cases, the flow equation is written and solved in terms of fluid pressures, fluid densities, and the intrinsic permeability of the porous media (Konikow and Grove 1977).

Most reported values of dispersion coefficient fall in a range from 0.01 to 1.0 times the scale of the measurement, although the ratio of αL to scale of measurement tends to decrease at larger scales (Anderson 1984; Gelhar et al. 1992). Field-scale dispersion (commonly called macrodispersion) results from large-scale spatial variations in hydraulic properties. Consequently, the use of relatively large values of dispersivity together with uniform hydraulic properties (Kij and ε) is inappropriate for describing transport in geological systems (Smith and Schwartz 1980).

Transient flow field by a mean steady-state flow field, which is commonly done, inherently ignores some of the variability in velocity and must be compensated for by using increased values of dispersivity (especially transverse dispersivity) (Goode and Konikow 1990).

Many analytical solutions have been developed for the flow equation; however, most applications are limited to well hydraulics problems involving radial symmetry (Walton 1962; Lohman 1972; Reed 1980).

Finite-element methods use assumed functions of the dependent variables and parameters to evaluate equivalent integral formulations of the partial differential equations. Huyakorn and Pinder (1983) present a comprehensive analysis and review of the application of finite-element methods to groundwater problems (Huyakorn and Pinder 1983).

The equations describing groundwater flow and solute transport are second-order differential equations, which can be classified on the basis of their mathematical properties. There are basically three types of second-order differential equations, which are parabolic, elliptic, and hyperbolic (Peaceman 1977).

Rubin (1983) discusses and classifies the chemical nature of reactions and their relation to the mathematical problem formulation. Bahr and Rubin (1987) compare kinetic and local equilibrium formulations for solute transport affected by surface reactions.

Huebner (1975) explained the four different approaches to formulate the finite-element method for a problem are: the direct approach, the variational approach, the weighted residual approach, and the energy balance approach.

# CHAPTER 3

# DEVELOPMENT OF MATHEMATICAL MODELS

## 3.1 TYPES OF MODELS

The mathematical equations that approximate the groundwater fate and flow and transport processes may be solved by different types of models. Some models may be exact solutions to equations that describe very simple flow or transport conditions (analytical model) and others may be mere approximations of equations that describe very complex conditions (numerical model). Many of the models may also simulate either one or more of the processes that govern groundwater flow or contaminant migration rather than all of the flow and transport processes.

For example, particle tracking models, like MODPATH, simulates the advective transport of contaminants but do not account for other flow and transport processes. For selecting a model for use at a site, it is essential to determine whether the model equations account for the key physical and chemical processes occurring at the site. Every model, whether it is a analytical model or a complex numerical model, may have usefulness and applicability in hydro-geological and remedial explorations.

### 3.1.1 Analytical Models

Analytical models are the simplest models derived by incorporating a lot of simplifying assumptions. These are an exact solution of a specific, often largely simplified, groundwater flow or transport equation. These equations are a simplification of more complex three-dimensional groundwater flow or solute transport equations. Before the development and widespread use of computers,

when human brain was used, there was a need to simplify the three-dimensional equations because it was not possible to solve these equations easily. These simplifications, consequently, resulted in reducing the groundwater flow to one dimension and the solute transport equation to one or two dimensions. These resulted in changes to the model equations that include one-dimensional uniform groundwater flow, homogeneous and isotropic aquifers, simple uniform aquifer geometry, simple flow or chemical reaction boundaries and uniform hydraulic and chemical reaction properties. Analytical models are usually steady-state and one-dimensional, although some groundwater flow models are two dimensional (e.g. analytical element models), and some contaminant transport models assume one-dimensional groundwater flow conditions and one-, two- or three dimensional transport conditions.

Due to the simplifications included in analytical models, it is not always possible to account for site conditions that vary with time or space. These scenarios includes variations in groundwater direction or flow rate, variations in hydraulic head or chemical reaction properties, fluctuating hydraulic stresses, or complex hydro-geologic or chemical boundary conditions.

Applications of Analytical models are most suitable at:

- Initial site assessments where a high degree of accuracy is not needed,
- Designing data collection plans prior to beginning field activities,
- An independent check of numerical model simulation results, or
- Sites where field conditions support the simplifying assumptions employed in the analytical models.

### 3.1.2 Numerical Models

Numerical models are used to solve the more complex equations that describe groundwater flow and solute transport. These complex equations generally

encompass multi-dimensional groundwater flow, solute transport and chemical reactions, although there are also one-dimensional numerical models. These numerical models use approximations (e.g. finite differences, matrix method or finite elements) to solve the differential equations describing groundwater flow or solute transport. The approximations require that the domain of the model and time be clearly mentioned. In this discretization process, the model domain is represented by a network of grid cells or elements, and the time of the simulation is represented by time interval. The graph and curve represents the continuous variation of a parameter across the model space or time domain. The bars represent a time interval step-wise approximation of the curve.

For any numerical model the accuracy depends upon the accuracy of the input data, the size of the space and time discretization (the lesser is the size of the discretization steps, the lesser is the possible error), and the numerical method used to solve the model equations. Unlike analytical models, mathematical or numerical models have the capability of representing a complex multi-layered hydro-geologic network. This is accomplished by dividing the network into discrete cells or elements. More applications in addition to complex three-dimensional groundwater flow and solute transport problems, numerical models may be used to simulate very simple flow and transport conditions, which may just as easily be simulated using an analytical model. However, numerical models are generally used to simulate problems which cannot be accurately described using analytical models.

## 3.2 DEVELOPMENT OF MODEL

Objectives of the model must be defined which explain the purpose of developing a groundwater model. These objectives of modeling will profoundly impact the modelling effort needed.

### 3.2.1 Hydro-geological Characterization

Appropriate characterization of the hydro-geological conditions at a site is necessary in order to understand the importance of relevant flow or solute-transport processes. The increase in the attempted application of natural attenuation as a remedial action, it is imperative that a thorough field characterization should be done. To gain such level of characterization requires more site-specific fieldwork than just an initial assessment, which includes more monitoring wells and groundwater samples, and an increase in the number of laboratory analytes and considering more field parameters. Without proper field characterization, it is not possible to select a desired model or develop a reliably calibrated model. In worst case, the following hydro-geological and geochemical information must be available for this characterization:

- Regional geologic data describing subsurface geology.
- Topographic data (including surface-water elevations)
- Enlisting the existing surface-water bodies and measured stream-discharge (base flow) data
- Cross sections of geological features drawn from soil borings and well logs.
- Well construction diagrams and soil boring logs.
- Duly measured hydraulic-head data.
- Estimates of hydraulic conductivity derived from aquifer and/or slug test data.
- Location and estimated flow rate of groundwater sources and sinks.
- Detection of chemicals and contaminants of concern in contaminant plume
- Horizontal and vertical extent of contaminant plume
- History, location, and mass loading or removal rate for contaminant sources or sinks.

- Direction and rate of contaminant migration
- Identification of downgradient receptors.
- Organic carbon content of sediments
- Appropriate geochemical field parameters (e.g. dissolved oxygen, pH)
- Appropriate parameters as geochemical indicator (e.g. electron acceptors and degradation byproducts)

### 3.2.2 Model Conceptualization

It is the process in which data describing site conditions are accumulated and assembled in a systematic way to describe groundwater flow and transport of contaminants processes at a site. Model conceptualization helps in determining the modelling approach and determining which model software to use.

Questions to be asked in developing a conceptual model include, but these are not limited to the following only:

- Are there adesufficient data to characterise the hydro-geological conditions at the site?
- In how many directions is groundwater flow is taking place?
- Can the contaminant transport or the groundwater flow be characterized as one-dimensional, two-dimensional or three-dimensional?
- What is the composition of aquifer system, wheather it is composed of more than one aquifer, and if the vertical flow between aquifers important?
- Is there recharge to the aquifer by precipitation or leakage from a river, drain, lake, or infiltration pond?
- Is the groundwater escaping the aquifer system by seepage to a river or lake, flow to a drain, or extraction by a well?

- Does it seem that the aquifer's hydrogeological characteristics remain relatively uniform with time and space domain, or do geologic data indicates considerable variation at the site?
- Are the boundary conditions well defined around the perimeter of the model domain, and do they have a hydro-geological or geochemical basis?
- Do groundwater-flow or contaminant source conditions remain constant, or do they change with time?
- Are there receptors located downgradient of the contaminant plume?
- Are geochemical reactions taking place in onsite groundwater, and are the processes understood?

### 3.2.3 Modelling Software Selection

A computer model software is selected after hydrogeological characterization of the site has been completed and the conceptual model developed. The selected model should be capable of simulating conditions faced at a site. There are few general guidelines which should be used in assessing the appropriateness of a model:

Analytical models should be used where:

- Site data show that groundwater flow or contaminant transport processes are relatively simple.
- An initial assessment of hydro-geological conditions or screening of remedial alternatives is needed.

Numerical or mathematical models should be used where:

- Site data show that groundwater flow or contaminant transport processes are relatively complex.

- Groundwater flow directions, hydrogeological or geochemical conditions, and hydraulic or chemical sources and sinks vary with space and time.

A one-dimensional groundwater flow or transport model should be used primarily for:

- Initial assessments where the degree of aquifer heterogeneity or anisotropy is not known.
- Sites where a potential receptor is immediately downgradient of a contaminant source.

Development of two-dimensional models should be, for:

- Problems which include one or more groundwater sources/sinks (e.g. pumping or injection wells, drains, rivers, etc.),
- Sites where the flow direction of groundwater is two dimensions(e.g. radial flow to a well, or single aquifer system with relatively small vertical hydraulic head or contaminant concentration gradients),
- Sites at which the aquifer has distinct variations in hydraulic properties,
- Contaminant migration problems where the impacts of transverse dispersion are important and the lateral, or vertical, spread of the contaminant plume must be approximated.

Three-dimensional flow and transport models should be used where:

- The hydro-geologic conditions are well known,
- Multiple aquifers are present,
- The vertical movement of groundwater or contaminants is important.

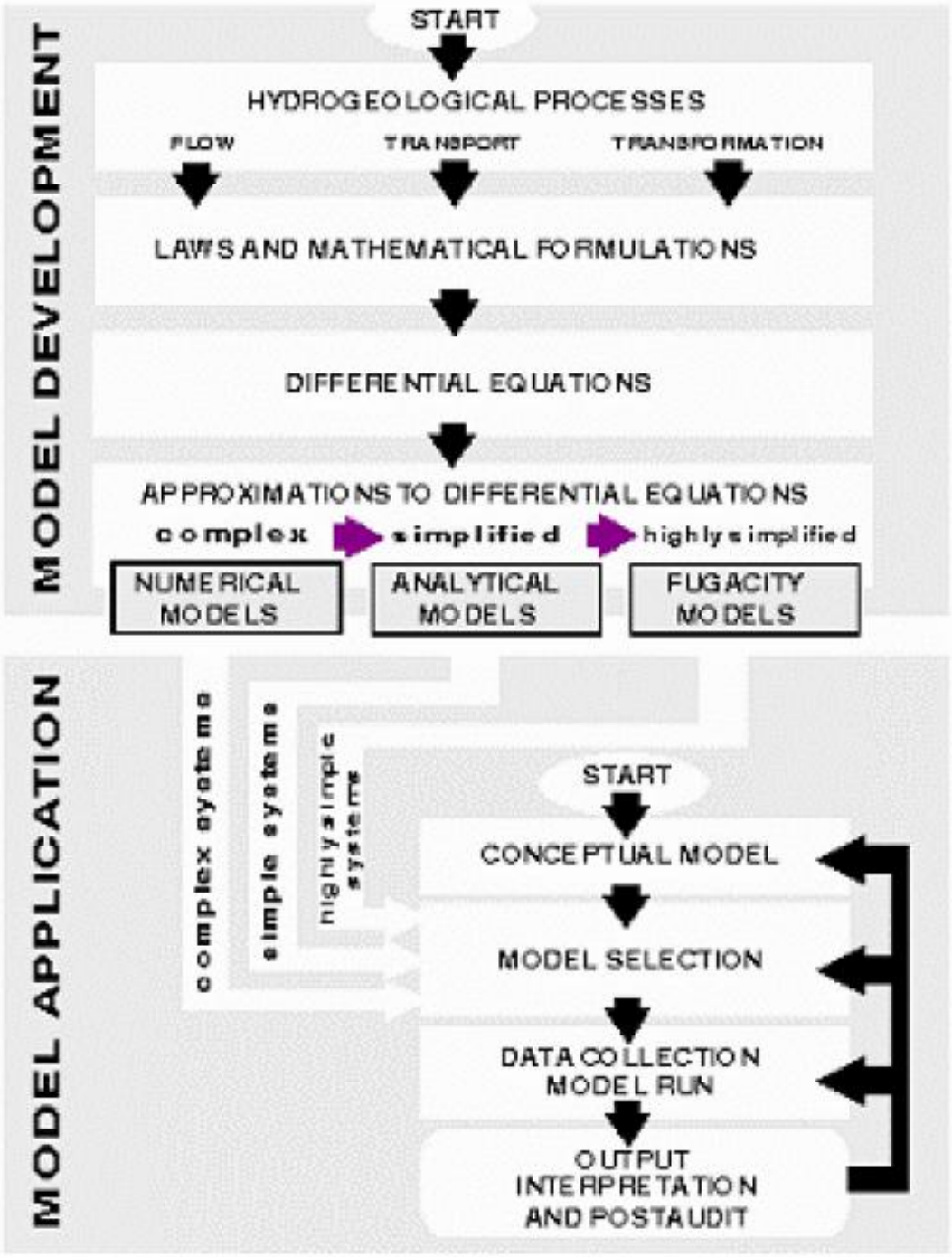


Fig 3.1: Flowchart of Development process of model

Model documentation report should demonstrate the rationale for selection of the suitable model software. The selection of model software program for use at a site is the responsibility of the model developer. Any suitable groundwater flow or fate

and transport model software may be used given that the model code has been already tested, verified and documented. However, it is recommended that the model developer contact the GMP at the starting of the exploration to discuss the selection of appropriate model software. If the software is not currently used by the GMP, a copy of the software and the documentation of the program must be submitted to the GMP along with the model documentation report. For example, analytical models can be used where field data show that groundwater flow or transport processes are relatively simple. Similarly, one-dimensional or two-dimensional or three-dimensional groundwater flow and transport models should be selected based upon the hydro-geological characterization and model conceptualization.

### 3.2.4 Model Design (Input Parameters)

The design of model includes all parameters that are used to develop a calibrated model. Model grid size and spacing, boundary conditions, layer elevation, hydraulic conductivity/transmissivity, recharge, any additional model input, dispersion coefficients transient or steady state modelling, degradation rate coefficients etc are included in the input parameters.

### 3.2.5 Model Calibration

Model calibration encompasses changing the values of model input parameters in an attempt to obtain the site conditions within some acceptable criteria. It requires that field conditions at a site be properly characterized. Lack of proper this site characterization may result in a model calibrated to a set of conditions that are not representative of actual field conditions.

The calibration process usually involves calibrating to steady-state and transient conditions. In steady-state simulations, no observed changes in hydraulic head or contaminant concentration are observed with time for the field conditions which is

being modelled. Change in hydraulic head or contaminant concentration with time (e.g. aquifer test, an aquifer stressed by a well-field, or a migrating contaminant plume) are involved in Transient calibration. These simulations are required to narrow the range of fluctuation in model input data since there are numerous choices of model input data values which may result in similar steady-state simulations. Models may be calibrated without simulating steady-state flow conditions, but not so easily. At a minimum, model calibration should include comparisons between model-simulated conditions and field conditions for the following data:

- Hydraulic head data,
- Direction of Groundwater flow ,
- Hydraulic-head gradient,
- Water mass balance,
- Contaminant concentrations (if needed),
- Contaminant migration rates (if needed),
- Migration directions (if appropriate), and
- Degradation rates (if appropriate).

These comparisons between measured and computed heads should be presented in maps, tables or graphs. A simple graphical comparison between measured and computed heads is shown in Figure 3.2. In this example, the closer the heads fall on the straight line, the better the "goodness-of-fit". Every model developer and model reviewer will use their professional judgment in evaluating the calibration results. There are no universally accepted "goodness-of-fit" criteria that apply in all cases. However, it is vital that the model developer makes all efforts to minimize the difference between model simulations and measured field conditions. For a good model usually, the difference between simulated and actual field conditions (residual) should be less than 10 percent of the variability in the field data across the model domain. Figure 3.3 shows plot showing residuals at monitoring wells

(calibration targets) . A plot in this format is useful to show the “goodness-of-fit” at individual wells.

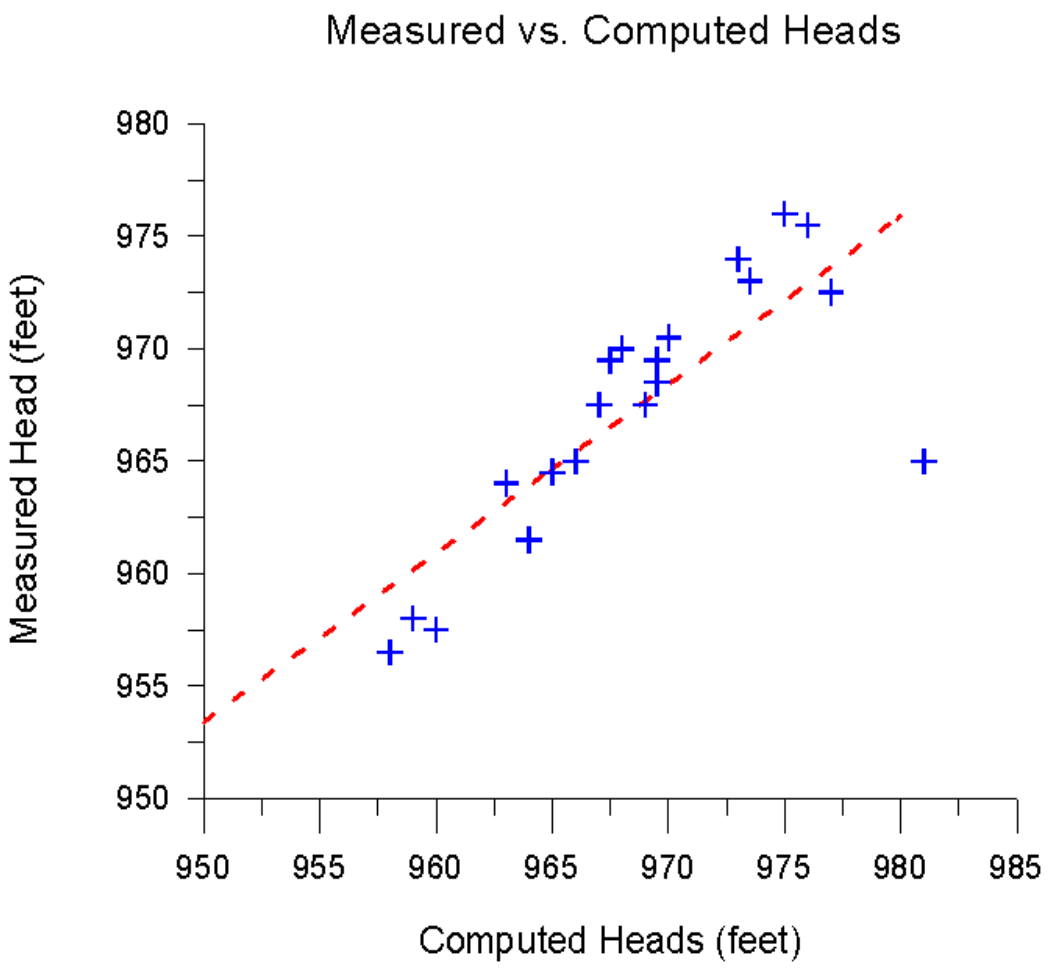


Figure3.2: Comparison between measured and computed hydraulic heads.

The model dveloper should also avoid the prejudice of adjusting model input data on a scale which is smaller than the distribution of field data. This process, referred to as "over calibration", results in a model that appears to be calibrated but has been based on a data set that is not supported by field data. For preliminary assessments, one can obtain useful results from models that are not even calibrated. Uncalibrated models are very useful in guiding data collection activities for hydro-geological investigations or as a screening tool in evaluating the relative effectiveness of remedial action alternatives.

### 3.2.6 Sensitivity Analysis

Sensitivity analysis is the process of varying model input parameters over a reasonable range (range of uncertainty in value of model parameter) and observing the relative change in model response. Typically, these data of the observed change in hydraulic head, contaminant transport or flow rate are noted. Data for which the model is relatively sensitive would require future characterization, while model-insensitive data would not require further field characterization.

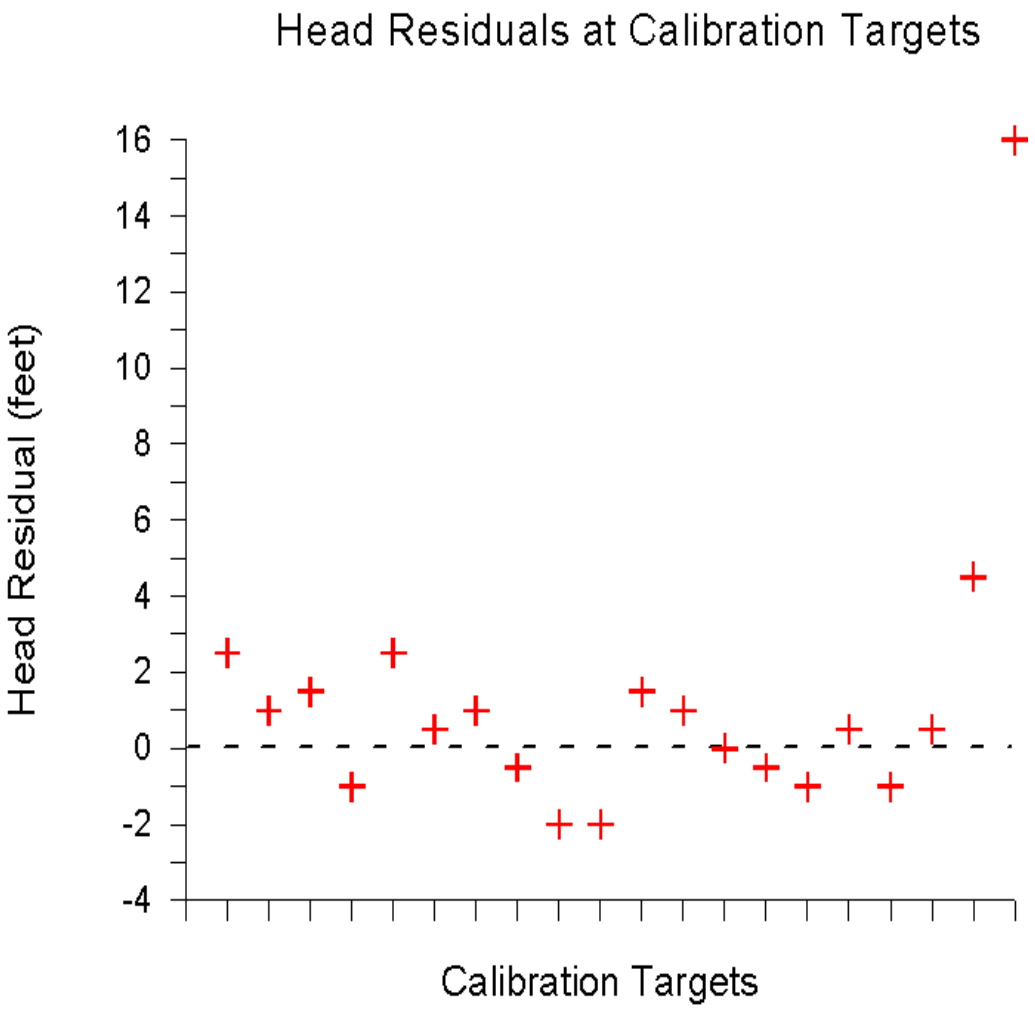


Figure3.3: Residuals from comparison of measured and computed heads at calibration targets.

The purpose of the sensitivity analysis is to demonstrate the sensitivity of the model simulations to uncertainty in values of model input data. The sensitivity of one model parameter relative to other parameters is also demonstrated. Sensitivity analyses are also beneficial in determining the direction of future data collection activities.

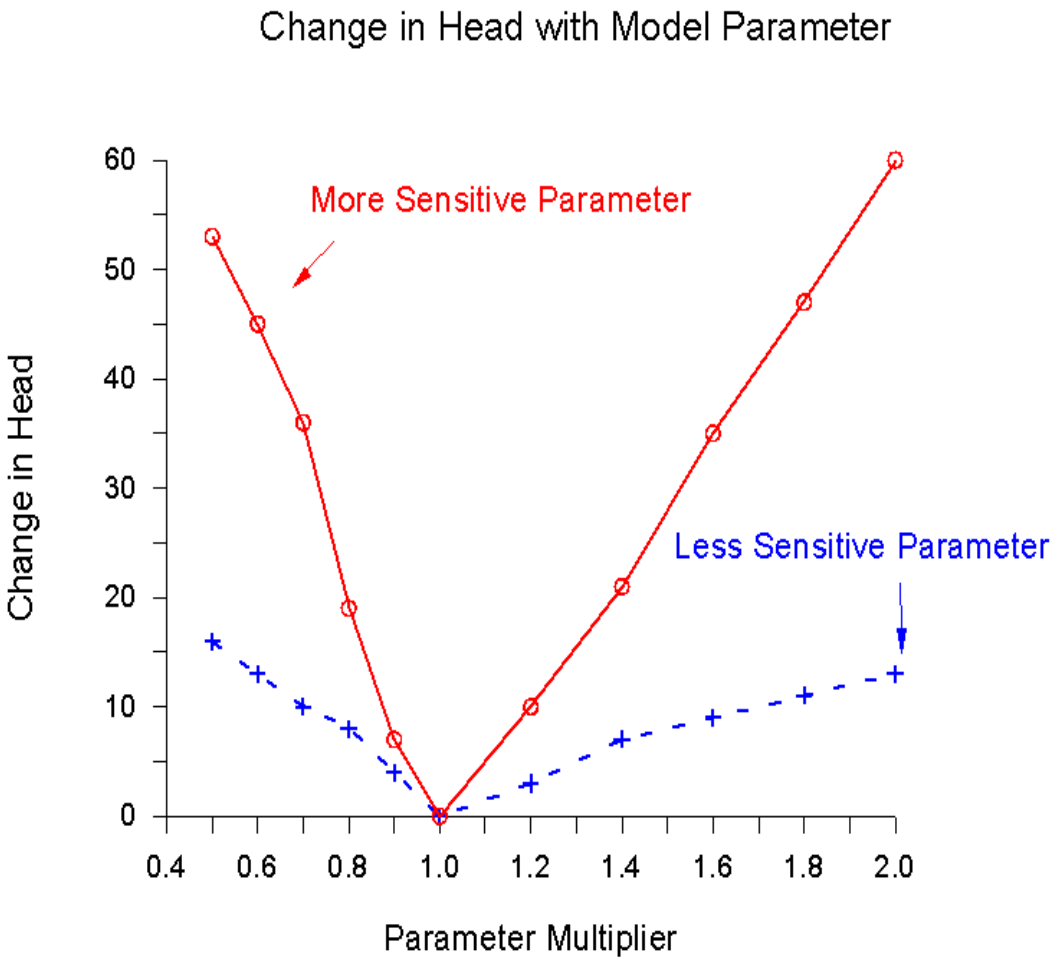


Figure3.4: Simulated change in hydraulic head resulting from change in parameter value.

### 3.2.7 Model Verification

A calibrated model uses selected values of hydro-geologic parameters, sources and sinks and boundary conditions to match historical field conditions. The process of model verification may result in further calibration or refinement of the model. After the model has successfully reproduced measured changes in field conditions, it is ready for predictive simulations.

### 3.2.8 Predictive Simulations

A model can be used to predict future groundwater flow or contaminant transport condition. The model may also be used to evaluate different remediation alternatives. However, errors and uncertainties in a groundwater flow analysis and solute transport analysis make any model prediction no better than an approximation. For this reason, all model predictions should be expressed as a range of possible outcomes that reflect the assumptions involved and uncertainty in model input data and parameter values.

In order to perform these tasks, the model, whether it is a groundwater flow or solute transport model, must be reasonably accurate, as demonstrated during the model calibration process. However, because even a well-calibrated model is based on insufficient data or oversimplifications, there are errors and uncertainties in a groundwater-flow analysis or solute transport analysis that make any model prediction no better than an approximation. For this reason, all model predictions should be expressed as a range of possible outcomes which reflect the uncertainty in model parameter values. The range of uncertainty should be similar to that used for the sensitivity analysis.

The following examples demonstrate, in a limited manner, how model predictions may be presented to illustrate the range of possible outcomes resulting in model input data uncertainty.

Figure 3.4 shows the range in calculated head at calibration targets at a particular point in time resulting from varying a model parameter over its range of uncertainty. If the purpose of the predictive simulations is to determine the future hydraulic head distribution in an aquifer, the upper and lower estimate of head should be presented so that appropriate decisions may be made.

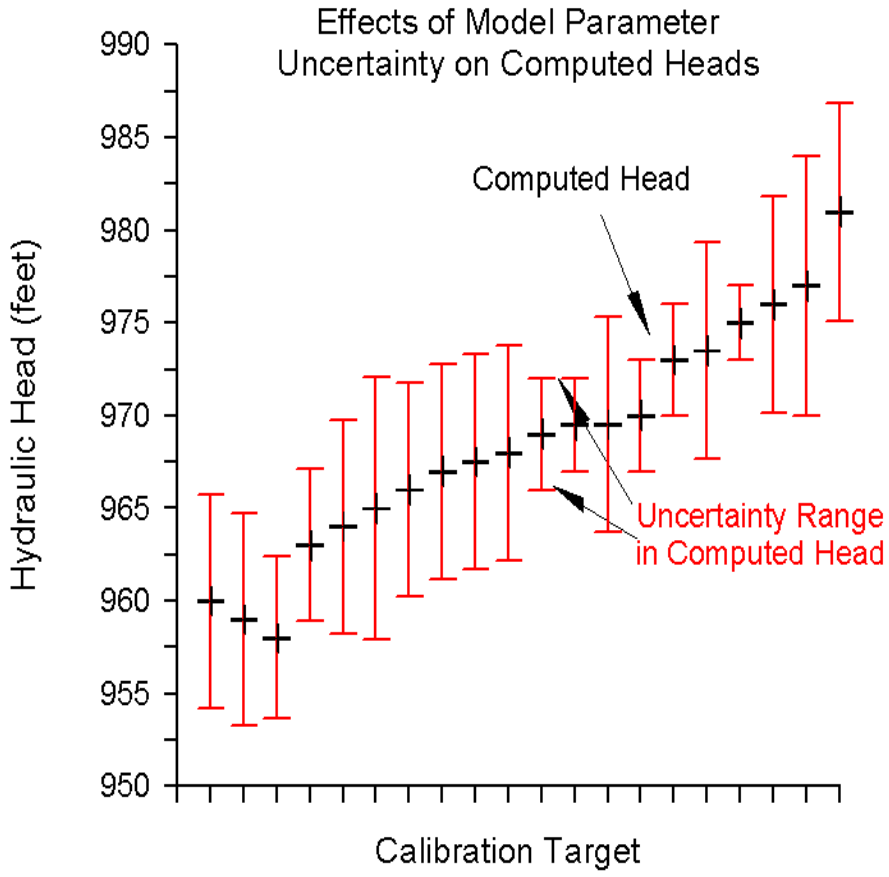


Figure3.5: Simulated uncertainty in hydraulic heads at calibration targets.

In Figure 3.5, hydraulic heads are predicted for a future time interval in response to changing stresses on the aquifer system. The predicted results using the calibrated flow model are presented as the black line. The red and blue lines show the hydraulic heads predicted using slightly different model input parameters which

result in values of hydraulic head which are five percent higher and lower than the heads predicted using the calibrated model. Again, the range in predicted heads should be presented so that appropriate, or conservative, decisions may be made regarding the groundwater resource.

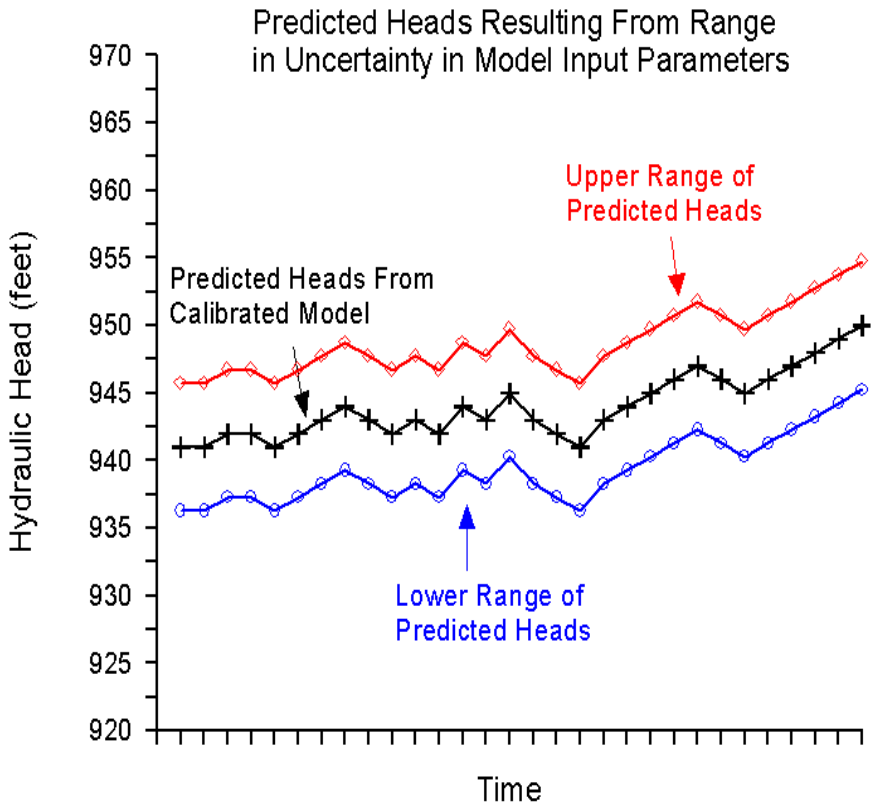


Figure 3.6: Predicted range in hydraulic heads.

Figure 3.6 shows an example of delineating a wellhead protection area (WHPA) for a public water-supply. These WHPAs were simulated using the range of hydraulic conductivity values reported from an aquifer test at a municipal well. The WHPA delineated using the low hydraulic conductivity value (shown in brown) is wider than and not as long as the WHPA delineated using the high value of hydraulic conductivity (shown in gold). In order to be protective of the public water supply, it's important that the delineated WHPA is conservatively estimated. In this

example, the final recommended WHPA is a composite of the two previously simulated WHPAs.

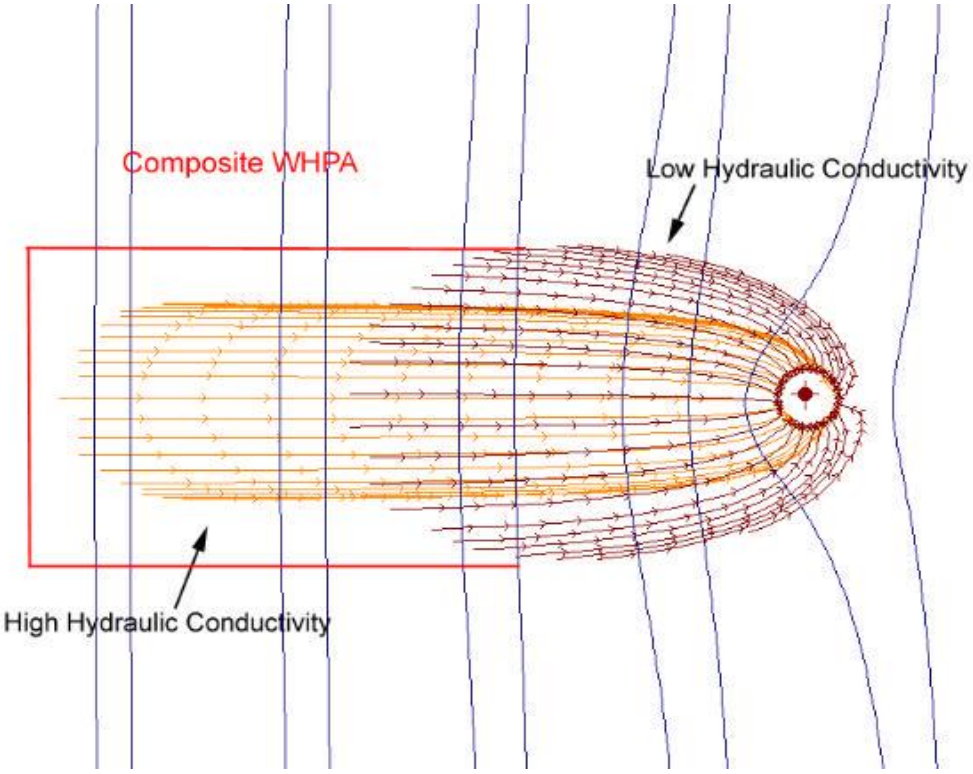


Figure 3.7: Simulated wellhead protection areas using range of hydraulic conductivities.

This final example (Figure 3.7) shows the simulated contaminant concentration downgradient from a source area. The purpose of the simulation was to estimate the contaminant concentration at the point of compliance, approximately 1000 feet downgradient from the source area. The difference between the two simulations shown in the figure is the value of organic carbon fraction used in each simulation. Increasing the organic carbon concentration increases the degree of attenuation of the contaminant plume. Since the organic carbon content of sediments is very seldom known with a high degree of certainty, and a single value is typically used in fate and transport models, it is best to present the simulation results as a range of

concentrations which might result. This can be said for any of the model inpu parameters used in fate and transport models.

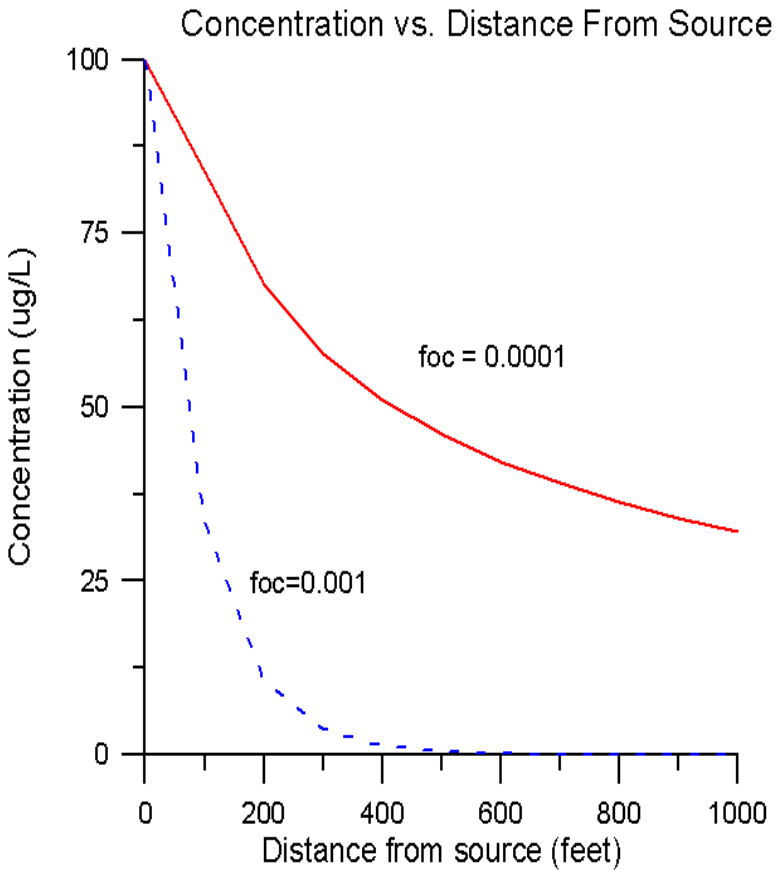


Figure3.8: Simulated contaminant concentrations.

### 3.2.9 Performance Monitoring Plan

Groundwater models are also used to predict the migration pathway and concentrations of contaminants in groundwater. Even though small in magnitude, the errors in predictive models gets accumulated and can result in gross errors in solutions projected forwarded with passage of time. Performance monitoring is required to compare future field conditions with model predictions.

Performance monitoring is required as a mean of physically measuring the actual behaviour of the hydro-geologic system and demonstrating compliance with

environmental status. Groundwater model simulations are estimates and may not be substituted in place of measurement of field data. Examples of applications of contaminant transport and groundwater modeling requiring performance monitoring would include, but not be limited to the following:

- Hydraulic containment systems for which certain geochemical and hydraulic head criteria, which measure the success of the remedial action, have been specified in a remedial action plan.
- Groundwater/surface-water interface (GSI) mixing zones for which the chemistry of the contaminant plume discharging to a surface-water body must meet appropriate criteria.
- Natural attenuation remedies in which a contaminant transport model predicts that site specific contaminants will reach regulatory limits prior to reaching a specified point.

The degree of performance monitoring required at a site depends on the conditions or actions which have been simulated and the associated level of risk to the down gradient receptors, if applicable. As an example, hydraulic containment of contaminant plumes by pump-and-treat systems would require extensive monitoring of hydraulic heads and possibly less frequent monitoring of groundwater quality. Hydraulic-head monitoring points should be at well distributed locations to demonstrate the desire hydraulic response. The groundwater chemistry Monitoring would be needed at locations down gradient of, or lateral to, the hydraulic containment system, with less frequent chemical monitoring at locations within the capture zone of the system. Sites at which contaminant biodegradation has been simulated would require extensive monitoring of appropriate chemical parameters and less frequent monitoring of hydraulic heads. Chemical monitoring would be required at a sufficient number of locations to evaluate the migration or mass removal of contaminants and obtain the groundwater quality at the designated points of compliance.

# CHAPTER 4

# GROUND WATER QUALITY MODELLING

A conceptual model is a hypothesis for how a system or process operates. This hypothesis can be expressed quantitatively as mathematical equations called mathematical model. Mathematical models are abstractions that process as equations, as the physical properties and geological features are known they are used as constants and details of state or potential in the system as variables. The word model has a lot of definitions and is used so regularly that it is sometimes difficult to derive the meaning of the word (Konikow and Bredehoeft 1992). Simplest way to define a model is as a representation of a real system or process taking place at the site. Groundwater models in use today are mostly deterministic mathematical models.

Deterministic groundwater models generally require the solution of partial differential equations. Principle of conservation of mass and energy is a universal law applied to all spatial objects. Deterministic mathematical models work on the principle of conservation of mass, momentum, and energy and explain cause and effect relations. The basic assumption undertaken is that given a high degree of understanding of the processes and knowledge of the parameters which effects the stresses on a system produce subsequent responses in that system, the response of the system to any set of stresses can be predetermined, even if the magnitude of the new stresses falls outside of the range of historically observed stresses. Exact solutions can often be obtained analytically, but for applying analytical models the degree of uncertainty in physical parameters and accuracy of data accumulated must be of higher degree of precision.

Heterogeneity of the medium or variation in the aquifer properties is characteristic of all geologic systems and has been found out to play important role in influencing groundwater flow and solute transport. Although homogeneous systems are absent in real world some deterministic models treat the properties of porous media as lumped parameters (essentially, as a black box), but this precludes the representation of heterogeneous hydraulic behavior in the model. It is better to apply distributed-parameter models because it gives proper representation to more realistic distributions of system properties thus giving more deterministic results. Numerical methods yield approximate solutions to the governing equation (or equations) through the discretisation of space and time. Within the discretised problem domain, the variable internal properties, boundaries, and stresses of the system are approximated. Deterministic, distributed-parameter, numerical models can relax the rigid idealised conditions of analytical models or lumped-parameter models, and they can therefore be more realistic and flexible for simulating field conditions.

The number and types of equations to be solved are determined by the concepts of the dominant governing processes. The coefficients of the equations are the parameters that are measures of the properties, boundaries, and stresses of the system; the dependent variables of the equations are the measures of the state of the system and are mathematically determined by the solution of the equations. When a numerical algorithm is implemented in a computer code to solve one or more partial differential equations, the resulting computer code can be considered a generic model. When the grid dimensions, boundary conditions, and other parameters (such as hydraulic conductivity and storativity), are specified in an application of a generic model to represent a particular geographical area, the resulting computer program is a site-specific model. The ability of generic models to solve the governing equations accurately is typically demonstrated by example applications to simplified problems.

## 4.1 GOVERNING EQUATIONS

Groundwater flow and transport processes are represented in mathematical equations are developed from the fundamental principle of quantum mechanics mainly conservation of mass of fluid or of solute. For a known representative volume of porous medium, a general equation for conservation of mass for the volume may be expressed as:

rate of mass accumulation = rate of mass inflow – rate of mass outflow + rate of mass production/consumption **.....(4.1)**

equation 4.1 which is the relation for Conservation of mass (or continuity equation) may be combined with a mathematical expression of the relevant process to obtain a differential equation describing flow or transport (Bear 1997; Domenico and Schwartz 1998; Freeze and Cherry 1979).

### 4.1.1 Groundwater Flow Equation

According to the Darcy's law the rate of flow of water through in a porous media like soil is directly co-related to the properties of the water, the properties of the porous media, and the gradient of the hydraulic head, , which can be summarised as:

$$q_i = - K_{ij} \frac{\partial h}{\partial x_j} \qquad \textbf{……(4.2)}$$

Where,

$q_i$ = specific discharge, $LT^{-1}$;

$K_{ij}$ = hydraulic conductivity of the porous medium (a second-order tensor), $LT^{-1}$;

h = hydraulic head, L.

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

$$\frac{\partial}{\partial x_i}\left[K_{ij}\frac{\partial h}{\partial x_j}\right] = S_s\frac{\partial h}{\partial t} + W^* \qquad \textbf{.....(4.3)}$$

Where,

SS = specific storage, $L^{-1}$;

t = time, T;

W = volumetric flux per unit volume, $T^{-1}$;

$x_i$ = Cartesian co-ordinates, L.

The summation convention of Cartesian tensor analysis is implied in Eqs.4.2 and 4.3. Eq.4.3 can generally be applied if isothermal conditions prevail, the porous medium only deforms vertically, the volume of individual grains remains constant during deformation, Darcy's law applies (and gradients of hydraulic head are the only driving force), and fluid properties (density and viscosity) are homogeneous and constant.

Aquifer properties can vary with space, and fluid stresses (W) can vary in space and time. If the aquifer is relatively thin as compared to its lateral dimensions, it may be appropriate to assume that groundwater flow is really two-dimensional. This allows the three-dimensional flow equation to be reduced to the case of two-dimensional areal flow, for which several additional simplifications are possible. The advantages of reducing the dimensionality of the equation include less stringent data requirements, smaller computer memory requirements, and shorter computer execution times to achieve numerical solutions. An expression similar to Eq.4.3

may be derived for the two-dimensional (for 2-D cases) areal flow of a homogeneous fluid in a confined aquifer and written as:

$$\frac{\partial}{\partial x_i}\left[ T_{ij} \frac{\partial h}{\partial x_i} \right] = S \frac{\partial h}{\partial x_j} + W \qquad \textbf{.....(4.4)}$$

Where,

$T_{ij}$ = transmissivity, $L^2T^{-1}$;

$T_{ij} = K_ij\ b$; b = saturated thickness of the aquifer, L;

S = storage coefficient (dimensionless); and

W = W*b is the volume flux per unit area, $LT^{-1}$.

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

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

### 4.1.2 Seepage Velocity

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

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

Where,

$V_i$ = seepage velocity, $LT^{-1}$;

$\varepsilon$ = effective porosity of the porous medium.

### 4.1.3 Solute-Transport Equation

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

Grove (1976) derived a generalized equation for solute transport, in which terms are incorporated to represent chemical reactions and solute concentration both in the pore fluid and on the solid surface, as:

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

where CHEM equals :

$\rho_b \frac{\partial C}{\partial t}$ (for linear equilibrium controlled sorption)

$\Sigma R_k$ (for S chemical rate controlled reactions)

$- \lambda (\varepsilon C + \rho_b C)$ (for decay)

where

$D_{ij}$ = coefficient of hydrodynamic dispersion, $L2T^{-1}$,

C' = concentration of the solute in the source or sink fluid, C is the concentration of the species adsorbed on the solid (mass of solute/mass of solid), is the bulk density of the sediment, $ML^{-3}$,

$R_k$ = rate of production of the solute in reaction k, $ML^{-3}T^{-1}$,

$\lambda$ = decay constant (equal to $\ln 2/T^{1/2}$), $T^{-1}$

Eq.4.6 represents the change in concentration due to hydrodynamic dispersion. This expression is analogous to Fick's Law describing diffusive flux. This Fickian model assumes that the driving force is the concentration gradient and that the dispersive flux occurs in a direction from higher concentrations towards lower concentrations. But, this assumption is not always consistent with field observations and is the subject of much ongoing research and field study.

The second term represents advective transport and describes the movement of solutes at the average seepage velocity of the flowing groundwater. The third term

represents the effects of mixing with a source fluid that has a different concentration than the groundwater at the location of the recharge or injection. The fourth term lumps all of the chemical, geochemical, and biological reactions that cause transfer of mass between the liquid and solid phases or conversion of dissolved chemical species from one form to another.

The chemical attenuation of inorganic chemicals can occur by sorption/desorption, precipitation/dissolution, or oxidation/reduction; organic chemical can adsorb or degrade by microbiological processes. If reactions are limited to equilibrium-controlled sorption or exchange and first-order irreversible rate (decay) reactions, then the general governing equation (Eq.4.6) can be written as:

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

Eq.4.7 can be represented in terms of the solute concentration in using the chain rule of calculus due to the temporal change in sorbed concentration, are:

$$\frac{\partial \overline{C}}{\partial t} = \frac{\partial \overline{C}}{\partial C}\frac{\partial C}{\partial t} \qquad \textbf{.....(4.8)}$$

Equilibrium relation for $\overline{C}$ and $d\overline{C}/dC$ can be substituted into the governing equation to develop a partial differential equation in terms of C only, as for equilibrium sorption and exchange reactions $d\overline{C}/dC$, as well as $\overline{C}$ is a function of C alone. The resulting single transport equation is solved for solute concentration.

Using the equilibrium relation sorbed concentration can then be calculated. The linear-sorption reaction considers that the concentration of solute sorbed to the porous medium is directly proportional to the concentration of the solute in the pore fluid, according to the relation,

$$\overline{C} = K_d C \qquad \textbf{.....(4.9)}$$

Where,

$K_d$ = distribution coefficient, $L^3M^{-1}$.

The curve between sorbed concentration to dissolved concentration is known as an isotherm. This reaction is assumed to be instantaneous and reversible. If that relation is linear, the slope (derivative) of the isotherm, $d\overline{C}/dC$, is known as the equilibrium distribution coefficient, $K_d$. Therefore, for linear isotherm,

$$\frac{\partial \overline{C}}{\partial t} = \frac{\partial \overline{C}}{\partial C}\frac{\partial C}{\partial t} = K_d \frac{\partial C}{\partial t} \qquad \textbf{.....( 4.10)}$$

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

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

**.....(4.11)**

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

$$R_f = 1 + \frac{\rho_b K_d}{\varepsilon} \qquad \textbf{.....(4.12)}$$

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

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

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

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

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

Where,

$\alpha_{ijmn}$ = dispersivity of the porous medium, L;

$V_m$ and $V_n$ = components of the flow velocity of the fluid in the m and n directions, respectively, $LT^{-1}$;

$D_m$ = effective coefficient of molecular diffusion, $L^2T^{-1}$;

$|V|$ = magnitude of the velocity vector, $LT^{-1}$, defined as $V= \sqrt{V_x^2 + V_y^2 + V_z^2}$

Two constants define the dispersivity of an isotropic porous medium. These are the longitudinal dispersivity of the medium, αL, and the transverse dispersivity of the medium, αT . These are related to the longitudinal and transverse dispersion coefficients by DL = αL|V| and DT = αT|V|. Most applications of transport models to groundwater problems that have been documented to date have been based on this conventional formulation.

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

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

## 4.2 Solution of Equations

Groundwater flow and transport can be solved by partial differential equations describing mathematically using either analytical solutions or numerical solutions. The advantages of an analytical solution, when it is possible to apply one, are that it usually provides an exact solution to the governing equation and is often relatively simple and efficient to obtain. Many analytical solutions have been developed for the flow equation; but its applications are limited to well hydraulics problems involving radial symmetry (Walton 1962; Lohman 1972; Reed 1980). For soving the solute-transport equation, analytical solutions are also available (Bear 1979; Javandel et al. 1984; Van Genuchten and Alves 1982; Wexler 1992). In general, obtaining the exact analytical solution to the partial differential equation requires that the properties and boundaries of the flow system be highly and perhaps unrealistically idealised.

Due to the errors in the mathematical modelling by simplifying assumptions of complex fields environment in most of the problems, the mathematical benefits of obtaining an exact analytical solution are probably outweighed that are required to apply the analytical model. For problems where the simplified analytical models are inadequate, the partial differential equations can be approximated numerically. For this, the continuous variables are replaced with discrete variables that are defined at grid blocks (or nodes). Thus, the continuous differential equation, which defines hydraulic head or solute concentration everywhere in the system, is replaced by a finite number of algebraic equations that defines the hydraulic head or concentration at specific points. This system of algebraic equations generally is solved using matrix techniques approaching a numerical model.

The equations describing groundwater flow and solute transport are second-order differential equations, which can be classified on the basis of their mathematical properties. There are basically three types of second-order differential equations,

which are parabolic, elliptic, and hyperbolic (Peaceman 1977). Such equations can be classified and distinguished based on the nature and magnitude of the coefficients of the equation. This is important because the numerical methods for the solution of each type have should be considered and developed separately for optimal accuracy and efficiency in the solution algorithm.

For solving the groundwater flow equation there are two major classes of numerical methods have come to be well accepted. These are the finite-difference methods and the finite-element methods. Both of these major classes of numerical methods include a variety of subclasses and implementation alternatives. Most of these numerical approaches require that the area of interest be subdivided by a grid into a number of smaller subareas (cells or elements) that are associated with node points (either at the centres of peripheries of the subareas).

In the partial differential equations as difference quotients finite-difference methods approximate the first derivatives (the differences between values of variables at adjacent nodes, both in space and time, with respect to the interval between those adjacent nodes). Finite-element methods use assumed functions of the dependent variables and parameters to evaluate equivalent integral formulations of the partial differential equations. Huyakorn and Pinder (1983) present a comprehensive analysis and review of the application of finite-element methods to groundwater problems (Huyakorn and Pinder 1983). In all of the two numerical approaches, the dis-cretisation of the space and time dimensions allows the continuous boundary-value problem for the solution of the partial differential equation to be reduced to the simultaneous solution of a set of algebraic equations. These equations can then be solved using either iterative or direct matrix methods. Both the numerical approaches have advantages and disadvantages, but there are very few groundwater problems for which either is clearly superior.

The finite-difference methods are simpler conceptually and mathematically, and are easier to program for a computer. The finite-difference methods are typically keyed

to a relatively simple, rectangular grid, which also eases data entry tasks. Finite-element methods generally require the use of more sophisticated mathematics but, for some problems, may be more accurate numerically than standard finite-difference methods. A major advantage of the finite-element methods is the flexibility of the finite-element grid, which allows a close spatial approximation of irregular boundaries of the aquifer and of parameter zones within the aquifer. An input data set is much more difficult for an irregular finite-element grid than for a regular rectangular finite-difference grid for the construction and specification. Therefore, the use of a model preprocessor, which includes a mesh generator and a scheme to efficiently number the nodes and elements of the mesh and to specify the spatial co-ordinates of each node, is better to effectively utilise the advantageous features of a finite-element model. Fig.4.1 illustrates a hypothetical aquifer system, which has impermeable boundaries and a well field of interest (Fig.4.1a), which has been discretised using finite-difference (Fig.4.1b) and finite-element (Fig.4.1c) grids. Figs.4.1b and 4.1c illustrate conceptually how their respective grids can be adjusted to use finer mesh spacing in selected areas of interest. The rectangular finite-difference grid approximates the aquifer boundaries in a sequence, resulting in some nodes or cells outside of the aquifer, whereas sides of the triangular elements of the finite-element grid can closely follow the outer boundary using a minimal number of overall nodes.

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

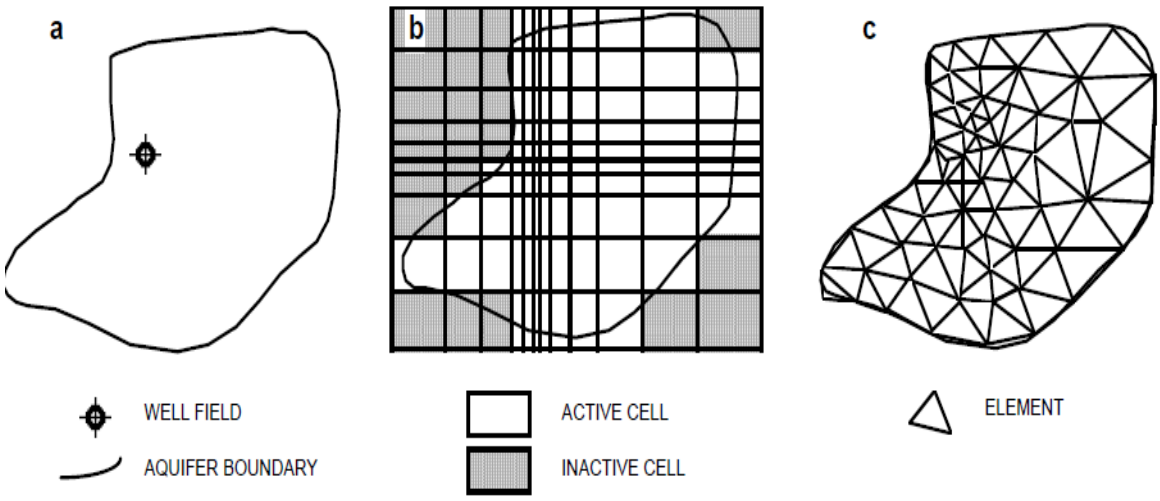


Figure4.1: Hypothetical application of finite-difference and finite-element grids to an irregularly bounded aquifer

For parabolic partial differential equations numerical methods are best to solve but these methods are not best for solving hyperbolic equations, and vice versa. Thus, no one numerical method or simulation model will be ideal for the entire spectrum of groundwater transport problems likely to be encountered in the field. Further compounding this difficulty is the fact that in the field, the seepage velocity of groundwater is highly variable, even if aquifer properties are relatively homogeneous (because of the effects of complex boundary conditions). Therefore, in low permeability zones or stagnation points, the velocity will be close to zero and the transport processes will be dominated by dispersion processes; in high permeability zones or stress points, the velocity may be several meters per day and the transport processes will be advection dominated. In other words, for the same system, the governing equation may be more hyperbolic in one area (or at one time) and more parabolic in nature in another area (or at another time).

Therefore, no matter which numerical method is chosen as the basis for a simulation model, it will not be ideal or optimal over the entire domain of the problem, and

significant numerical errors may be introduced somewhere in the solution. The transport modelling effort must recognise this inherent difficulty and strive to minimise and control the numerical errors. But finite-difference and finite-element models are commonly applied to transport problems, other types of numerical methods have also been applied to transport problems, including method of characteristics, particle tracking, random walk, Eulerian-Lagrangian methods, and adaptive grid methods. All of these have the ability to track sharp fronts accurately with a minimum of numerical dispersion. Documented models based on variants of these approaches include Konikow and Bredehoeft (1978), Sanford and Konikow (1985), Prickett et al. (1981), and Zheng (1990).

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

Most mechanical dispersion actually arises from variations in velocity about the mean, so at least partly is an advective-based process as conventional solute-transport equation is a Fickian model. Transport in stratified porous media may be non-Fickian in nature (Gelhar et al. 1979; Matheron and De Marsily 1980). Thus,

no matter how accurately we can solve the governing solute-transport equation, that equation itself is not necessarily a definitive and sufficient description of the processes controlling solute transport at the scale of most field problems. In general, the more accurately a model can represent or simulate the true velocity distribution, the less of a problem will be the uncertainty concerning representation of dispersion processes.

The reaction terms included in Eq.4.6 are mathematically simple ones, but it does not necessarily represent the true complexities of many reactions. Also, particularly difficult numerical problems arise when reaction terms are highly non-linear, or if the concentration of the solute of interest is strongly dependent on the concentration of other chemical constituents. In reality, isotherms may not be linear and may not be equilibrium controlled. Rubin (1983) discusses and classifies the chemical nature of reactions and their relation to the mathematical problem formulation. Bahr and Rubin (1987) compare kinetic and local equilibrium formulations for solute transport affected by surface reactions. For field problems in which reactions are significantly affecting solute concentrations, simulation accuracy is less limited by mathematical constraints than by data constraints. That is, the types and rates of reactions for the specific solutes and minerals in the particular groundwater system of interest are rarely known and require an extensive amount of data to assess accurately. Yeh and Tripathi (1989) review hydrogeochemical transport models and discuss various mathematical approaches to modelling transport of multiple reacting species.

### 4.2.1 FINITE-DIFFERENCE METHODS

The partial differential equations describing the flow and transport processes in groundwater include terms representing derivatives of continuous variables. Finite-difference methods are based on the approximation of these derivatives (or slopes of curves) by discrete linear changes over small discrete intervals of space or time. If

the intervals are sufficiently small, then all of the linear increments will represent a good approximation of the true curvilinear surface.

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

$$\left[\frac{\partial h}{\partial x}_{d}\right] = \frac{h_o - h_1}{\Delta x} \qquad \textbf{.....(4. 15)}$$

Note that the observation wells are spaced an equal distance apart. Similarly, a reasonable approximation for the second derivative, ð2h/ðx2 , at point 0 (the location of the centre well) can be given as:

$$\left[\frac{\partial^2 h}{\partial x^2}\right] = \frac{\left[\frac{\partial h}{\partial x}_{e}\right] - \left[\frac{\partial h}{\partial x}_{d}\right]}{\Delta x} = \frac{\frac{h_2 - h_0}{\Delta x} - \frac{h_o - h_1}{\Delta x}}{\Delta x} = \frac{h_1 + h_2 - 2h_o}{(\Delta x)^2}$$

**.....(4. 16)**

If we also consider wells 3 and 4 shown in Fig.4.2b, located on a line parallel to the y-axis, we can similarly approximate $\partial 2h/\partial y2$ at point 0 (the same point 0 as in Fig.4.2a) as (Bennett 1976):

$$\frac{\partial^2 h}{\partial x^2} = \frac{h_3 + h_4 - 2h_o}{(\Delta y)^2}$$

**.....(4. 17)**

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

$$\frac{\partial^2 h}{\partial x^2} + \frac{\partial^2 h}{\partial y^2} = \frac{h_1 + h_2 + h_3 + h_4 - 4h_o}{a^2} \qquad \textbf{.....(4. 18)}$$

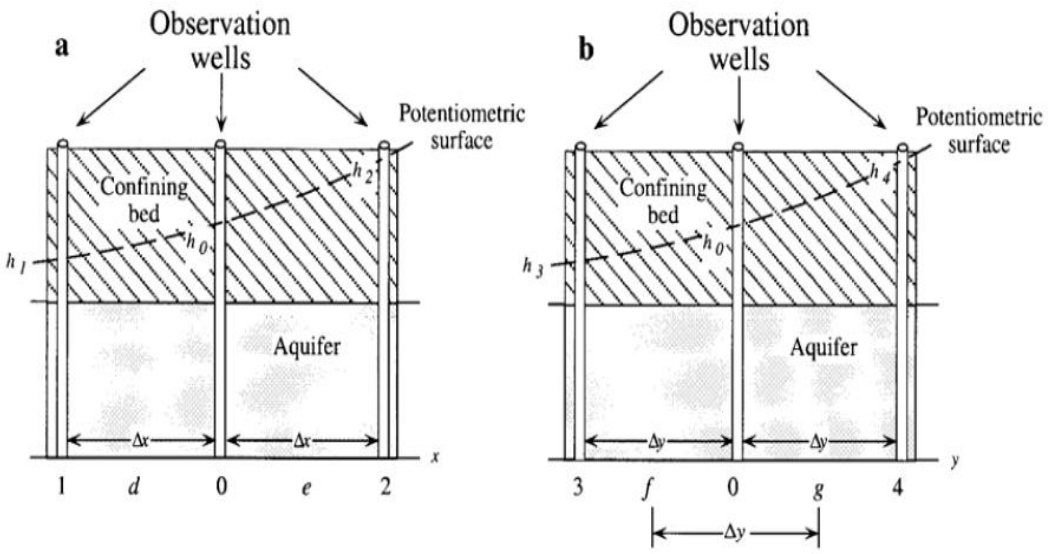


Figure4.2: Cross section through confined aquifer

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

We must also consider the discretisation of time, which may be viewed as another dimension, and hence represented by another index. If we consider a representative segment of a hydrograph (see Fig.4.3), in which head is plotted against time for a transient flow system, n is the index or subscript used to denote the time at which a given head value is observed. The slope of the hydrograph at any point is the

derivative of head with respect to time, and it can be approximated as $\partial h/\partial t \approx \Delta h/\Delta t$. In terms of the heads calculated at specific time increments (or time nodes), the slope of the hydrograph at time n can be approximated by:

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

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

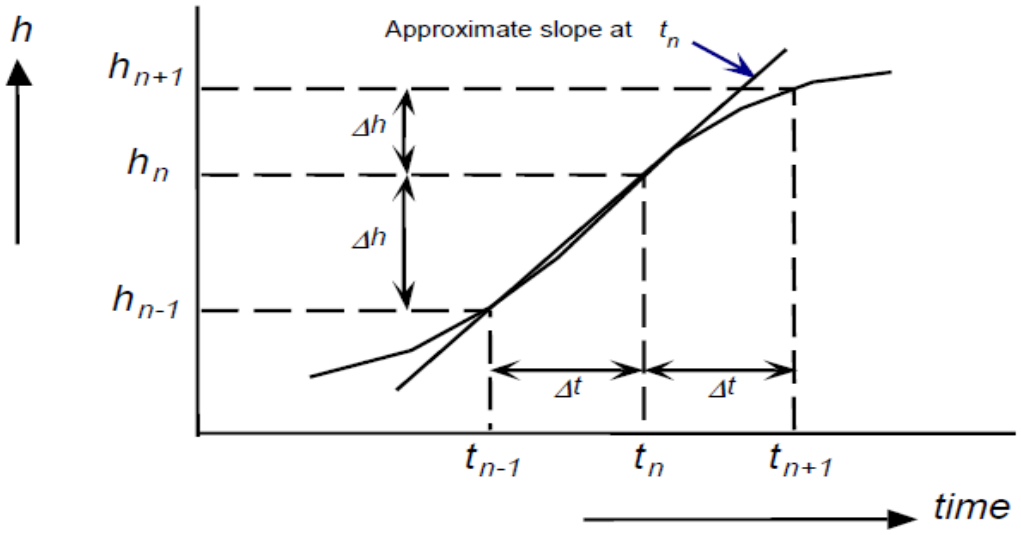


Figure4.3: Part of a hydrograph showing that the derivative (or slope, $\partial h/\partial t$) at time node $t_n$ may be approximated by $\Delta h/\Delta t$ (Konikow 1996).

We are calculating the derivative at $t = n\Delta t$ in Eq.4.19 by taking a "forward difference" from time n to time n+1, and by taking a "backward difference" in Eq.4.20. In terms of solving the groundwater flow equation for a node (i,j) of a finite-difference grid, we have to consider heads at five nodes and at two time

levels, as illustrated in Fig.4.4. In Fig.4.4a, we have expressed the spatial derivatives of head at time level n, where all values are known, and the time derivative as a forward difference to the unknown head at time step n+1. Then for every node of the grid we will have a separate difference equation, each of which contains only one unknown variable. Thus, these equations can be solved explicitly. Explicit finite-difference equations are thus simple and straightforward to solve, but they may have stability criteria associated with them. That is, if time increments are too large, small numerical errors or perturbations may propagate into larger errors at later stages of the computations.

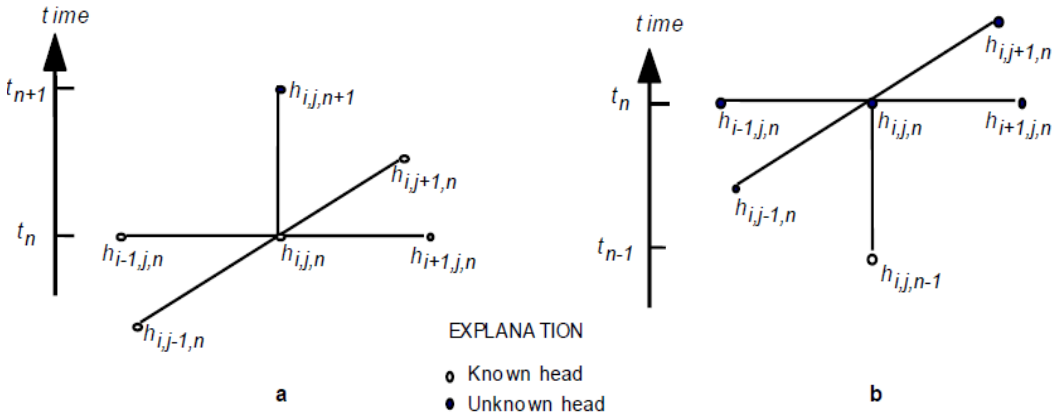


Figure4.4: Grid stencil showing discretisation of time at node (i,j) in two-dimensional finite-difference grid: (a) explicit (forward-difference) formulation and (b) implicit (backward-difference) formulation (Konikow 1996).

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

advantage of generally being unconditionally stable. Most available groundwater flow models solve an implicit finite-difference approximation to the flow equation.
We may next consider a two-dimensional groundwater flow equation for a heterogeneous, anisotropic aquifer, in which the co-ordinate system is aligned with the major axes of the transmissivity tensor. This may be approximated by the following finite-difference equation for representative node (i,j) as:

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

**.....(4. 21)**

Where,

$q_{i,j}$ = volumetric rate of withdrawal or recharge at the i,j node, $L^3T^{-1}$.

This formulation inherently assumes that any stresses, such as represented by $q_{i,j}$, are applied over the entire surface area of cell i,j rather than at a point (or at node i,j). This implies that if a pumping well is represented at node i,j, then the head will be calculated as if it were being withdrawn from a well that had a borehole surface area equal to $\Delta x \Delta y$ rather than its actual value. In Eq.21 the transmissivity terms represent the harmonic means of the transmissivity of the two adjacent cells. The harmonic mean can be shown to be appropriate and consistent with the assumption that transmissivity is constant and uniform within each cell but may be different between cells. Other types of means for interblock transmissivity may be more appropriate for other assumptions about the transmissivity distribution, such as smoothly varying transmissivity (Goode and Appel 1992).

### 4.2.2 FINITE-ELEMENT METHODS

Finite-element method (FEM) is used for obtaining approximate solutions to a wide variety of problems in physics and engineering, which is a numerical analysis technique. The method was originally applied to structural mechanics but is now used in all fields of fluid and continuum mechanics. The four different approaches to formulate the finite-element method for a problem as given by Huebner (1975) are: the direct approach, the variational approach, the weighted residual approach, and the energy balance approach. The weighted residual or variational approach are the two methods which are used to solve the problems related to the groundwater most frequently.

The finite-element method (FEM) uses a concept of "piecewise approximation". In which the aquifer which is to be modeled is divided into a set of elements or pieces. Theoretically, the elements can be of different shapes and sizes. One shape elements, most commonly either triangular or quadrilateral elements are used by most FEM computer programs. In the groundwater model MODFE (Torak 1993; Cooley 1992) triangular elements are used, whereas in the groundwater model SUTRA (Voss 1984) quadrilateral elements are used. Point values of the dependent variable (for example, head, pressure, or concentration) are calculated at nodes, these nodes are the corners or vertices of the elements, and the value of the dependent variable is described by a simple equation within the element. This simple equation is called a basis function and each node that is part of an element has an associated basis function.

Linear equations are the simplest basis functions that are usually used. The solution to the differential equation for flow (Eq.4.3) or transport (Eq.4.6) is approximated by a set of elements in which the dependent variable only varies linearly within the element, but the entire set of elements approximates the complex distribution of head or concentration. Huyakorn and Pinder (1983), Huebner (1975), Zienkiewicz

(1971), Wang and Anderson (1982), and Cooley (1992) provide more comprehensive explanations of the method.

### 4.2.3 MATRIX SOLUTION TECHNIQUES

As shown above, both the methods the finite-difference and finite-element approximations tend to an algebraic equation for each node point. Direct or iterative methods are the two basic methods which may be adopted to numerically solve the set of algebraic equations. In direct methods, a sequence of algebraic operations is used only once to solve the matrix equation, which leads to a solution which is exact but for machine round-off error. While iterative methods arrive at a solution by method of interpolation and a process of successive approximation. They are done by initial assumptions at the solution, and then improving these assumptions by some iterative process until an error criterion is satisfied to required exactness. Therefore, in these techniques, convergence and the rate of convergence are of concern.

Direct methods can be further subdivided into:

1. solution by determinants,
2. solution by successive elimination of the unknowns, and
3. solution by matrix inversion.

These direct methods have two main drawbacks. The first disadvantage is one of computer data input requirements, including large storage (memory) requirements and prolonged computation times for bigger problems. The matrix method have two advantages, it is sparse (contains many zero values) and several techniques have been proposed to minimise computational effort,. However, for finite-difference and finite-element methods, even for three-dimensional problems storage requirements may still prove to be unavoidably large. For the second problem with direct methods due to many arithmetic operations are involved, round-off errors can accumulate for certain types of matrices.

Iterative approach reduces the need for storing large matrices, which make them attractive to solve problems with large no of unknowns. A lot of schemes have been developed; a few of the more commonly used schemes include iterative alternating-direction implicit procedure, successive over-relaxation methods, and the strongly implicit procedure.

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

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

### 4.2.4 BOUNDARY AND INITIAL CONDITIONS

Additional information about the physical state of the process is required to obtain a unique solution of a partial differential equation corresponding to a given physical process. This additional data is supplied by boundary and initial conditions. For

steady-state problems, only boundary conditions are required, whereas for transient problems, boundary and initial conditions must be specified.

The boundary conditions are combination of the geometry of the boundary and the values of the dependent variable or its derivative normal to the boundary. In physical terms, the boundary conditions are usually of three types, for groundwater models:

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

There is a third type of boundary condition, which might be used, for example, to represent leakage or exchange between a stream and an adjacent aquifer, where the leakage may change over time with the change in the head in the aquifer changes, even though the head in the stream might remain fixed. A no-flow boundary is a special case of the second type of boundary condition. The types of boundaries appropriate to a particular field problem require careful consideration.

The value of the dependent variable given at every point inside the boundary at the start of the simulation is called initial condition. Often, the initial conditions are specified to be a steady-state solution. However, initial conditions are specified so that transient flow is occurring in the system at the start of the simulation, it should be recognised that heads will change during the simulation, not only in response to the new pumping stress, but also due to the initial conditions (Franke et al. 1987).

# CHAPTER 5

# DEVELOPMENT OF MODEL FOR NITRATE CONTAMINATION

## 5.1 CONCEPTUAL MODEL FOR UNSATURATED WATERFLOW CONDITION

There are two assumptions taken for the development of the model for unsaturated flow conditions. Each and every layer of the soil medium is homogeneous and isotropic porous. The soil water flow can be simplified two dimensional plane (Fig5.1) according to the axisymmetric characteristics of water infiltration under water storage pit irrigation condition. The unsaturated water flow for water storage pit irrigation is described by the two-dimensional cylindrical coordinate form of the Richards' equation:

$$\frac{\partial \theta}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left[rK(h)\frac{\partial h}{\partial r}\right] + \frac{\partial}{\partial z}\left[K(h)\frac{\partial h}{\partial z}\right] - \frac{\partial K(h)}{\partial z} \qquad \textbf{.....(5.1)}$$

Where,

$\theta$ = volumetric water content ($cm^3/cm^3$)

h = soil water pressure (cm)

k = soil unsaturated hydraulic conductivity (cm/min)

z = depth taken, positive downwards (cm)

r = horizon, positive rightwards (cm)

t = time (min)

To solve Eq.(5.1), the unsaturated soil hydraulic properties should first be determined accurately. These properties include the soil water retention curve, h,

and the unsaturated hydraulic conductivity, K. these can be described by Van Genuchten equations, as follows

$$\theta (h) = \theta_r + (\theta_s - \theta_r) [1+ |\alpha h|^n ]^{-m} \quad \textbf{.....(5.2)}$$

$$K (h) = K_s S^l_e [ 1 – (1 – S_e^{1/m})^m ]^2 \quad \textbf{.....(5.3)}$$

$$Se = (\theta - \theta_r) / (\theta_s - \theta_r) \quad \textbf{.....(5.4)}$$

Where,

$\theta_r$ = residual water content ($cm^3/cm^3$)

$\theta_s$ = saturated water content ($cm^3/cm^3$)

$k_s$ = saturated hydraulic conductivity (cm/min)

$s_e$ = effective water content

$\alpha$ = inverse of the air entry value

n = pore size distribution index

m = 1-1/n (n>1)

The pore connectivity parameter l was estimated to be 0.5 as an average for many soils in hydraulic conductivity conditions.

We will use this model for further studies and calculations.

## 5.2 NITROGEN TRANSPORT AND TRANSFORMATION IN SOIL

The first order decay chain of urea is describes as follows:

$$CO(NH_2)_2 \longrightarrow NH^+_4 \longrightarrow NO^-_3 \begin{cases} \nearrow N_2 \\ \searrow N_2O \end{cases} \quad \textbf{.....(5.5)}$$

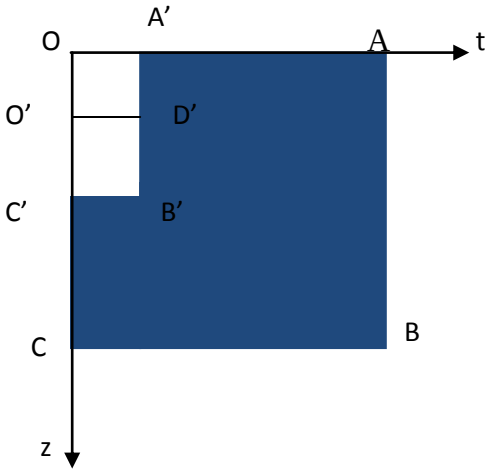


Figure 5.1: Profile of water storage pits irrigation

The transport of soil nitrogen in the unsaturated soil is commonly described by the general convection-dispersion equation.

$$\frac{\partial \theta c_1}{\partial t} = \frac{\partial}{\partial r_i}\left[\theta D_{ij,1}\frac{\partial c_1}{\partial r_j}\right] + \frac{1}{r}\left[\theta D_{rj,1}\frac{\partial c_1}{\partial r_j}\right] - \frac{\partial q_i c_1}{\partial r_i} - \frac{q_r c_1}{r} - u_{w,1}\theta c_1$$

**.....(5.6)**

$$\frac{\partial \theta c_k}{\partial t} + \frac{\partial p_d s_k}{\partial t} = \frac{\partial}{\partial r_j}\left[\theta D_{ij,k}\frac{\partial c_k}{\partial r_j}\right] + \frac{1}{r}\left[\theta D_{rj,k}\frac{\partial c_k}{\partial r_j}\right] - \frac{\partial q_i c_k}{\partial r_i} - \frac{q_r c_k}{r} - u_{w,1}\theta c_k$$

$$-u_{s,k}pc_k + u_{w,k-1}\theta c_{k-1} + u_{s,k-1}pc_{k-1} \qquad \textbf{.....(5.7)}$$

Where,

$c_k$ = concentration of substance k in liquid phase ($mg/cm^3$)

$s_k$ = concentration of substance k in solid phase (mg/g)

$\rho_d$ = dry bulk density ($g/cm^3$)

$D_{ij}$ = the dispersion coefficient tensor for the liquid phase ($cm^2/min$)

k = k-th substance

$\mu_w$ = first-order rate constants for solutes in the liquid phase (1/min)

$\mu_s$ = first-order rate constants for solutes in the solid phase (1/min)

$q_i$ = i-th component of Darcian water flux (cm/min)

$r_i$ = spatial coordinates

Eq. no 5.6 represents the first urea species, while Eq. no 5.7 represents ammonium and nitrate. The point which should be noted is that the first-order decay coefficient μ acts as sink in Eq. 5.6 and as a source in Eq. 5.7.

The adsorption isotherm relating $s_k$ and $c_k$ is described by a linear equation of the form:

$$s_k = k_{d,k} c_k \qquad \textbf{.....(5.8)}$$

Where,

$K_{d,k}$ = distribution co-efficient of species k

The component of dispersion tensor, $D_{ij}$ in liquid phase is given by

$$\theta D_{ij} = D_T q \delta_{ij} + (D_L - D_T) q_i q_j / q + \theta D_w \tau_w \delta_{ij} \qquad \textbf{.....(5.9)}$$

Where,

$D_w$ = molecular diffusion co-efficient in free water ($cm^2$/min)

$\tau_w$ = tortousity factor in liquid phase (-)

q = absolute value of darcian fluid flux density (cm/min)

$\delta_{ij}$ = kronecker delta function

$D_L$ = longitudinal dispersivity (cm)

$D_T$ = transverse dispersivity (cm)

The tortousity factor is evaluated in model as a function of the water contents using the relationship:

$$\tau_w = \theta^{7/3}/\theta_s^{\,2} \qquad \textbf{.....(5.10)}$$

## 5.3 INITIAL CONDITIONS AND BOUNDARY CONDITIONS

**1) The initial conditions** are given by:

$h(r,z,t) = h_0$ and $c_k(r,z,t) = c_{k0}$ at $t = 0$ **.....(5.11)**

Where,

$h_0$ = initial pressure head (cm)

$c_{k0}$ = initial concentration of substance k ($mg/cm^3$)

**2) Boundary conditions**

**a) At the soil surface (OA):** the evaporation and the precipitation are not considered, a zero flux is assumed (second type)

$$-K(h)\frac{\partial h}{\partial z} + K(h) = 0 \qquad -\theta D_{zz}\frac{\partial c}{\partial z} + q_z c = 0 \qquad t>0$$

**.....(5.12)**

**b) At the right margin (AB) and the lower boundary (CB)**

At the right margin (AB):

$h(r_{max},z,t) = h_o$ $\qquad$ $c_k(r_{max},z,t) = c_{ko}$ **.....(5.13)**

At lower boundary (CB):

$h(r,z_{max},t) = h_o$ $\qquad$ $c_k(r,z_{max},t) = c_{ko}$ **.....(5.14)**

**c) At the boundary (C'C) and the side (A'D'):** considering the symmetry of water and solute movement, second type is used

$$-K(h)\frac{\partial h}{\partial r} = 0 \qquad -\theta D_{rr}\frac{\partial c}{\partial z} + q_r c = 0$$

**.....(5.15)**

**d) At the infiltration side (D'B'):** a urea-nitrogen and water boundary condition (third type) are used, nitrate-nitrogen boundary condition (second type) is used:

$h(r_o,z,t) = h_i$ $\quad c_1(r_o,z,t) = c_{1i}$ $\quad -\theta D_{rr} \frac{\partial c_k}{\partial z} + q_r c_k = 0$ **.....(5.16)**

$r_0$ = radius of water storage pit (cm)

$h_i$ = i-th pressure potential of the infiltration side (cm)

$c_{1i}$ = urea-nitrogen concentration ($mg/cm^3$)

e) The bottom boundary condition (C'B'): a zero flux is assumed:

$-K(h) \frac{\partial h}{\partial z} + K(h) = 0$ $\quad -\theta D_{rr} \frac{\partial c}{\partial z} + q_z c = 0$ **.....(5.17)**

## 5.4 MODEL PARAMETERS

**A) Soil hydrodymanic parameters**

The soil saturated hydraulic conductivity and the soil water characteristic curve were determined by using a constant-head permeameter and a centrifuge, respectively. All the experimental data were fitted by the RETC, namely, $\theta_r$, $\theta_s$, $k_s$, $\alpha$ and n were 0.022 $cm^3/cm^3$, 0.468 $cm^3/cm^3$, 0.007422 cm/min, 0.00687 and 1.424, respectively (Jingling Li, 2011).

**B) N-transformation Parameters**

Urea, ammonium and nitrate were considered for the nitrogen species simulations. In the mathematical model, the N-transformation processes include urea hydrolysis, mineralization, nitrification and denitrification. The parameters of nitrification, denitrification and absorption coefficient (2.18 $g/cm^3$) were determined by indoor laboratory, volatilization of ammonium and subsequent ammonium transport by gaseous diffusion was neglected, these N-transformation parameters were 0.00038 [8] 1/min, 0.0000014 [9] 1/min, 0.000042 1/min, 0.0000039 1/min, respectively (Jingling Li, 2011).

## 5.5 NUMERICAL SOLUTION

The finite difference method is used to obtain a solution of the (5.1), (5.6) and (5.7) subject to the imposed initial and boundary conditions. the calculation region is divided into a series of rectangular grid subregions (Fig 5.2), the node is located in the center of subregion which is the control volume, where W, E, N, S and P is the node of calculation region , w-e-n-s is the control volume, w, e, n and s is located in intermediate point of W-P,P-E,N-P and P-S, respectively, the shadow region is the control volume of P node. Applying the basic idea of the finite difference method, the discrete equation was deduced by control volume integral method, and realized by numerical method.

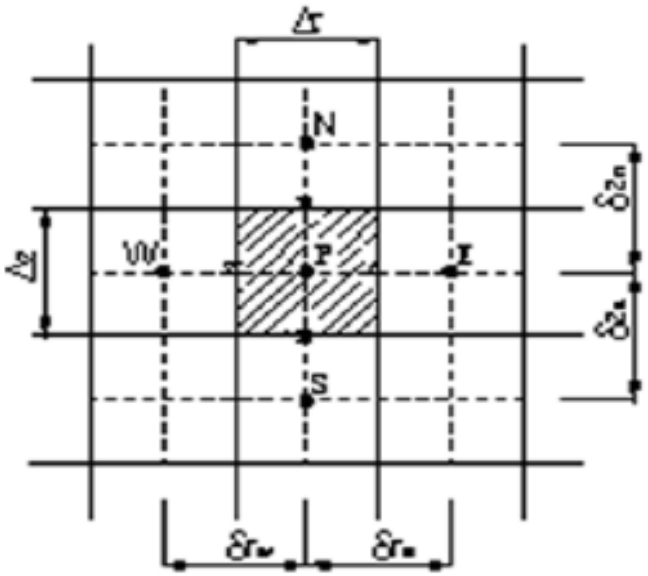


Figure 5.2: Profile of two- dimensional grid system

## 5.6 SOLUTION OF THE MODEL

The finite difference method of mathematical modeling has been used for the solution of convective dispersion equation of transport of nitrogen in the soil sample

subjected to initial and boundary conditions. The soil data has been taken as per Jingling, 2011. The physiochemical properties of sample are detailed as follows:

Table 5.1: Physiochemical properties of sample

| S.No. | Parameters | Values |
|---|---|---|
| 1 | Initial water content | 0.024 $cm^3/ cm^3$ |
| 2 | Saturated water content | 0.486 $cm^3/ cm^3$ |
| 3 | Field Capacity | 0.27 $cm^3/ cm^3$ |

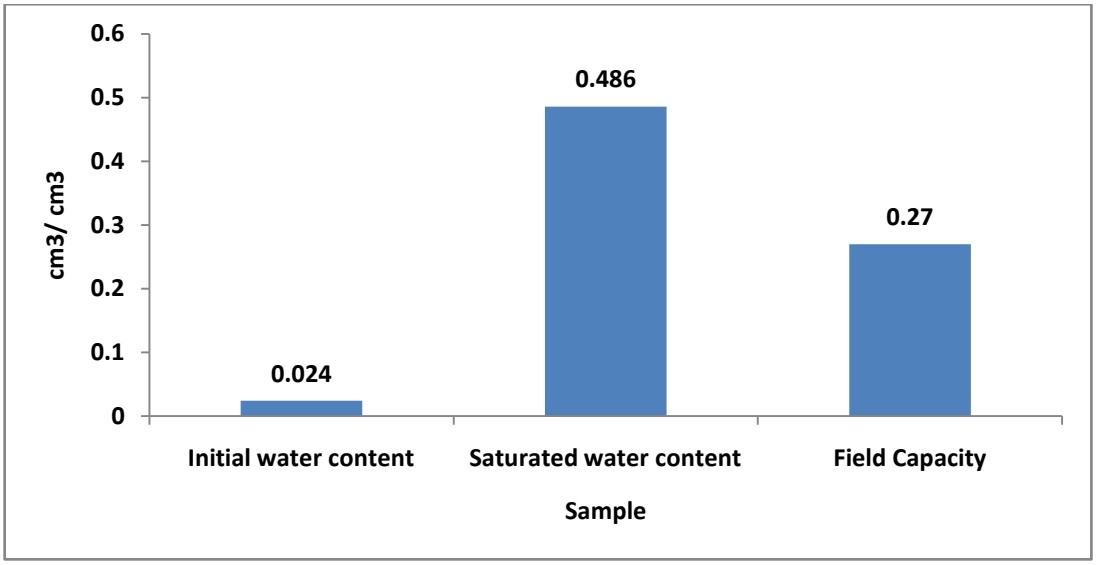


Figure 5.3: Physiochemical properties of sample

Test performed were setup consisted of a $30^0$ wedge shaped plexiglass containers, 120 cm high and with a 100 cm radius, the water storage pit was located at the corner of the soil container, the bottom of the water storage pit is impermeable by water. The completely mixed air –dry soil was passed through a 2 mm sieve and picked in the container with 5 cm increments to obtain a constant bulk density of 1.4 $g/cm^3$. The nutrient solution was added to the soil through a Mariotte tube with a flexible hose. The irrigation amount was 6L and the urea nitrogen concentration is 700 mg/L.

Table 5.2: Particle Size Analysis

| S.No. | Soil sample | Percentage |
|---|---|---|
| 1 | Sand | 21 % |
| 2 | Silt | 70 % |
| 3 | Clay | 9 % |

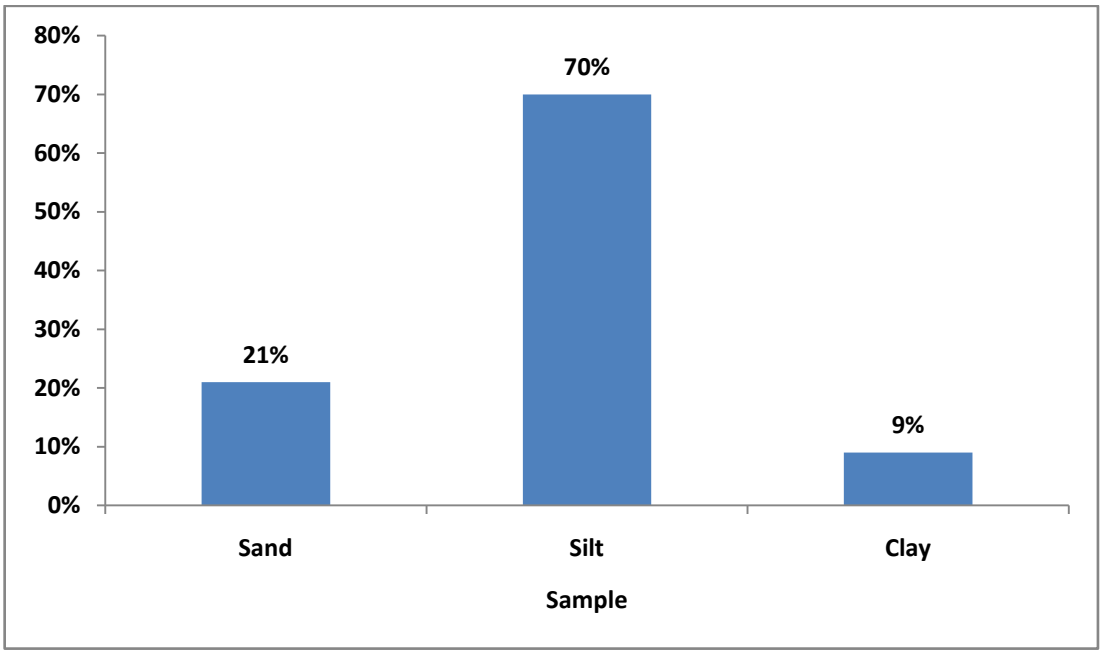


Figure 5.4: Particle Size Analysis

Table 5.3: Sample Content Analysis

| S.No. | Parameters | Values |
|---|---|---|
| 1 | Organic Content | 1.1 % |
| 2 | Total Nitrogen | 0.068 % |
| 3 | Total Phosphorus | 0.08% |
| 4 | Total Potassium | 2.14 % |
| 5 | Alkanied Nitrogen | 148.9 mg/kg |
| 6 | Nitrate | 58.8 mg/kg |
| 7 | Ammonia | 4.8 mg/kg |

## 5.7 RESULT AND ANALYSIS

### 5.7.1 Water content

At different radial direction, the simulated and measured values of water content during the simulation period are varied greatly for the water storage pit irrigation. The average error between all the measured and simulated values was -6.4% ~5.7% and have good relation between the simulated and measured water content. Results show that water content increased gradually with the increase of distance from the storage pit. But there was little water content on the soil surface, while there was maximum water content near the bottom of the pit of water storage. With the time, the water distribution becomes more homogeneous, which results in water content to be distributed mainly in middle deep layer of soil, which can prevent water effectively from the evaporation.

### 5.7.2 Ammonia and Nitrogen Concentration

Simulated ammonia and nitrogen concentration for the water storage pit irrigation are compared with the measured values. The results of the comparison, shows that the ammonia nitrogen content has increased gradually in the early period and then decreased subsequently after the seventh day, major reason of the decrease in the value of the ammonia and nitrogen concentration is the completion of the urea hydrolysis. Ammonia was majorly distributed in 30-70 cm depth, while there was little ammonia in 0-10 cm depth, this will reduce effectively the nitrogen loss which is caused by ammonia volatilization in water storage pit irrigation.

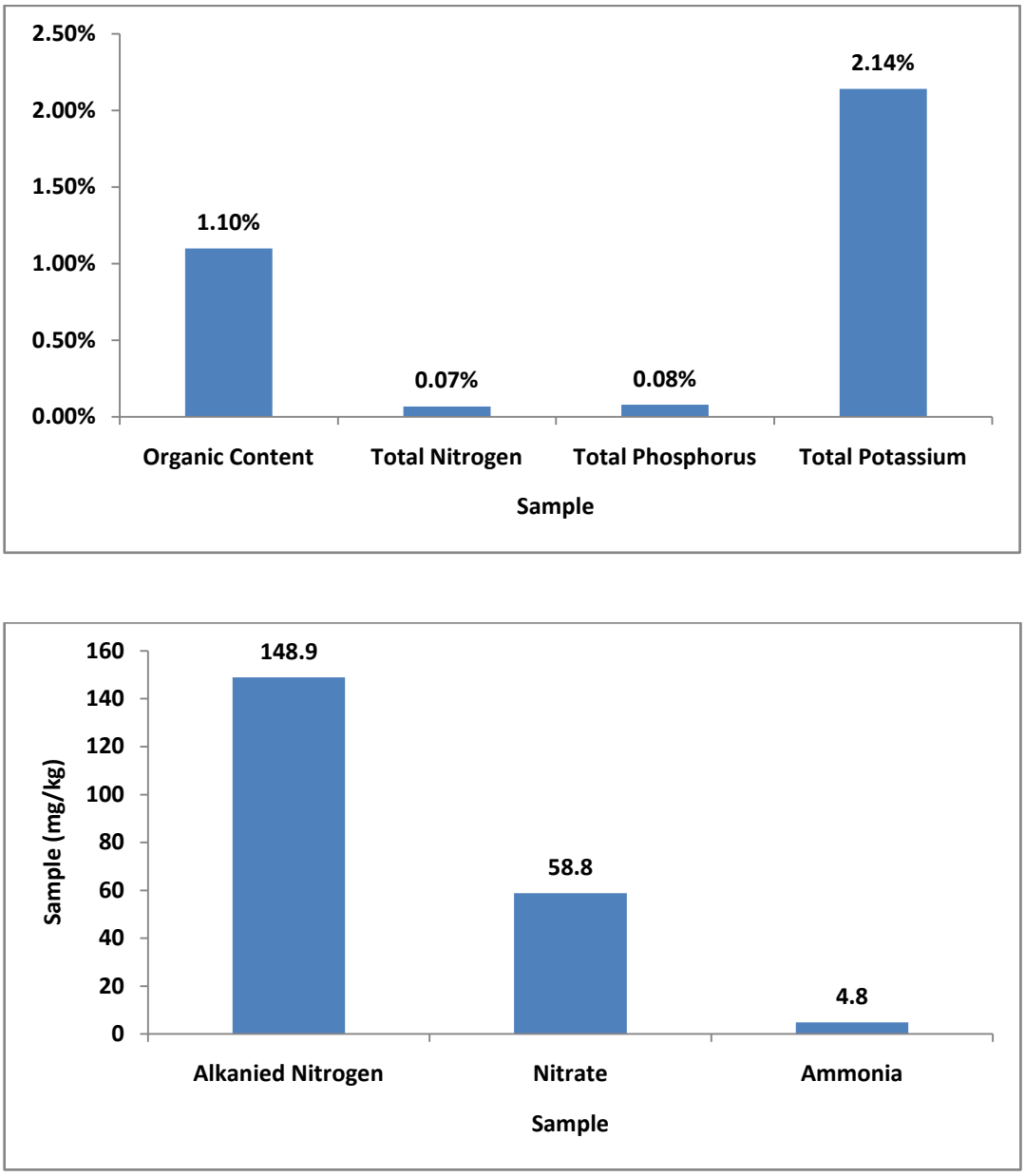


Figure 5.5: Sample Content Analysis

According to the results of the analysis, the root menu square error between the measured and simulated values of ammonia was 0.326 and 0.317 respectively. Better agreement was found between simulated and measured values.

### 5.7.3 Nitrate Nitrogen Concentration

The nitrate concentration for the water storage pit irrigation is compared with the measured values and the results obtained from the comparison, shows that nitrate concentration increased with the horizontal distance. But the nitrate concentration in the edge of wetting soil were more than the water near storage pit, a possible explanation for the characteristics of nitrate distribution might be the possible effect of repellent action between the nitrate in and soil colloid. During the 1-7 days redistribution with the increase of nitrification, the nitrate concentration in 30-70 cm depth increased significantly within 1-7 days. According to the analysis, the root menu square error between the measured and simulated values of nitrate content was 0.365 and 0.612 respectively. The simulated nitrate nitrogen concentration agreed reasonably well with the measured values for all the depth.

# CHAPTER 6

# CONCLUSION & RECOMMENDATIONS

## 6.1 Conclusion

Although about 71% of the earth is occupied by water only 2% of all these resources are in the form of fresh water. Most portion of the fresh water is stored in polar, sub-polar and mountains in the form of permafrost. With the rapid rate of growing population and subsequent increasing pressure on the water resources these water deposits are unable to fulfill the demand hence we need alternative solution in form of water deposits from groundwater resources. With excessive drawing from these water bodies and intermixing of contaminants to the groundwater, its monitoring and preservation is an important issue and has attracted a lot of concentration from environmentalists, hydrologists and civil bodies. Modeling of the groundwater resources can provide with sustainable solution to the rising problem.

Mathematical models are important tools, which are frequently used in studying groundwater systems. In general, mathematical models are used to simulate (or to predict) the groundwater flow and in some cases the solute and/or heat transport. Predictive simulations must be viewed as estimates, dependent upon the quality and uncertainty of the input data. Models may be used as predictive tools, however field monitoring must be incorporated to verify model predictions. The best method of eliminating or reducing modeling errors is to apply good hydro-geological judgment and to question the model simulation results. If the results do not make physical sense, find out why.

Mathematical modeling in India is practice for research and educational purposes only. It is the high situation we should implement the results and the proper remediation based on detailed and precise modeling of the site. These can help in

reducing the stress on water resources and can save the environment. By regulation of the flow and transport of contaminants we can avoid the serious problems of groundwater pollution.

Mathematical models are an approximate tool to find the solution to a problem, so it requires thorough study of hydro-geology and the physical parameters of the field. Its use in agriculture and water supply can help in gross progress of a nation like India. Errors must be reduced and the sources of contamination must be taken care of in order to save our groundwater resources for humen generations to follow in the future.

Delhi is a large city with huge population flowing in from different parts of the country every year. The groundwater resource management is essential for this cosmopolitan city. The situation of groundwater contamination in delhi is not that serious right these days but it will cause a huge problem in future. This is the high time we should awake before any catastrophe takes place.

## 6.2 Recommendations

- Alternate sources of drinking water having less nitrate contamination must be used.
- People must be made aware of the problems associated with use of contaminated water.
- Use of fertilizers should be optimized in a proper managed way in order to reduce the groundwater contamination.
- Laboratories and research centres must be established in the area should be established.
- Organic manure must be used more to limit the nitrate infiltration.
- Proper management of avoiding leachate percolation be adopted.
- Methods for removal of nitrate from water should be developed and it must be employed in worst affected regions.

- Denitrification techniques must be adopted.
- With promotion of nitrate consumption from denitrifying bacteria and plants must be encouraged.

## 6.3 Application of the study

The present study on the modeling of ground water for transport of nitrate and ammonia contaminants has been conducted for the contaminations due to irrigational studies. This can help us in management of fertilizers and other chemical's use in the field conditions.

The results of this study will be useful to individuals, municipalities, and regulators who all have an interest in maintaining safe drinking water supplies. An understanding of the mechanisms controlling nitrate contamination will be useful in modifying well construction methods and placing new wells to prevent contamination and in designing mitigation measures for already contaminated wells.

## 6.4 Scope of the study

There is a very bright scene of this modeling study on groundwater in future. There should be thorough study conducted on the pollutants and the nature of flow and transport of contaminants in groundwater at the fields. The interrelation between the intermixing of pollutants and groundwater through leakage from surface sources to the groundwater must be studied in details.

The study can be carried into a much larger frame by its application to other sources of contaminants as well as varying the nature of the pollutants. This is very useful tool in management of our scarce and depleting water resources. By simulation of these numerical models we can understand the nature in a more convincing way.

# REFERENCES


1. Anderson, M.P. and W.W. Woessner, 1992, Applied Groundwater Modelling. Academic Press, Inc., San Diego, CA., 381 p.

2. American Society for Testing and Materials, 1993, Standard Guide for Application of a Ground-Water Flow Model to a Site-Specific Problem. ASTM Standard D 5447-93, West Conshohocken, PA, 6 p.

3. American Society for Testing and Materials, 1995, Standard Guide for Subsurface Flow and Transport Modelling. ASTM Standard D 5880-95, West Conshohocken, PA, 6 p.

4. Bear, J., and A. Verruijt, 1987, Modelling Groundwater Flow and Pollution. D. Reidel Publishing Company, 414 p.

5. Franke, O.L., Bennett, G.D., Reilly, T.E., Laney, R.L., Buxton, H.T., and Sun, R.J., 1991, Concepts and Modelling in Ground-Water Hydrology -- A Self-Paced Training Course. U.S. Geological Survey Open-File Report 90-707.

6. Kashyap, Deepak, 1989, Mathematical Modelling for Groundwater Management – Status in India. Indo-French Seminar on Management of Water Resources, 22-24 September, 1989, Festival of France-1989, Jaipur, pp. IV-59 to IV-75.

7. Kinzelbach, W., 1986, Groundwater Modelling: An Introduction with Sample Programs in BASIC. Elsevier, New York, 333 p.

8. Kumar, C. P., 1992, Groundwater Modelling – In. Hydrological Developments in

India Since Independence. A Contribution to Hydrological Sciences, National Institute of Hydrology, Roorkee, pp. 235-261.

9. Kumar, C. P., 2001, Common Ground Water Modelling Errors and Rem ediation. Journal of Indian Water Resources Society, Volume 21, Number 4, October 2001, pp. 149-156.

10. McDonald, M.G. and A.W. Harbaugh, 1988, A Modular Three-Dimensional Finite-Diference Ground- Water Flow Model, USGS TWRI Chapter 6-A1, 586 p.

11. Pinder, G.F., and J.D. Bredehoeft, 1968, Application of the Digital Computer for Aquifer Evaluation, Water Resources Research, Vol. 4, pp. 1069-1093.

12. Wang, H.F. and M.P. Anderson, 1982, Introduction to Groundwater Modelling. W.H. Freeman and Company, San Francisco, CA, 237 p.

13. Website - Kumar Links to Hydrology Resources: http://www.angelfire.com/nh/cpkumar/hydrology.html

14. Website - Scientific Software Group: http://www.scisoftware.com/

15. Website - USGS Ground-Water Software: http://water.usgs.gov/nrp/gwsoftware/