

**A Conceptual Framework for Ground-Water Solute-Transport Studies
with Emphasis on Physical Mechanisms of Solute Movement**



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By Thomas E. Reilly, O. Lehn Franke, Herbert T. Buxton, and Gordon D. Bennett



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A CONCEPTUAL FRAMEWORK FOR GROUND-WATER SOLUTE-TRANSPORT STUDIES
WITH EMPHASIS ON PHYSICAL MECHANISMS OF SOLUTE MOVEMENT
by

Thomas E. Reilly, O. Lehn Franke, Herbert T. Buxton, and Gordon D. Bennett

ABSTRACT

Analysis of solute transport in ground-water systems involves a complex, multi-discipline study that requires intensive and costly investigation. This report examines the physical mechanisms of solute transport, advection and dispersion, and explains how they relate to one another and the scale of study.

A step-by-step framework for conducting a study of the physical mechanisms is given that encourages the use of simulation to help understand the ground-water system under study. This framework is intended to aid both first-time project leaders of solute-transport studies who already have considerable experience in ground-water flow studies and technically oriented administrators.

INTRODUCTION

In recent years, project activities in both the Federal and Cooperative Programs of the U.S. Geological Survey have reflected the growing importance of ground-water contamination particularly from point sources. Today, these programs are continuing to allocate significant resources for the study of the complex problems related to the movement of contaminants in ground-water systems.

During the last decade, research into problems of solute transport by the worldwide community of ground-water hydrologists and geochemists has been intensive. While the outcome of this effort has greatly increased our understanding of solute transport, the significant realization has emerged that solute-transport problems are very complex and generally involve large degrees of uncertainty in defining the relevant physical and chemical parameters. This high level of uncertainty in defining solute-transport problems is worthy of emphasis. Many years of collective experience in the development and application of ground-water flow models taught hydrologists the many pitfalls and uncertainties that arise in any attempt to achieve a quantitative understanding of ground-water flow systems. It is probably fair to say that ground-water solute-transport problems involve a level of complexity and related uncertainty that is several times, perhaps an order of magnitude, greater than the more familiar ground-water flow problems that do not involve transport of solutes.

Given the complexity of solute-transport problems, the question arises as to what goals are realistic for such studies. Regardless of the complexity and uncertainty of solute-transport systems, an increased understanding of the system under study is an attainable goal.

Many tools are available to the hydrologist for studying solute transport; they range from basic mapping and hand calculations to powerful numerical simulation. Proper application of these tools can lead to an improved understanding of a given flow and transport problem, even though it may not be possible to develop a reliable predictive model for most situations. Finally, a model, or the development of a model, should never be viewed as an end in itself. The principal goal of hydrologic and geochemical studies is to increase our understanding of systems and processes; models are simply tools to this end.

Purpose and Scope

The purpose of this report is to provide first-time project leaders of solute-transport studies who already have considerable experience in ground-water flow studies, and technically oriented administrators who wish to acquire additional insight into the nature of solute transport, with a conceptual framework for field studies of solute transport in ground water. This framework emphasizes the two physical transport mechanisms of advection and dispersion.

The following brief presentation is not a "handbook of information" but provides a general guide or "road map" to approach and think about solute-transport studies and indicates some common complications and pitfalls. These general guidelines must be individually tailored to meet the specific challenges encountered in the particular physical system under study.

This conceptual framework is presented for an important class of solute-transport studies which address the movement of solutes in ground water from point sources near the land surface. The principal goal of these studies is an increased understanding of the processes that control the spatial and temporal distribution of solutes in the ground-water system.

This report focuses on physical mechanisms of solute transport. Chemical mechanisms are often critical and must be addressed; however, the scope of this work is such that only brief mention of chemical aspects will be made. Any rigorous analysis of solute transport in an existing contaminant plume, including studies that focus on mechanisms related primarily to chemical and microbiological effects, requires a detailed quantitative definition of (a) the ground-water flow field in three dimensions and (b) the distribution of solutes in the contaminant plume in three dimensions at one point in time and preferably at more than one point in time. These two fundamental elements of all solute-transport studies are discussed in considerable detail.

The framework outlines a practical and achievable hierarchy of tasks to develop a continuously improved understanding of the system. Numerical simulation is presented as a vehicle for acquiring increased understanding of the flow system and the processes that control solute transport, rather than as a tool for prediction.

General References

The physical processes of solute transport and methods of simulating them are currently the subject of much discussion, debate, and research. Review papers by Gelhar and others (1985), Gillham and Cherry (1982), and Anderson (1984) have clearly presented the state of the art. The classical approach using the advection-dispersion equation is being questioned and the mathematical representation of dispersion is being debated.

The classical equations that describe solute transport in ground water have been rigorously developed by Bredehoeft and Pinder (1973) and Konikow and Grove (1977). These equations represent the physical mechanisms of: 1) advection of solutes due to the average movement of the fluid, and 2) dispersion (or mixing) due to variations in the fluid movement from the average advective movement. Classical derivations, such as these, are based on the assumption that dispersion is analogous to molecular diffusion. The validity of this assumption is discussed in the following sections.

This report emphasizes the importance of simulation in increasing our understanding of the transport of solutes through ground-water systems. The role of simulation has been similarly discussed in reports by Konikow (1981) and Pinder (1984).

PROBLEM FORMULATION

The systems concept used in the study of ground-water flow is equally useful in considering solute transport. By use of the systems concept to provide an appropriate format, the information needed to define both types of problems is listed in figure 1. This comparison of information needs illustrates the greater demand for information and the implied higher level of complexity of solute-transport studies, and demonstrates that the quantitative definition of a solute-transport problem requires an accurate representation of the ground-water flow system.

Both ground-water flow and solute-transport problems are treated mathematically as boundary-value problems (Freeze and Cherry, 1979, p. 67-69 and 389-391). Boundary-value problems are characterized by a governing differential equation (usually a partial differential equation) and by a set of boundary and initial conditions particular to the problem under study. The differential equation is actually a mathematical model of the physical processes of fluid flow and associated transport of solutes.

In ground-water flow problems, the dependent variable is generally expressed in terms of head, drawdown, or pressure as a function of space and time (fig. 1); boundary conditions are usually defined in terms of heads and flows; and the parameters that must be specified are the hydraulic parameters--hydraulic conductivity (or transmissivity), and the storage coefficient (or specific storage). In contrast, the dependent variable in solute-transport studies is concentration of solute as a function of space and time (fig. 1); boundary conditions relating specifically to solute transport are often defined as representing either (a) constant solute concentration or (b) constant input or flux of solute.

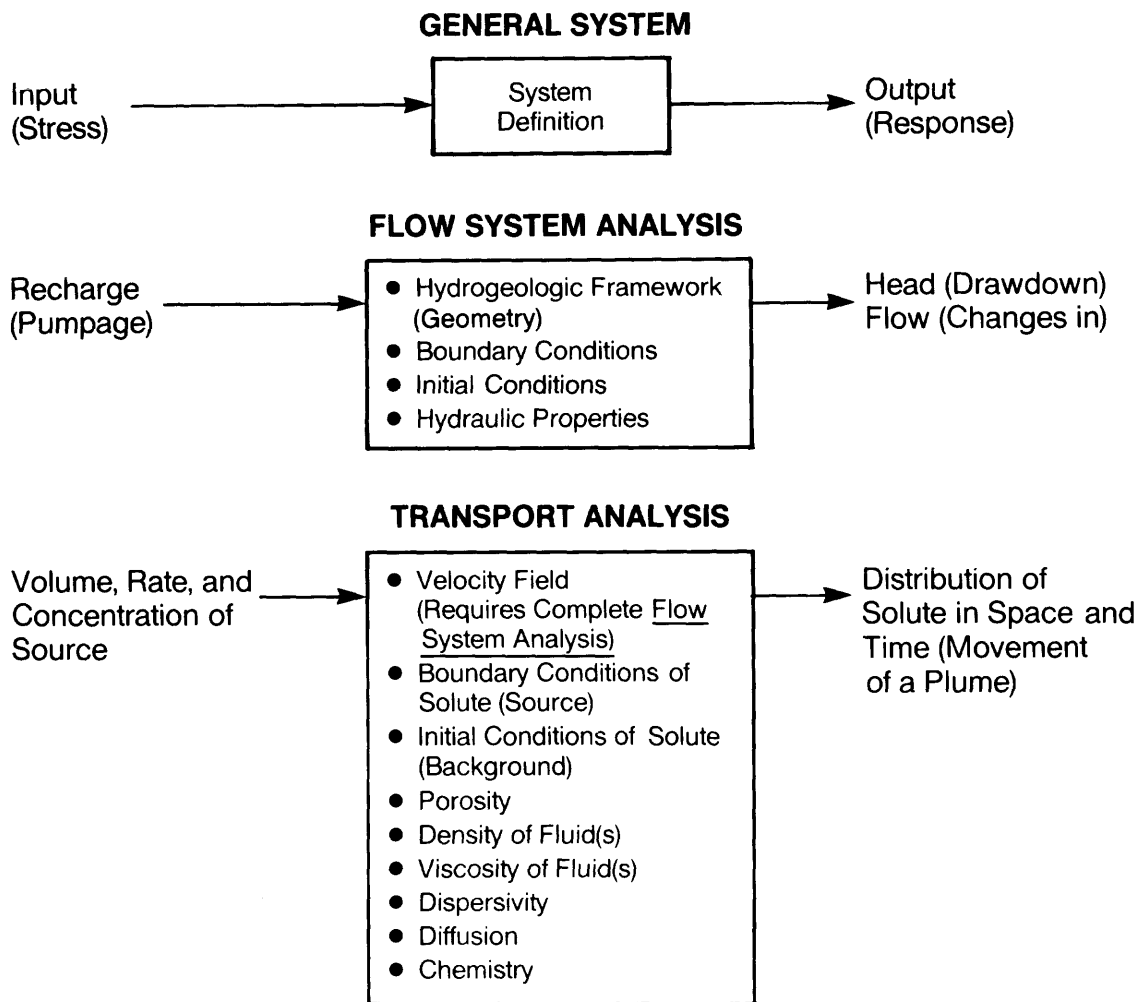


Figure 1. Information necessary to describe ground-water flow systems and solute transport, presented with a simple systems approach.

The number of parameters required for transport analysis is significantly greater than for flow system analysis alone. The transport analysis not only requires a flow-system analysis first, but requires a flow-system analysis with fine enough resolution to define the velocity field with sufficient detail to represent the advective movement of the contaminant plume. Additional parameters that must be specified include the effective porosity of the porous medium and a characterization of its mixing properties as expressed by coefficients of dispersion, diffusion or hydrodynamic dispersion. Furthermore, if significant variations in density and/or viscosity of the fluid exist within the flow system, these fluid properties and their dependence on pressure and concentration must be defined explicitly. Finally, a quantitative representation of solute concentrations as a function of space and time requires that chemical reactions between solutes or with the porous medium, including the effects of micro-organisms and the decay of radioactive constituents, be defined by quantitative relationships.

FRAMEWORK FOR THE STUDY OF SOLUTE-TRANSPORT PROBLEMS

The purpose of this section is to propose a general design for a hydrologic study involving solute transport. A flow chart that represents an overview and summary of the investigative process, is shown in figure 2. In figure 2, a number of the arrows connecting boxes indicate feedback loops. These feedback loops represent a "going back" to reevaluate data and/or previous assumptions--a key concept that will be mentioned frequently in the following discussion. Additional feedback loops could certainly be added to figure 2, but were omitted to prevent the illustration from becoming unduly complex.

No set of guidelines can encompass all the highly complex and variable situations one may encounter in the field. These guidelines are designed to provide a general philosophy and direction for solute-transport investigations that must be modified as needed to address individual situations.

Overview

The tasks indicated in boxes I through V of figure 2 represent the initial stages of the investigation. The major phases of scientific analysis are those indicated in boxes VI through IX; they are the focus of the following sections. Box X represents a synthesis of all the information gathered during steps I through IX to obtain the best possible understanding of solute transport in the unique ground-water system under study.

The framework presented in figure 2 is recursive in character. That is, the methods of analysis are applied early in the investigative process (box III), before any new data collection is undertaken. Then, new data collection and re-analysis takes place. If required, additional data are collected and analyzed until a sufficient understanding is attained.

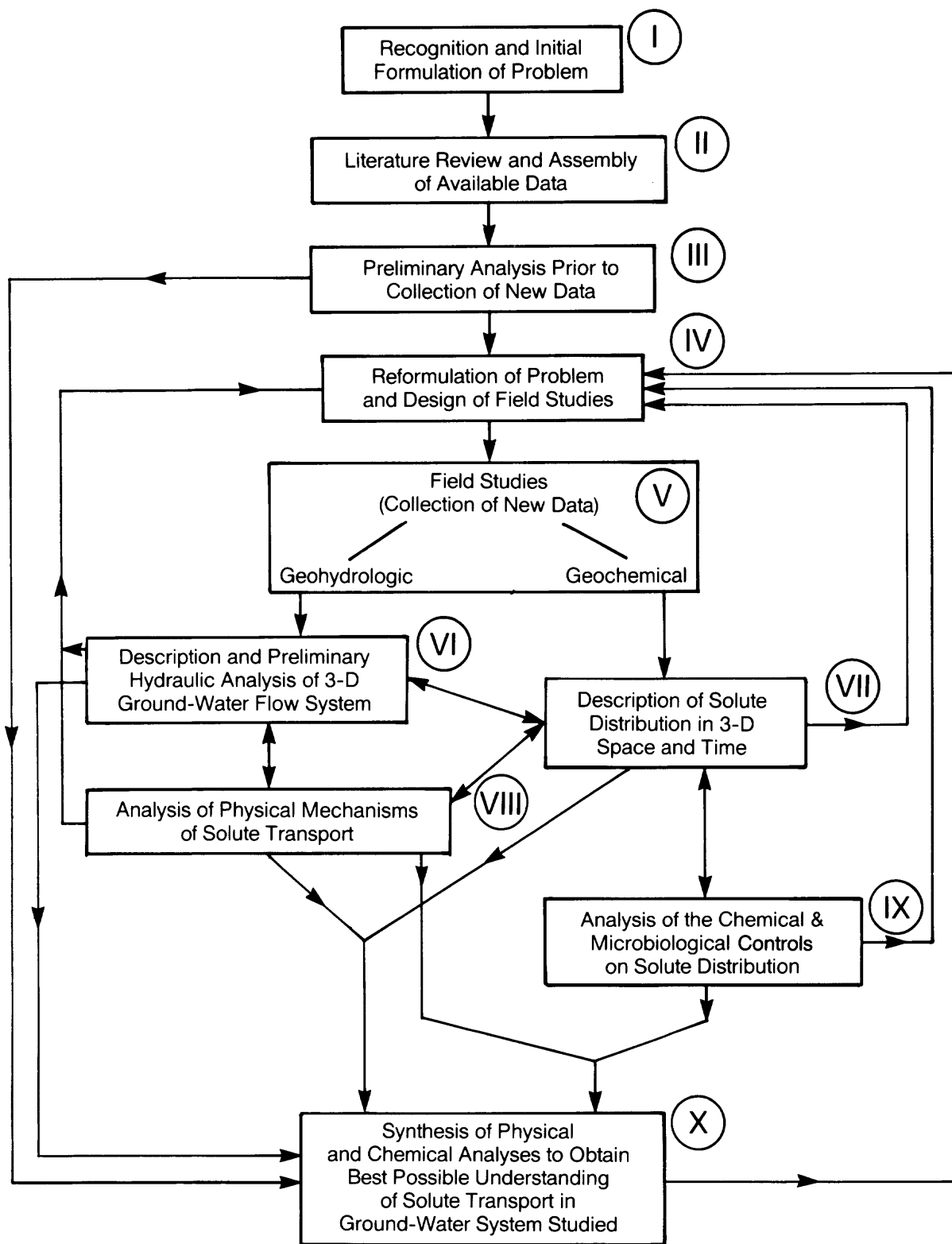


Figure 2. Framework for the study of solute-transport problems.

Initial Stages of the Investigation

Generally, an investigation involving solute transport is initiated because someone either (a) has evidence for or strongly suspects present contamination of the subsurface environment or (b) foresees the future likelihood of contamination of the subsurface environment. A list of the various combinations of circumstances by which contamination of the subsurface environment is either known or suspected, which may serve as a rather general classification of problem types, is given in table 1 along with appropriate examples.

The most common type of problem undertaken is the first, in which the source of contamination is either known or suspected. For example, in the case of ground-water contamination near the Rocky Mountain Arsenal, Colorado, crops downgradient from the arsenal were adversely affected by chloride-rich ground water whose source (unlined disposal ponds) could be identified easily within the arsenal grounds (Konikow, 1977). Once a source of contamination is known or suspected, practical questions often provide the impetus for initiation of a formal study.

The initial phase of a solute transport investigation is represented by the first three boxes in figure 2. It has three major goals:

1. to describe the general operation of the ground-water flow system under investigation and identify the specific area (surrounding the contamination site) for more intensive study;
2. to formulate specific questions, such as which chemical constituents are involved and whether streams or springs should be sampled; and
3. to perform a preliminary evaluation of the problem based on existing data to help define the intensity and technical level at which the planned investigation should proceed.

The initial phase, in effect, constitutes a "mini-investigation." All existing data on the geology, hydrology, and geochemistry of ground and surface waters in the area of interest are collected from the literature and available unpublished records. The analysis of these data (figure 2, box III, preliminary analysis) represents the first attempt to synthesize all the available technical information and serves as a foundation for the subsequent conduct of the study. This step is in fact an initial form of the analyses outlined in steps VI-IX.

The preliminary analysis is the basis for deciding on the next step in the investigation. Either (a) continuing the study is not necessary, desirable, or feasible--that is, to some extent the questions posed for the study have been answered; or (b) additional investment of resources in the study is warranted. If additional investment of resources is warranted, then this analysis should help to determine which data are to be collected and to define a reasonable approach for the study.

Table 1.--Types of problems or sets of circumstances that may initiate a hydrologic study involving solute transport from contamination sources near land surface

Problem Type	Initial Circumstance	Example	Comments and Emphasis
History-matching problem	Contamination incident from an identified source	A spill or accident has occurred, allowing a hazardous chemical into the subsurface environment. The plume may or may not have been observed.	Define a complete plume configuration for at least one "snapshot" in time. Preliminary analysis is integral to design of initial field studies. Phased drilling program can optimize network. Because of the short duration of studies and slow ground-water velocities, maximizing time between snapshots of plume gives more insight.
Hypothetical prediction problem	Anticipation of contamination incident	Proposed waste-storage or disposal-site evaluation, or contingency planning at an existing site.	Geochemical field studies are limited to background water-quality and the geochemical character of the medium. Confidence in the results of such an analysis is limited because no plume data are available to calibrate ground-water flow paths or velocities, or geochemical controls.
Detection problem	Observed contamination from an unknown source	Contamination is observed in a highly industrialized area with several potential sources.	Identification of source may have legal implications. Detailed geochemical analysis for constituents that are unique to a single source can play an important role. Chemical reactions may disguise the character of the plume.

Procedures and problems in the conduct of field studies (boxes IV and V in figure 2) are a specialty in themselves. Some excellent reports on the subject, such as those by Gillham and others (1983 and 1985), Scalf and others (1981), and Claassen (1982), are available. An important consideration in the design and execution of field studies, particularly in the design and installation of monitoring networks, is the high level of uncertainty regarding physical and chemical parameters and mechanisms in any study involving solute transport. Many monitoring-well networks have been installed which either did not sample the contaminant plume at all or did so inadequately. These uncertainties suggest that, depending in part on the availability of field data prior to the collection of new data, a monitoring network should be installed and sampled in two or more phases. Such a stepwise procedure permits time for sampling and further technical analysis during the development of the monitoring network which may be applied immediately to locate additional monitoring wells in locations that might provide the greatest amount of useful information. Thus, a monitoring network should not be designed at the start of the project but should evolve as more information and understanding are attained, despite increased practical and administrative difficulties.

Hydraulic Analysis of the Ground-Water Flow System

The hydraulic analysis in a solute-transport investigation is composed of the same basic elements as a typical ground-water flow-system analysis, but differs somewhat in its emphasis. Because the ultimate goal of a solute-transport investigation is to understand the movement of a contaminant through the ground-water system, the associated flow-system analysis emphasizes hydraulic characteristics which control the three-dimensional pattern of ground-water flow in the area of the contaminant plume. In contrast, the typical flow-system analysis focuses on the general, more regional operation of the ground-water system.

Ground-water velocities are typically low; therefore, the movement of a contaminant is usually on a scale of hundreds or thousands of feet. However, contaminant plumes are embedded in regional ground-water systems that are usually on a scale of miles, if not tens or hundreds of miles. Although the details of the flow system in the immediate vicinity of the contaminant plume are of the utmost importance, an understanding of the regional ground-water flow system is required in order to understand the local system. For example, the spatial and temporal distribution of ground-water flow that enters the local study area significantly affects contaminant movement. This distribution of flow is controlled by the operation of the entire ground-water system and can be sensitive to regional system boundaries or other characteristics of the system that are distant from the plume. Small temporal changes in the distribution of flow passing through the local area may not perceptibly affect the local distribution of hydraulic

head, but nevertheless may have a major effect on the actual path of a particle of water over a period of years. Thus, definition and understanding of the regional as well as local ground-water flow system are essential.

A general outline for the hydraulic analysis is presented in Table 2. Although the items are listed in what the authors consider to be a logical order, they are presented not as a rigid series of steps but rather as a guide to stimulate thought, highlight important topics, and provide a constructive approach to the hydrologic analysis.

Frequent references to regional and local scale further emphasize the importance of evaluating the effects of different-scale hydrologic characteristics in solving the transport problem. The effort allotted to data collection and analysis in order to define the relationship between the local and regional scales is problem-dependent and must be considered individually for each study.

Elements 1, 2, and 3 of Table 2 stress development of a concept of the structure and operation of the ground-water system and indicate that the relationship of regional and local scale characteristics should be considered early.

Preparing water budgets (item 4) represents the first attempt to quantify or approximate the gross fluxes through the hydrologic system and to identify their sources and sinks. For example, quantitative estimates of baseflow of local streams, defining reaches that are gaining, losing, and hydraulically disconnected, provide valuable insight into the quantity of shallow ground-water flow. In addition, identifying where water enters and leaves the ground-water system (internal sources and sinks can be considered separately) provides a general picture of the flow pattern through the system.

Preparation of a water budget implies careful definition of a three-dimensional control volume which is enclosed by a three-dimensional surface. This control volume is the portion of the ground-water system that is isolated for study. This emphasis on volumes and three-dimensional surfaces underlines the fact that flow patterns in all natural ground-water systems are fundamentally three dimensional.

Identifying where water enters and leaves the ground-water system as part of the water-budget analysis leads to a conceptualization of boundary conditions starting at locations of inflow and outflow. For example, if sporadic areal recharge to the water table from precipitation is an important source of water to the ground-water system, the hydraulic boundary condition at this physical boundary might be conceptualized as a constant areal flux or an areal flux that varies as a function of time. (For further discussion of boundary conditions see Franke, Reilly, and Bennett, 1987.) In transport investigations, especially those in which ground-water flow rates and velocities will be used at a detailed scale, measurements of flow rates either within the natural system or at boundaries are an important check on water-transmitting properties and ultimately flow rates and velocities.

Table 2.--Outline for preliminary hydraulic analysis of the ground-water flow system associated with a contaminant plume.

1. Identify the extent and physical boundaries of the natural (regional) ground-water flow system and develop an initial concept of its operation.
 2. Identify an appropriate local area for intensive study which includes the contaminant plume.
 3. Define formal boundary conditions for the regional ground-water system, which indicate the flow of ground water into and out of the system; place special emphasis on natural boundaries within the local area of interest.
 4. Evaluate the relationship between the regional flow system and the flow system in the local area primarily by developing a water budget for the regional ground-water system and the local area of intensive study as accurately as available data permit.
 5. Define the internal geometry (hydrogeologic framework) at the appropriate scale throughout the system.
 6. Define the regional and local distribution of hydraulic potential (head) with appreciation for the three-dimensional nature of natural flow systems by preparing appropriate water-level maps starting with the water table and hydrogeologic cross-sections that include available information on head with depth.
 7. Estimate the spatial distribution of hydraulic (water-transmitting) properties.
 8. Conceptualize the approximate ground-water flow pattern and estimate ground-water flow rates through both the regional and local systems using hand calculations and compiled data.
 9. Develop a flow model of the regional ground-water system.
-
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In order to refine further the general flow pattern that was developed through items 1-4, it is necessary to define the internal geometry of the ground-water system (item 5, internal heterogeneities with respect to the three-dimensional distribution of hydraulic conductivity). This definition includes details of the thickness and areal extent of aquifers and confining units both laterally and in vertical sequence. Although we have defined previously how and where water enters and leaves the system, these internal heterogeneities have a major effect on the paths of water movement within the ground-water system. Further discussion of the various scales of heterogeneities in ground-water systems and their effects on the distribution of ground-water velocities is presented in the next section.

An early step in defining the flow pattern of constant-density ground-water flow is mapping the spatial distribution of hydraulic head, or potential (item 6). Mapping head involves more than mechanically contouring water levels measured in observation wells. Head varies in three dimensions, and ground water moves throughout the three-dimensional aquifer system in response to existing three-dimensional head gradients. Because any map representation is two-dimensional, head maps represent a two-dimensional simplification of a three-dimensional surface (as in the case of a potentiometric surface map of an aquifer). Often, to represent the three-dimensional hydraulic head distribution in a ground-water system, head maps are prepared in sets--on the regional scale, a map for each aquifer in a vertical sequence of aquifers, accompanied by a series of vertical cross-sections showing a "slice" of the three-dimensional surface. At the local scale, maps in the vicinity of a plume might be prepared at a much larger scale and smaller contour interval than regional maps, accompanied by vertical cross-sections.

After preparing equipotential maps and cross-sections and conceptualizing the approximate pattern of flow through the ground-water system, the spatial distribution of ground-water flow is estimated, with greatest emphasis in the area of the contaminated site (item 8). According to Darcy's law, the rate of flow per unit area (specific discharge) is the product of the hydraulic gradient and the hydraulic conductivity of the medium:

$$q = -K \frac{dh}{dl}$$

where:

q = Darcian velocity or specific discharge (L/T),

K = hydraulic conductivity of medium (L/T),

$\frac{dh}{dl}$ = hydraulic gradient (L/L).

Thus, to define the actual distribution of flow through different parts of the system, it is first necessary to define the system's water-transmitting properties (item 7). These include the horizontal and vertical hydraulic conductivities of the porous media. In simple isotropic and homogeneous systems the average path of a water particle aligns with the hydraulic gradient (flow is perpendicular to equipotential surfaces). However, in natural systems which are inevitably heterogeneous and anisotropic, the water-transmitting properties may have to be defined in all three coordinate axis directions to assess the actual path of ground-water flow.

At this phase of the investigation, a number of simple calculations can be made to assess the consistency of data and to gain additional insight into the transport problem. These calculations can determine gross quantities of water moving through the system and approximate ground-water velocities and times of travel for advective ground-water movement. These simple calculations can be compared to measured discharges (for example, base flows of streams) and the known extent of the contaminant plume to ascertain whether estimates of water-transmitting parameters are physically reasonable, as well as to provide a baseline for comparison between the advective and dispersive transport of conservative and non-conservative constituents, discussed further in the next section.

Ground-water flow modeling is the most powerful tool available to the hydrologist for hydraulic analysis (item 9). Development of a ground-water model allows a quantitative representation of our concept of the ground-water flow system using all the information and hydrologic insight gained from the previous steps in the hydraulic analysis. After defining mathematically the boundary conditions, internal geometry, and water-transmitting characteristics, the model solves for the distribution of head and flow through the simulated system. The simulated values are then compared to measured head and flow values to assess the validity of our concept of the system. A model of the regional ground-water system also offers a means to quantify the water budget for the local area selected for more detailed investigation and to test the sensitivity of this budget to realistic variations in system representation.

Ground-water flow models can now be developed with sufficient size (number of nodes) to represent entire ground-water systems in three dimensions. The flexibility of variable-grid models allows the representation of the system to reflect added detail in the area of concern, while still providing an accurate regional representation. Techniques of coupling models of regional and local scales have also been employed (Buxton and Reilly, 1987) and will be discussed later. This technical capability is useful in the hydraulic analysis phase of the study, because a three-dimensional simulation of the regional flow system greatly enhances our understanding of its physical operation.

A contamination study by Konikow (1977) exemplifies some of these ideas on regional and local hydraulic analysis. Konikow defined the hydrogeologic framework for his contamination study of the Rocky Mountain Arsenal, Colorado, with four maps--the bedrock surface, a composite water table over

a period of several years (fig. 3), saturated thickness of unconsolidated materials, and transmissivity of saturated unconsolidated materials (water-table aquifer). Figure 3 shows several areas where buried bedrock exists above the water table in the surrounding unconsolidated sediments. Initially, these features, which play a significant role in determining the pattern of ground-water flow in the study area, were not recognized. Because the areal distribution of the contaminant plume was extensive and the saturated thickness of the unconsolidated sediments containing the plume was generally less than 50 feet, the hydraulics of the flow system and the distribution of contaminants were approximated by a two-dimensional numerical simulation. Although the analysis was simplified to two dimensions, this study clearly illustrates the importance of understanding the regional ground-water flow field.

Solute Distribution in Three-Dimensional

Space and Time

The purpose of this task (figure 2, box VII) is to describe as accurately as possible the distribution of chemicals and related characteristics in the ground-water system in three-dimensional space and time. In conjunction with an understanding of the three-dimensional flow field, this information is essential for any description and understanding of the transport system. Again, although often the quantitative methods of transport analysis may be simplified to one or two dimensions, natural systems are characteristically three-dimensional, and our understanding of the transport processes must be based on an accurate and thorough description and understanding of the system in nature.

A logical first step in this task is the careful definition of the background or ambient ground-water chemistry in the neighborhood of the contaminant plume. This includes chemical analyses of water samples as well as determination of the soil and rock mineralogy. This information is important in two ways. A comparison of background chemistry and the chemical content of contaminating fluids may suggest possible reactions between the two. In addition, if a chemical constituent of interest in the contaminating fluids also occurs in the natural waters, this background occurrence may materially affect the spatial extent of the contaminant plume that can be defined with confidence.

For example, in Konikow's (1977) study of the Rocky Mountain Arsenal plume, the contaminating source fluid contained chloride concentrations as high as 5000 mg/l, and background chloride concentrations ranged from about 40 - 150 mg/l. As a result, the lowest contour of equal chloride concentration used to depict either the contaminant plume in nature or a simulated plume was 200 mg/l. However, the 200 mg/l chloride contour did not indicate the maximum extent of contaminant migration, but was used to illustrate the path of the plume and a minimum extent.

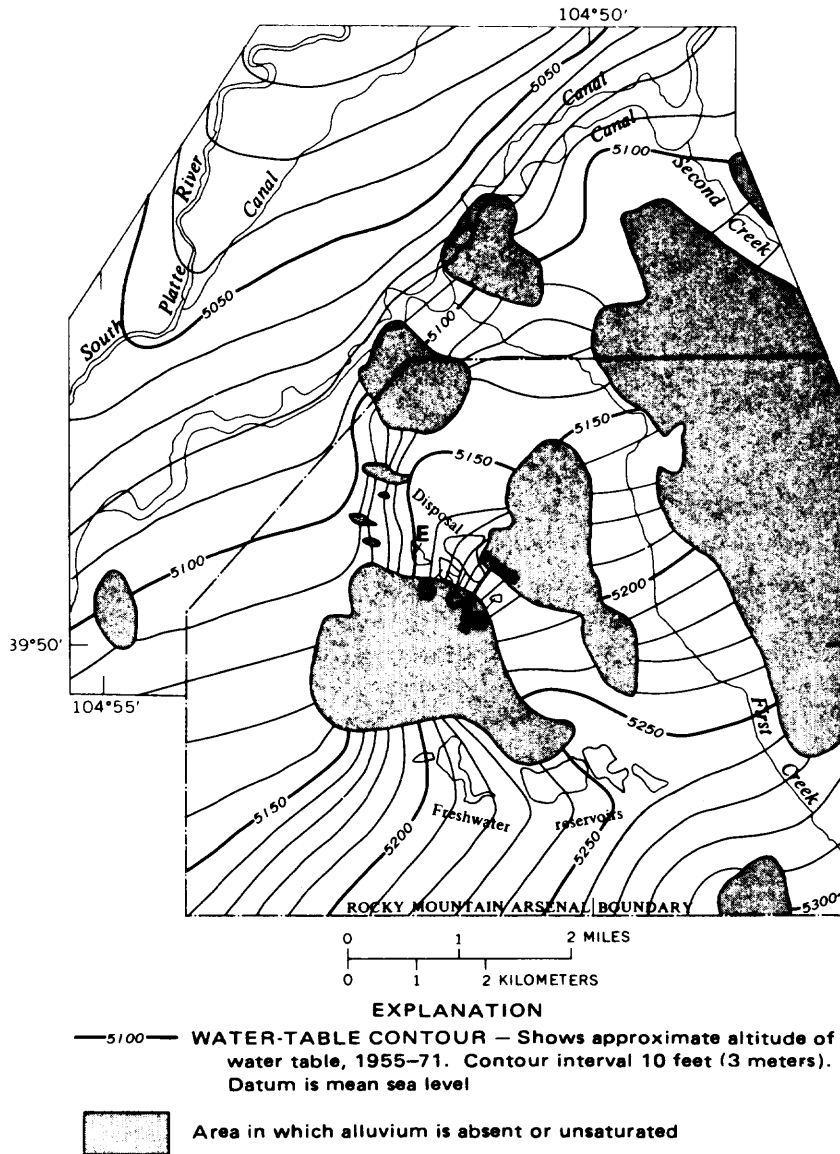


Figure 3. General water-table configuration in the alluvial aquifer in and adjacent to the Rocky Mountain Arsenal, Colorado, 1955-1971 (from Konikow, 1977).

The next step is to compile information on the source of contamination. Such information might include the location and extent of the source; history of use (for example, the times at which different sections of a landfill were put into operation); type of source, such as a one-time spill (volumetric source), waste lagoon (possible constant-head source), waste spreading on the land surface (specified-rate source), or leachate produced from recharge moving through the waste material; and the rate of introduction of solute into the ground-water system (loading rate) as a function of time. If possible, the chemical composition of the undiluted source fluid should be analyzed as completely and accurately as possible to determine the suite of constituents and their expected maximum concentrations in the ground-water system.

Unfortunately, both flow and transport field studies often suffer from a poor quantitative definition of the source input or loading rate. This is particularly true for transport studies of waste-disposal sites. For these sites, it is more often the rule than the exception that little historical information exists, either volumetric or chemical, on the input of solutes and other contaminants to the ground-water system. Thus, an accurate comparison between the loading rate and the quantities of contaminants observed in the ground-water system through sampling is seldom possible.

If a contaminant is introduced at or near land surface and is separated from the water table (upper limit of the saturated zone) by several feet or more of unsaturated earth material (unsaturated zone), the chemical composition of the contaminating fluid at the water table may differ significantly from the composition of the source fluid at the surface. For example, Robertson (1974) mapped a strontium-90 contaminant plume associated with a disposal well. However, no strontium-90 was detected in the ground water beneath the disposal ponds (that also contained a high concentration of strontium-90) which Robertson (1974) attributed to the presence of a thick unsaturated zone.

A number of mechanisms may be active in the unsaturated zone to effect these changes, including oxidation, adsorption, and microbial activity. A general characterization of the unsaturated zone to identify these mechanisms would include its thickness, grain-size distribution, mineralogy of grains, organic carbon content, and average quantity of fluid flow per unit area. Further discussion of the role of the unsaturated zone in solute transport may be found in Yaron and others (1984) and Warrick and others (1971).

In general, a problem involving solute transport in the saturated ground-water system is greatly simplified if the effect of the unsaturated zone can be neglected. If the unsaturated zone significantly alters the composition of the source, it is prudent to consider the contaminant concentration in the ground water at the water table immediately beneath the source as the source concentration for a contaminant-transport study in the saturated ground-water system.

The third and major part of the task is a description of the distribution of solutes in the three-dimensional ground-water system. This task is difficult because usually samples are available only for discrete points in the flow field and these point measurements must be extrapolated to describe a continuum. The number of point measurements (usually monitoring wells) required to define the solute distribution depends primarily on the ground-water flow system, the contaminants in the plume, and the time of first contamination.

The chemical composition of the source provides a basis for selecting constituents to be sampled in the ground-water system. Of particular importance is to identify and sample a "conservative" constituent--an ion, chemical group or chemical indicator that appears to be non-reactive (chemically, biologically, or radioactively) or whose aggregate value does not depend on the various possible types of chemical reactions taking place. The distribution of a conservative constituent is exceedingly important in approximating the physical transport parameters (discussed in the next section). Selection of other constituents to be sampled (both conservative and non-conservative) might be based on toxicity, presence in drinking water standards, or some particular characteristic of interest (for example, association with a particular chemical reaction).

LeBlanc (1984a), in his study of a contaminant plume resulting from disposal of treated sewage effluent into sand beds, sampled and studied the spatial distribution in the ground-water system of eleven physical properties and chemical constituents. He found three constituents--chloride, sodium, and boron--to be essentially conservative. Chloride was considered to be conservative and was used to delineate the contaminant plume in studies by Konikow (1977) and Robertson (1974), whereas Kimmel and Braids (1980) mapped specific conductance for this purpose.

Non-conservative constituents often can be identified by comparing the areal extent of their plumes with those of a relatively conservative constituent--for example, comparing the strontium-90 and chloride plumes reported by Robertson (1974) or the phosphorous (fig. 4A) and chloride (fig. 4B) plumes reported by LeBlanc (1984a). The cadmium and chromium plumes studied by Perlmutter and Lieber (1970) were not associated with conservative constituents and were not mapped with consideration of whether these constituents were conservative or non-conservative. A subsequent study of the same site (Ku and others, 1978) indicated that significant quantities of cadmium and chromium were sorbed on amorphous iron oxyhydroxide and iron oxide coatings on the aquifer grains, suggesting that if a conservative constituent had been identified in the earlier study, the sorption of metals might have been more apparent in the earlier study.

After chemical data from monitoring wells have been assembled, the areal extent and concentration of selected chemical species are plotted on maps and vertical cross-sections. The contaminant plume is three-dimensional and exists in a three-dimensional flow field; any map projects some aspect of the plume onto a two-dimensional surface. It is sometimes useful to prepare maps of the areal extent and concentration of selected chemical species or physical characteristics of water for specific surfaces, such as

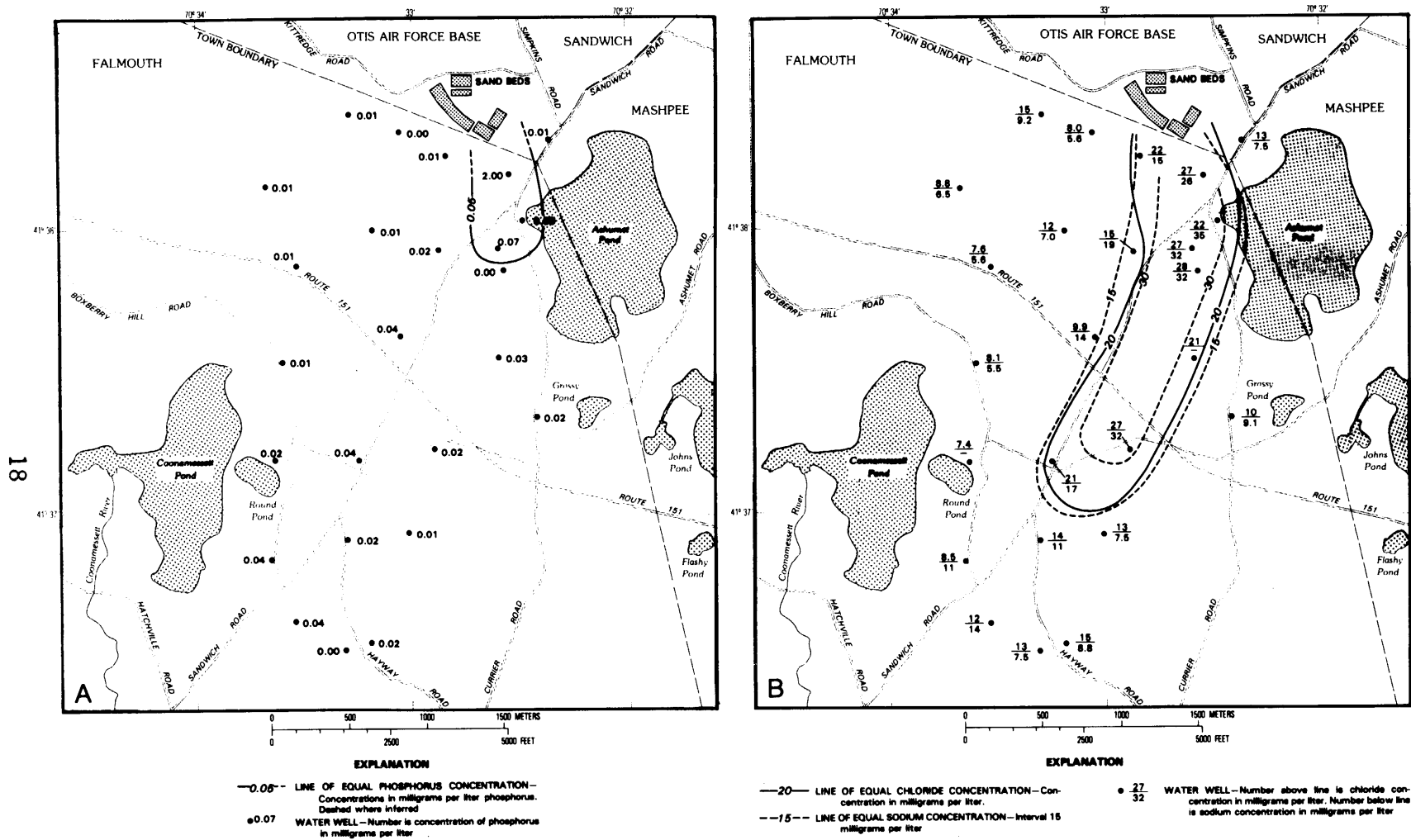


Figure 4 Areal distribution of non-conservative and conservative constituents in ground water at Cape Cod, Massachusetts, May 1978 through May 1979: (A) phosphorous; (B) chloride (from LeBlanc, 1984a).

at the water table, 20 feet below the water table, and so on. This mapping procedure was followed by Kimmel and Braids (1980) because the measured values of specific conductance depicted no discernible pattern in map view without this vertical perspective based on depth below the water table.

Vertical cross-sections, both longitudinal and transverse, that show the extent and concentration of selected chemical species are invaluable for depicting the three-dimensional geometry of the contaminant plume. Locating longitudinal sections parallel to streamlines and transverse sections approximately perpendicular to the general direction of plume movement makes their interpretation more straightforward and physically meaningful. Careful cross-checking for consistency between maps and vertical cross-sections is critical.

The contaminant plumes studied by LeBlanc (1984a) on Cape Cod, Cherry (1983) in Ontario, Canada, and Kimmel and Braids (1980) and Perlmutter and Lieber (1970) on Long Island, N. Y. were mapped in considerable detail in three dimensions based on point measurements of one or more chemical constituents or physical characteristics of the water. As an example, the vertical distribution of boron in the plume studied by LeBlanc (1984a), depicted in one longitudinal and two transverse vertical sections, is shown in figure 5. In all four studies the longitudinal axis of the contaminant plume downgradient from the source lies at some depth below the water table--generally, with some thickness of virtually uncontaminated aquifer between the water table and the top of the plume. This observed vertical distribution of contaminant results from the regional streamline pattern in the study areas. These streamlines travel downward as they move from the source as a result of intermittent areal recharge from precipitation over the entire land surface.

These four studies exemplify the situation in which the three-dimensional distribution of contaminants in a plume gives a clear picture of the average ground-water flow pattern which could not be obtained easily from field measurements of head. Hence, there is feedback where understanding of the flow field helps to explain the chemical distribution, and knowledge of the chemical distribution helps to explain the flow field.

At this juncture, a valuable check on the consistency of the field data is to compare the estimated mass of a chemical species in the plume with the estimated mass from the source. This comparison (depending on the accuracy of the estimates) might indicate the degree of consistency between the estimated mass of conservative constituents from the source and in the plume and also might indicate possible chemical reactions or microbial degradation if this comparison shows a large discrepancy.

If data from previous time periods are available, the next step is to document the historical movement of the plume by 1) preparing hydrographs of concentration for selected chemical constituents at selected points in the ground-water system; 2) preparing maps showing constituent concentrations at different times; and 3) examining changes in concentrations of specific constituents through time to estimate rates of plume movement or to indicate differences in rate of movement between species, which might reflect chemical reactions. Again, the estimated mass of each solute in the source should be compared to the estimated mass in the plume for each time period mapped.

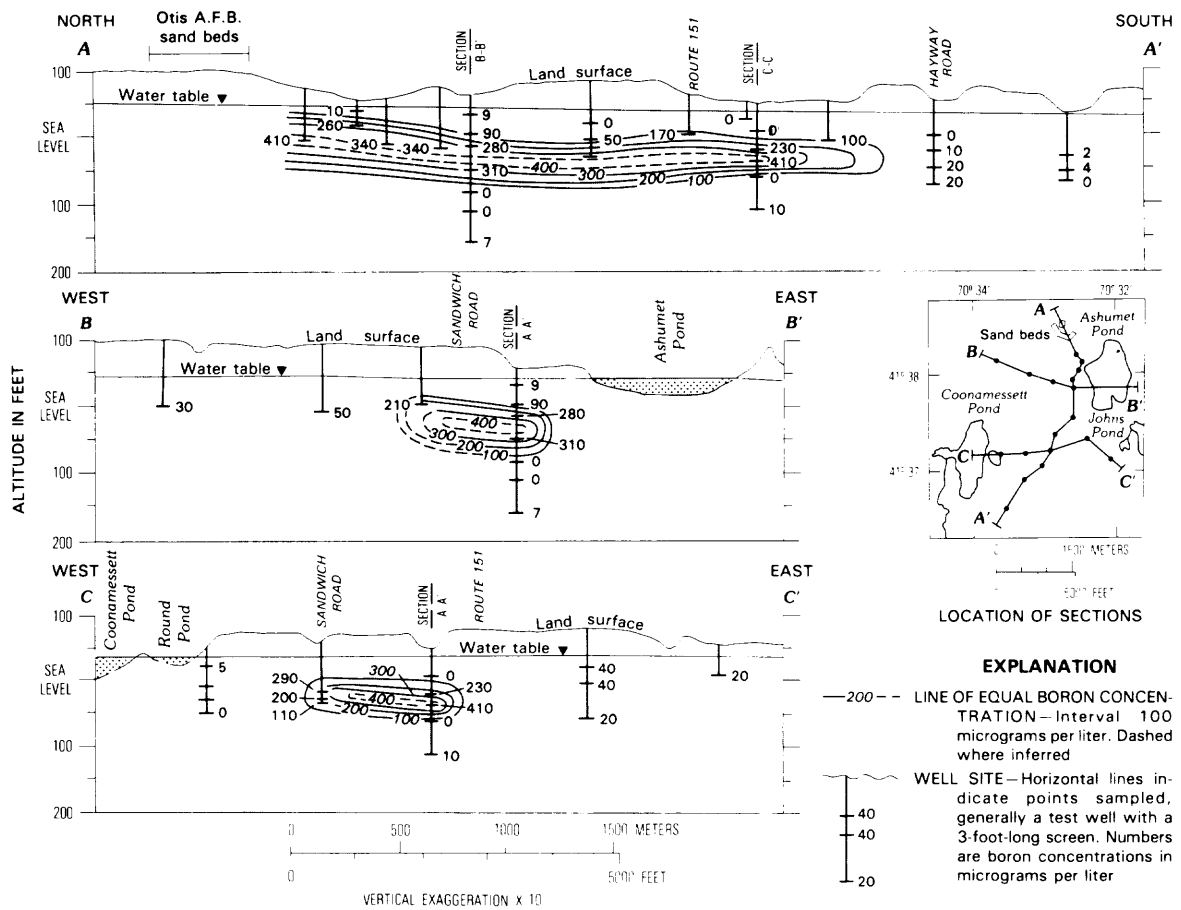


Figure 9. Vertical distribution of boron in ground water, May 1978 through May 1979.

Figure 5. Vertical distribution of boron in ground water at Cape Cod, Massachusetts, May 1978 through May 1979 (from LeBlanc, 1984a).

These activities, data compilations, and presentations can be carried out by a competent hydrologist who does not have an extensive background in geochemistry, but who is assisted by literature research and consultation with geochemists. The analysis of chemical and microbiological controls discussed below, however, requires greater chemical expertise.

Physical Mechanisms of Solute Transport

The following section on physical mechanisms of solute transport in ground-water systems (fig. 2, box VIII) (1) defines and describes the two physical mechanisms advection and dispersion; (2) emphasizes the interdependence of these mechanisms and the importance and implications of the scale of analysis in transport studies, and (3) addresses the primary goal of the study of physical mechanisms--to define a working approximation of the three-dimensional ground-water velocity field affecting the contaminant plume, by building upon the information and knowledge gained in the hydraulic analysis and description of solute distribution (fig. 2, boxes VI and VII).

Advection is the process by which solutes are transported by the bulk motion of the flowing ground water (Freeze and Cherry, 1979, p. 75). The bulk motion of the flowing ground water is characterized by the average linear velocity (v), which is defined as:

$$v = - \frac{K}{n} \frac{dh}{dl}$$

where:

K = hydraulic conductivity (L/T),

n = porosity (dimensionless),

h = hydraulic head (L), and

l = distance along a flowline (L).

Although thus far, analyses have been possible on a qualitative level, quantitative methods (analytical or numerical modeling) which can calculate the specific paths of particles of ground water in the vicinity of the contaminant plume are needed to understand the ground-water velocity field and approximate the physical movement of the plume. Hydraulic conductivity and porosity values are needed to make these quantitative estimates. These parameters, used to calculate the average linear velocity, usually vary significantly in three dimensions in natural ground-water systems and depend on the size of the volume of aquifer over which they are averaged.

A major part of understanding the physical mechanisms is development of a representation of the ground-water system in the local area around the plume which includes sufficient hydrogeologic detail to define

a suitable approximation of the ground-water velocity field. This can only be achieved through a detailed model in the area of the plume which relies on the hydraulic analysis to (1) estimate boundary conditions and (2) provide an initial estimate of fine-scale hydrogeologic features in the local area. However, an accurate representation of the local system can only be achieved through application and sensitivity analysis with the local model. Thus, understanding is built in a recursive manner. One must understand the system to develop a model, but the model should help one understand the system better. The "feedback" or recursive nature of the analysis results in a continually evolving and improving representation and understanding of the system.

An additional complexity introduced in this phase of the analysis is that the Darcian velocities developed with a flow model differ from the actual velocities required for transport analysis in that the average linear velocity (v) is the Darcian velocity (q) divided by porosity (n); that is

$$v = q/n.$$

Thus, a new spatially varying parameter, the porosity (n) of the porous material in the neighborhood of the point at which velocity is calculated, is introduced. Errors in estimating the magnitude and distribution of porosity produce proportional errors in estimates of actual ground-water velocity.

A more subtle difference between the velocity field developed with a flow model designed for basic hydraulic analysis (box VI) and the velocity field required for transport analysis (box VIII) is the scale at which the physical processes are considered. In the analysis of ground-water flow, the flow field is usually studied at a scale that is much larger than the scale of a contaminant plume because an accurate definition of boundary conditions is required for a physically reasonable simulation. At this larger scale, the properties of the porous medium and variations in velocity are averaged. In the analysis of the velocity field for transport analysis, however, a more detailed scale is needed. This finer scale enables variations due to the heterogeneous nature of the porous media to be represented if possible. It also enables more resolution in describing changes in velocity (both magnitude and direction) due to the three-dimensional movement of the ground water in response to local conditions.

Regardless of the degree of detail included in the representation of the flow field used to calculate the ground-water velocities, however, variations between actual and calculated velocities remain that cannot be accounted for explicitly. In any calculation of advective transport, whether by numerical model or by using an analytical solution, we assume that the velocity is uniform or varies in a simple way over specified regions of the flow field. For example, suppose a uniform flow in the x direction is simulated using the array of model nodes shown in figure 6. In calculations of solute transport using numerical models, velocity in the x direction is assumed to be uniform or vary in a simple way (such as bilinear inter-

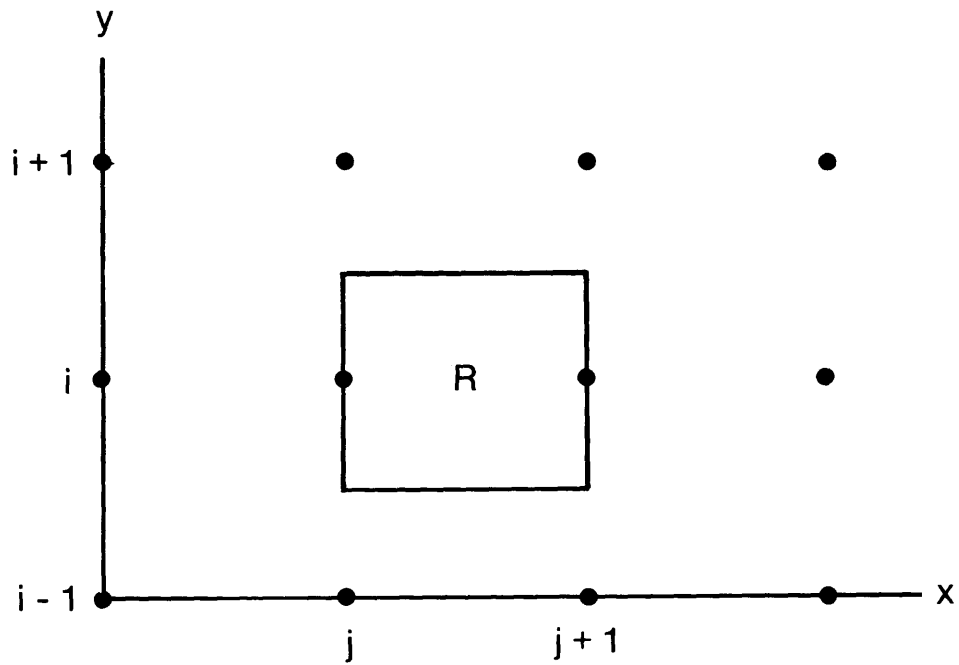


Figure 6. Diagram showing an array of model nodes with region R between two representative nodes.

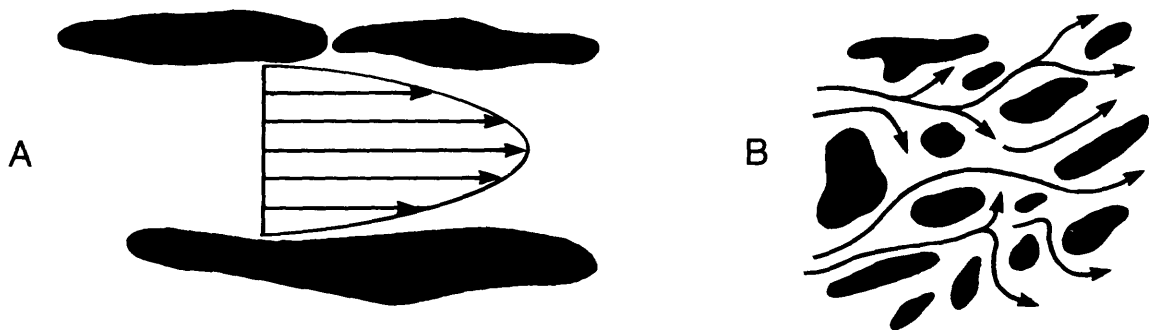


Figure 7. (A) Approximate fluid velocity distribution in a single pore; and (B) Tortuous paths of fluid movement in an unconsolidated porous medium.

polation) in both magnitude and direction over the rectangular region R, which extends between adjacent nodes in the x direction. This uniformity is vertical as well as areal--that is, within the area R, velocity is assumed to be constant over the vertical depth interval represented by the simulation. By contrast, the actual ground-water velocity in the block of aquifer represented by R would exhibit spatial variation over a range of scales.

At the microscopic (pore) scale, velocity varies from a maximum along the centerline of each pore to zero along the pore walls, as shown in figure 7A; both the centerline velocity and the velocity distribution differ in pores of different size. In addition, flow direction changes as the fluid moves through the tortuous paths of the interconnecting pore structure, as shown in figure 7B.

At a larger (macroscopic) scale, local heterogeneity in the aquifer causes both the magnitude and direction of velocity to vary as the flow concentrates along zones of greater permeability or diverges around pockets of lesser permeability. In this discussion, the term "macroscopic heterogeneity" is used to suggest variations in features large enough to be readily discernible in surface exposures or test wells, but too small to map (or to represent in a mathematical model) at the scale at which we are working. For example, in a typical problem involving transport away from a landfill or waste lagoon, macroscopic heterogeneities might range from the size of a baseball to the size of a building.

Figure 8, which shows some results of laboratory tracer experiments in heterogeneous media by Skibitzke and Robinson (1963), illustrates the effects of macroscopic heterogeneity. The net effect is to increase the spreading of the solute in the system. These effects tend to increase progressively with the scale of the heterogeneities. At a still larger scale, we can envision heterogeneities that could be mapped at the scale at which we are working, and which could be taken into account in our calculations of advective transport, but which simply have not been recognized in the field or accounted for in simulation. Mercado (1967 and 1984) showed this effect in an analysis of the spreading of injected water that was caused by stratified layers of different permeabilities.

The velocity variations described for these three scales share certain characteristics:

- (1) they may occur both areally and vertically over the region R (fig. 6);
- (2) they influence the distribution of ions or tracers moving through the system; and
- (3) they are not represented in calculations of advective solute movement through the region R that are made using the uniform model velocity.

Using the velocity from the model, a tracer front introduced at the left side of region R would be predicted to traverse R as a sharp front moving with the average linear velocity of the water. In reality, however, a tracer front becomes progressively more irregular and diffuse as it moves

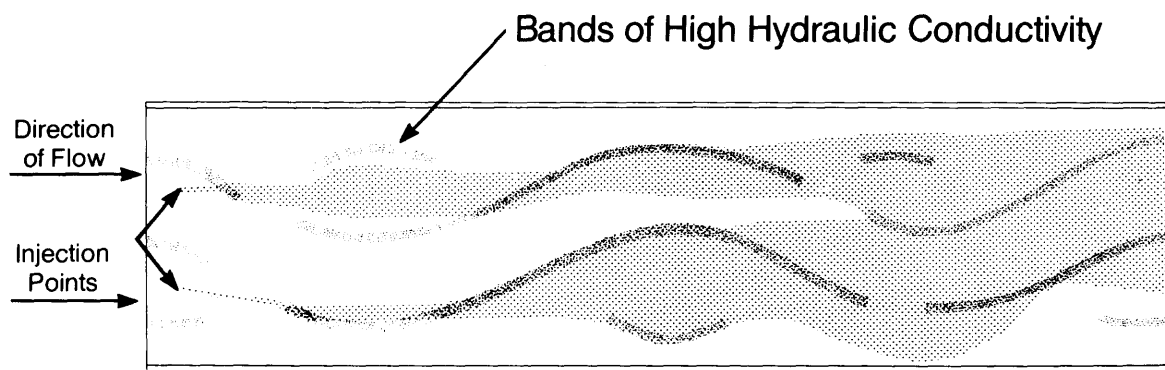


Figure 8. Results of a laboratory experiment to determine the effects of macroscopic heterogeneity on a tracer (modified from Skibitzke and Robinson, 1963).

through a porous medium. If we consider a vertical plane through the aquifer at the left edge of region R, the actual velocity varies in both magnitude and direction from one point to another; and the same holds true in the flow direction. Thus each tracer particle enters R at a velocity that is generally different from that of its neighbors, and each particle experiences a different sequence of velocities as it crosses R from left to right. Instead of a sharp front of advancing tracer as shown in figure 9A, we see an irregular advance as in 9B with the forward portion of the tracer distribution becoming broader and more diffuse with time. The pore-scale or microscopic velocity variations contribute only slightly to this overall dispersion; macroscopic variations contribute more significantly, while "mappable" variations generally have the largest effect.

If it were possible to generate a model or a computation that could account for all of the variations in velocity in natural aquifers, dispersive transport would not have to be considered (except for molecular diffusion); sufficiently detailed calculations of advective transport could theoretically duplicate irregular tracer advance observed in the field. In practice, however, such calculations are impossible. Field data at the macroscopic scale is never available in sufficient detail, information at the "mappable" scale is rarely complete, and descriptions of microscopic scale variations are never possible except in a statistical sense. Even if complete data were available, however, an unreasonable computational effort would be required to define completely the natural velocity variations in an aquifer.

The more closely we represent the actual permeability distribution of an aquifer, the more closely our calculations of advective transport will match reality; the finer the scale of simulation, the greater will be the opportunity to match natural permeability variations. In most situations, however, when both data collection and computational capacity have been extended to their practical limits, calculations of advective transport will fail to match field observation, so that we must find a tractable method of adjusting or correcting such calculations.

Historically, the effort to develop such a method of correction followed the diffusion model. Diffusion had been successfully analyzed as a process of random particle movement which, in the presence of concentration change, results in a net transport proportional to the concentration gradient in the direction of decreasing concentration. In the case of a moving fluid, the random movement ascribed to diffusion was viewed as superimposed on the motion arising from the fluid velocity. Thus, the net movement of any solute particle could be regarded as the vector sum of an advective component and a random diffusive component.

By analogy, it was assumed that solute transport through porous media could be viewed in the same way, as the sum of an advective component in which solutes move with the average linear velocity of the fluid, and a random "dispersive" component superimposed on the advective motion (Saffman, 1959). In effect, dispersion became the net transport with respect to a point moving with the average linear velocity of the fluid. Because the dispersive motion of solute particles was assumed to be random, the flux was taken to be proportional to the concentration gradient.

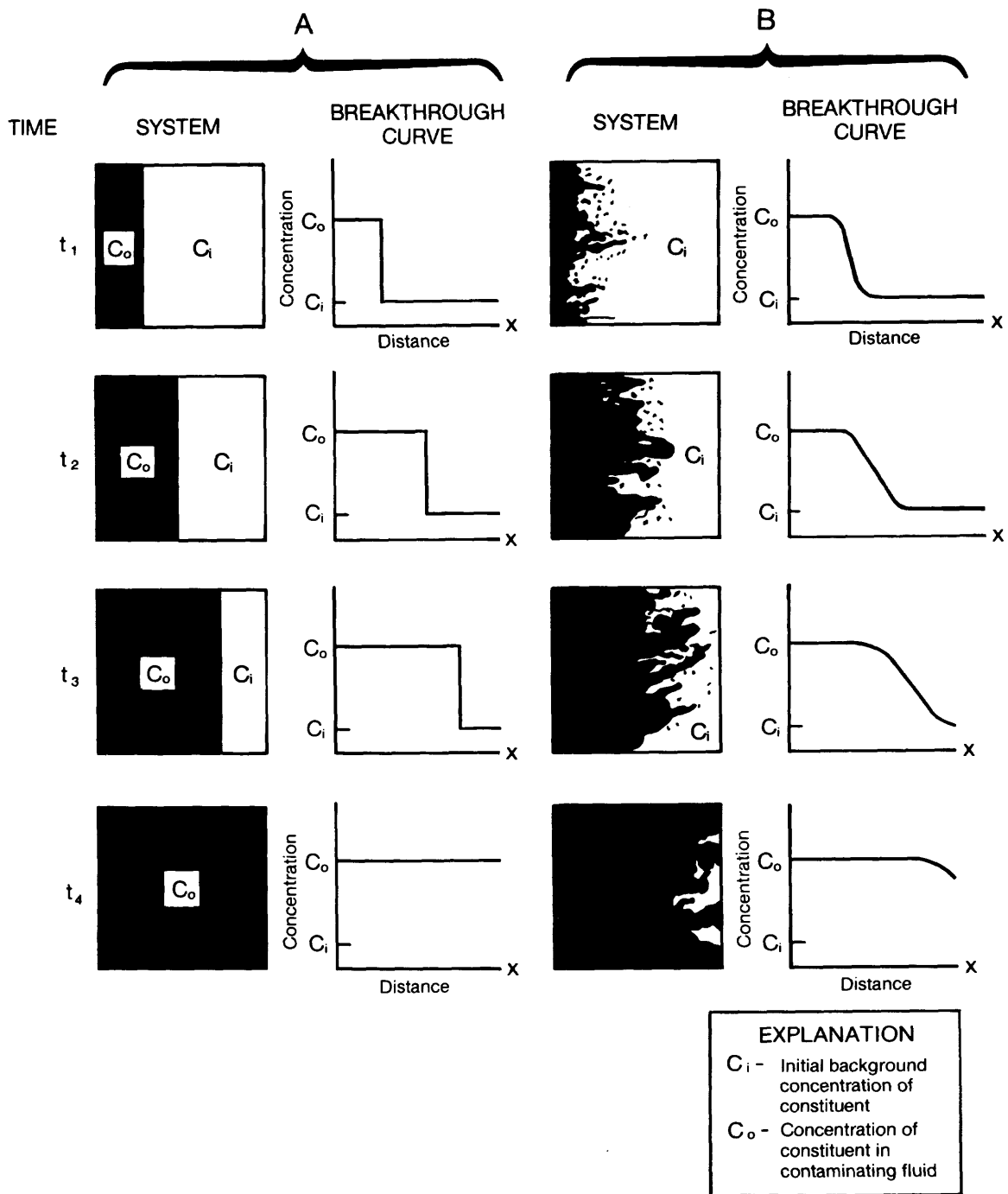


Figure 9. Advance of a tracer for: (A) a sharp front and (B) an irregular advance.

While many difficulties have been perceived with the concentration-gradient approach, no satisfactory alternatives have yet been found. Currently, we know that some method is required to adjust and correct the results of advective transport calculations. The method commonly employed is to postulate an additional transport proportional to the concentration gradient in the direction of decreasing concentration; however, the coefficient of proportionality is treated as a function of the average flow velocity.

This approach can be derived or justified mathematically if assumptions similar to those used in the analysis of molecular diffusion in moving liquids are made--that is, if the actual velocity of particles through the system can be described as the sum of two components, the average velocity used in advective calculation, and a random deviation from the average velocity. To the extent that scale variations represent random deviation from the velocity used in advective transport calculation, and to the extent that they occur on a scale which is significantly smaller than the size of the region used for advective calculation (for example, region R of figure 6), dispersion theory may adequately describe the differences between advective calculation and field observation. However, if the velocity variations are not random, or occur on a scale which is large relative to the region used for advective calculation, the suitability of the dispersion approach is questionable. Moreover, even when the approach appears to be justified, determination of the coefficients needed to implement it must usually be approached empirically (for example, through model calibration). The range of validity of the quantities determined in this manner is uncertain.

Variations in velocity arise predominantly from variations in the permeability and effective porosity of the porous medium, on each of the relevant scales. In theory, therefore it should be possible to describe the dispersive transport process through statistical analysis of variations in aquifer permeability. Gelhar and Axness (1983) have attempted this by using a stochastic analysis of permeability variation at the macroscopic scale to generate dispersivity values. The utility of this approach is currently limited by the difficulty in obtaining the necessary data on the statistics of permeability variation. However, Gelhar has demonstrated that in the limit, as distances of transport become large, a concentration-gradient approach is justified on theoretical grounds.

Because dispersive transport actually represents an aggregate of the deviations of actual particle velocities from the velocity used in advective transport calculation, coefficients of dispersion must be varied as the overall velocity of flow varies in order to create agreement between computed and observed results. As overall flow velocities in the system are increased, the magnitude of velocity deviations from the average velocity used in advective calculation must increase as well; therefore, dispersive transport is dependent on average flow velocity.

The description of dispersion in terms of velocity variation implies that problem scale must be a factor in any calculation of dispersive effects. As the size of the region used for advective transport calculation (for

example, region R in figure 6) is increased, more heterogeneities will be included in that region. If a very small region of calculation is chosen (for example, corresponding to the size of a laboratory column), the dominant heterogeneities within it will be those at the pore scale; dispersive effects and dispersion coefficients will be correspondingly small. As the region R becomes larger, macroscopic and ultimately "mappable" heterogeneities are dominant. Thus as larger regions of calculation are taken, the dispersive effects tend to increase in magnitude, the coefficients required for their description become more difficult to determine, and the applicability of the conventional concentration-gradient approach becomes questionable. In general, the scale at which advective transport calculations are made (for example, the scale of discretization in a model analysis) should reflect the existing level of knowledge of heterogeneities in the system. The scale should be fine enough so that the effects of all recognized heterogeneities can be accounted for by advective transport, yet coarse enough so that individual regions of advective calculation are large with respect to their unknown internal heterogeneities, which must be described by dispersive terms.

Thus, in any calculation of the physical mechanisms of solute transport, advection and dispersion are interrelated, and the appropriate values of dispersion depend on the scale at which the advective field is quantified. Because of this, dispersion is frequently used to account for unknowns in the flow field at the scale of interest. The uncertainties involved in defining a numerical coefficient (coefficient of dispersion) to quantify dispersion in a given field situation have been referred to as the "ignorance factor" in our understanding of advective movement. For this reason dispersion coefficients used in field scale problems should not be extrapolated from other sites or laboratory experiments. The best dispersion coefficients for a particular field problem at a particular scale of interest are obtained through trial and error analysis of historical information--that is, the dispersion coefficient is varied until it best reproduces the history of the contaminant plume. Because dispersion is not a distinct physical process that can be isolated from other factors, any estimate of future conditions (prediction) requires a sensitivity analysis to determine possible ranges of dispersive transport at the specific site. Predictions of plume migration over a distance significantly greater than the observed plume extent affects the scale of the transport problem and, therefore, may affect the value of the dispersion coefficient that best represents field conditions.

Characteristics and uncertainties other than lithologic heterogeneities contribute to the ignorance factor. These include temporal variations in velocity not explicitly taken into account; errors in map location of sampling points, lengths and position of well screens; and misinterpretation of data from long well screens and other sampling biases. Understanding the advective flow field in as much detail as possible at the scale of interest is one of the best ways to minimize the ignorance factor. Aside from detailed measurements based on actual historical information or tracer tests over the time and distances of interest, numerical simulation is the best approach to obtain a quantitative estimate of the velocity (advective flow) field. However, analyses by hand calculation involving flow nets and analytical solutions are also useful in estimating the velocity field or in checking simulation results. Regardless of the approach used to estimate the velocity field,

it is imperative that a sensitivity analysis be used to obtain insight into the effect of uncertainties in estimates of the parameters on the analysis of the velocity field.

Accurate simulation of the velocity field in the neighborhood of the contaminant plume may require a much finer scale of discretization than is used in the regional analysis of ground-water flow. To derive maximum benefit from the finer scale of discretization in the form of a more accurate local distribution of ground-water velocities requires that the variations in porosity and hydraulic parameters also be defined accurately at this finer scale. Robertson's (1974) study of several plumes at the National Reactor Testing Station used two differing scales of discretization (fig. 10) to study contaminant plumes--a relatively fine scale for the area including the contaminant plume, and a coarser grid designed to simulate the regional ground-water flow system.

The adequacy of the flow model to generate a physically meaningful velocity field may also be related to the dimensionality of the flow simulation. Because all natural flow systems are three-dimensional, three components are needed to completely define the velocity vector at a point in the flow system. In many situations it is useful and convenient to approximate the three-dimensional system in nature with a two or even one-dimensional simulation. Two-dimensional flow models in the (approximately) horizontal plane are a common example of this approach. Again, the specific situation under study and the requirements for the results of the simulation will determine whether such a simplification of the problem is warranted. In many cases such a simplification will provide a very adequate simulation. However, it is important to recognize that flow at the scale of interest in transport studies is almost always three-dimensional in nature.

In simulating advection and dispersion for a field situation, the flow field can be simulated using a three-dimensional flow model which can then be used as boundary conditions for a two-dimensional transport (simulating advective and dispersive movement) model. This two-dimensional representation of the physical mechanisms of solute transport has both conceptual and computational advantages. Conceptually it is easier to understand the response of a two-dimensional system to changes in parameters; and computationally transport models require considerably finer grid sizes as well as increased computer storage and computation time compared to flow models, and have only been applied with consistent success in one- or two-dimensional applications. However, averaging the solute concentrations that exist in three-dimensional space in the natural system into either a one- or two-dimensional representation can introduce at the outset a significant approximation that may not be valid. LeBlanc (1984b) used a two-dimensional transport (and flow) simulation, but recognized and discussed the consequences of this simplification in the analysis of the actual three-dimensional plume.

At this stage in the analysis, the importance of identifying conservative chemical constituents or parameters, mapping their three-dimensional distribution in the contaminant plume, and using this information in the analysis of the physical mechanisms of solute transport becomes manifest. The credibility of the physical transport simulation is enhanced considerably by comparison between simulated results and field data on conservative

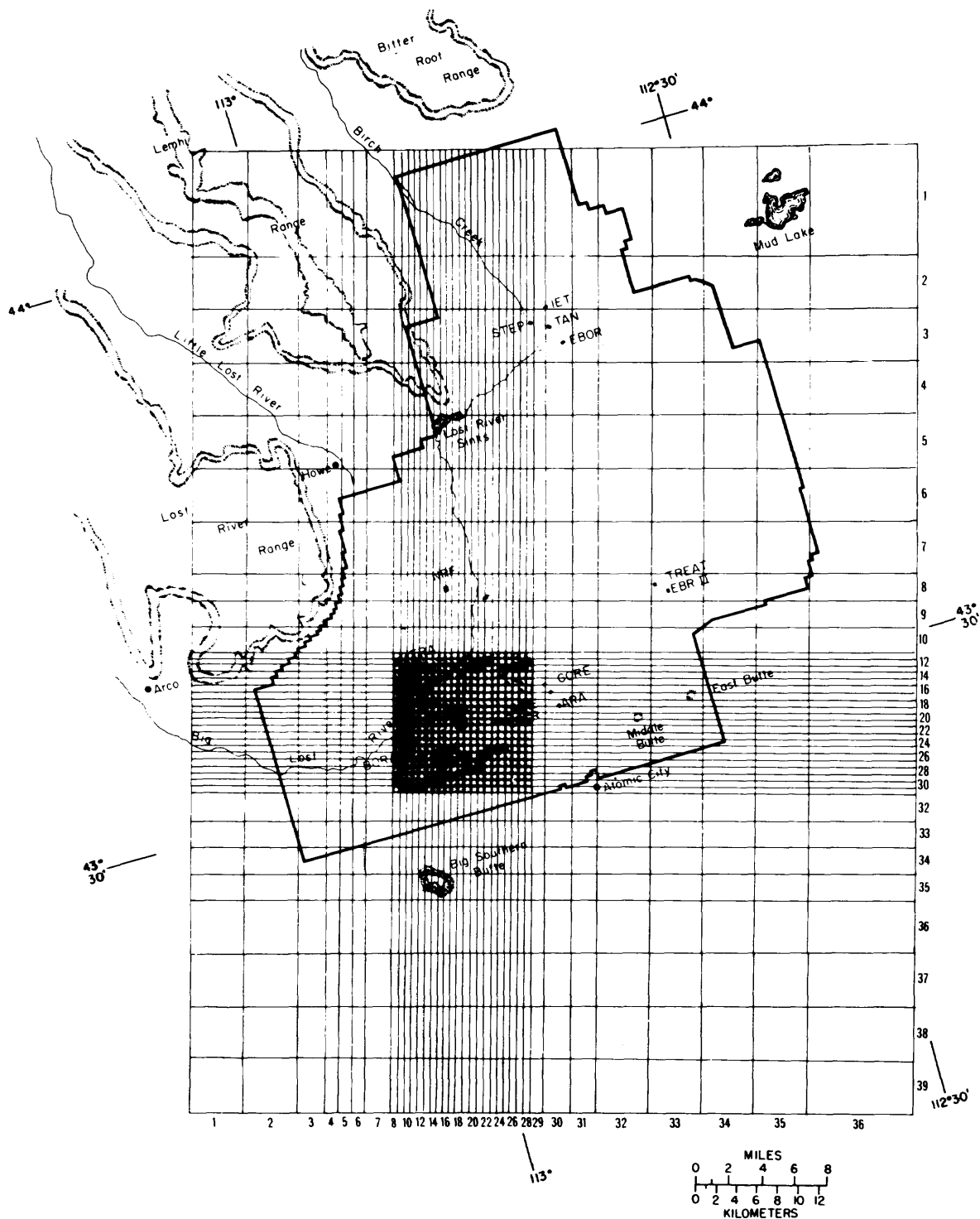


Figure 10. Finite-difference grid map used by Robertson (1974) showing two scales of analysis. Flow simulation included entire grid, whereas solute transport model included only shaded part (smallest nodal spacing).

constituents. If no conservative parameters exist, then a larger degree of uncertainty usually will be associated with the physical mechanisms. Once a physically reasonable representation of the velocity field is defined (or at least the velocity field is bounded through use of the sensitivity analysis), the advective movement of ground water can be determined. This analysis involves using either (1) "stream functions" to define flow paths as in a flow net for steady-state conditions, (2) a numerical particle-tracking algorithm to define path lines, or (3) some other numerical technique. Once the path lines are defined using the refined velocity field, various time-of-travel estimates assuming piston or plug flow at the average linear velocity can be made for the movement of contaminants.

In conclusion, numerical tools are generally necessary for defining the physical mechanisms of solute transport. The scale required to analyze the advective movement of a solute may differ considerably from the scale required to analyze regional ground-water movement. To accommodate both scales of interest, two flow models can be coupled--the regional model (fig. 2, box VI) providing boundary conditions for the local model that simulates the advective movement of ground water in and near the contaminant plume.

Furthermore, the chemical boundary conditions (source location in space and time, source concentration, capability of solute to leave the simulated area) used in assessing advective movement and dispersion generally involve considerable uncertainty and must be critically evaluated. In the process of determining a reasonable estimate for the coefficient of hydrodynamic dispersion (which is the coefficient in the governing differential equation which quantifies the dispersive process and includes molecular diffusion), a chemically conservative substance or parameter in the contaminant plume should be used for reference. Following this procedure ensures the necessary focus on the physical processes of dispersion as opposed to more complex combinations of mixing and chemical or microbial reactions.

Finally, because of the introduction of additional physical parameters, such as porosity and dispersion, and uncertainties associated with definition of sources (chemical boundary conditions), sensitivity analysis should always be used to bound the estimates (predictions) of future contaminant movement.

Chemical and Microbiological Controls on Solute Transport

Although chemical and microbiological controls on solute transport are not discussed in detail, they are included in the flowchart (fig. 2, box IX) to acknowledge their significant, if not dominant, role in a complete analysis of a solute transport problem. The purpose of this phase of the analysis is to understand the chemical environment as thoroughly as available data and present-day chemical concepts permit by explaining the sources and sinks of the various constituents observed in the contaminant plume. These sources and sinks can affect greatly the distribution of the various

constituents in the plume. The Stanford-Waterloo Research Project (United States Environmental Protection Agency, 1986) shows the effect of chemical reactions on the distribution of a constituent. Figure 11 contrasts the areal extent of a conservative (chloride) and two non-conservative organic compounds documented by this study.

The level of analysis applied to this phase of the study can range from relatively simple to state-of-the-art chemical concepts. The appropriate level of complexity is determined by the purpose of the project, the chemical composition of the native water and mineralogy of the earth materials, and the chemical composition of the contaminants. Analysis can range from consideration of a single chemical reaction, as applied to phosphorus on Cape Cod, Massachusetts (figure 4A) by LeBlanc (1984a), to more sophisticated analysis that assumes multiple interrelated chemical reactions, such as the study of a landfill in Delaware by Baedecker and others (Baedecker and Apgar, 1984; and Baedecker and Back, 1979) and of the Borden Landfill, Borden, Ontario, by Nicholson and others (1983).

The relevant chemical processes, reviewed by Cherry and others (1984), and their incorporation into mathematical solute transport models, reviewed by Rubin (1983), are current topics of research. Historically, multisolute analysis has been based on an equilibrium concept (reactions classified by Rubin (1983) as "sufficiently fast" and reversible). Chemical equilibrium models (Plummer, Parkhurst and Thorstenson, 1983), which do not account for the physical transport mechanisms of advection and dispersion, are capable of increasing our understanding of the chemical system under these sufficiently fast conditions. The other major class of reactions is classified as "insufficiently fast" and/or irreversible reactions (Rubin, 1983). This type of analysis is based on reaction rate equations in which the chemical coefficients for large groups of solutes may be difficult to determine, and the mathematical formulation of the equations is more complex.

At present, numerical simulations of solute transport that account for advection and dispersion usually include only extremely simplified chemical reactions. For example, Gillham and Cherry (1982) state: "In models that include the effects of advection, dispersion, and reaction, the reaction term rarely describes more than the effects of reversible linear sorption represented by linear isotherms." However, research is continuing in this area and limited multisolute simulations with realistic chemical reactions are being attempted (Lewis and others, 1986).

Regardless of the level of study to be undertaken, the magnitude of changes in the chemical composition of water and aquifer materials in the contaminant plume that occur in space and time because of (1) inorganic reactions, (2) organic reactions, and (3) microbiologically controlled reactions must be evaluated. A hydrologist can often evaluate the importance of some of the simpler and better understood chemical reactions; however, investigation of more complex chemical mechanisms generally requires the combined efforts of geochemists, organic chemists, and microbiologists.

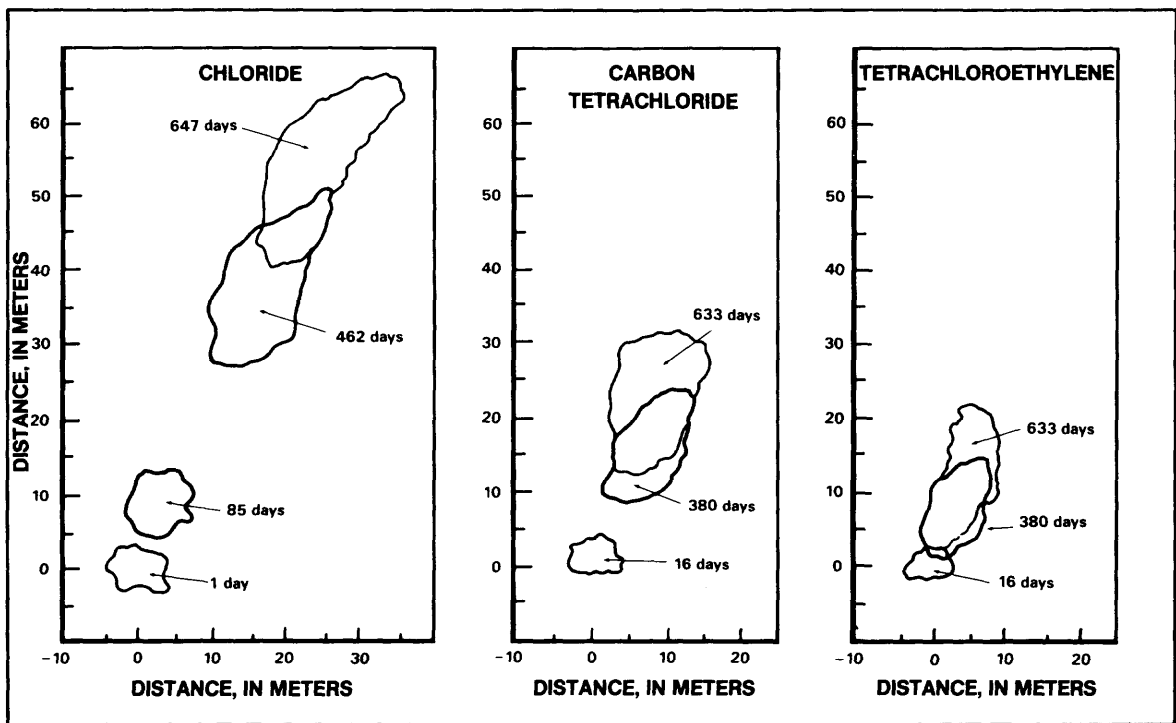


Figure 11. Location of three chemical plumes at selected time intervals at the Stanford-Waterloo Project site. Time contours shown are depth averaged. (U.S. Environmental Protection Agency, 1986).

Synthesis of Physical and Chemical Analyses

Although the final synthesis phase of the transport study is represented as box X at the bottom of the flow chart in figure 2, attempts at synthesis take place continuously throughout the entire study. In short, the synthesis of the physical and chemical analyses to obtain the best possible understanding of solute transport in the ground-water system is the integration of the hypothesized chemical and physical mechanisms used to describe the transport that has been observed.

Levels of integration for the hypothesized chemical and physical mechanisms range from a summary of observations and possible reasons for these observations to a complete, complex, state-of-the-art numerical analysis involving physics, chemistry, and microbiology. As noted previously, the flow chart in figure 2 shows an exit point from the preliminary analysis phase (box III) indicating that it is possible for a sufficient understanding to be achieved from information already available at that stage.

Whatever the technical level of the study, however, the final integration of the chemical and physical mechanisms should result in an integrated description of the contaminant plume that is devoid of technical inconsistencies. Uncovering inconsistencies at any stage of the study offers opportunities to explore other explanations that may result in a better understanding of processes and mechanisms. Numerical simulation is valuable because it integrates quantitatively the effects of the various components and mechanisms assumed to be operating and thereby points out inconsistencies between model results and field data. Thus, numerical simulation is the best way to test hypotheses and integrate the various pieces.

An increased understanding of the system and physical mechanisms evolves from the integration of all the "pieces". Furthermore, at this stage, investigators must reassess all assumptions made throughout the study to ensure their validity.

If a reasonable understanding of the ground-water system and associated mechanisms of physical and chemical transport has been attained, then a prediction (or preferably 'estimate') of future events may be acceptable. However, the uncertainties and error involved in transport analysis make future estimates tentative at best. Thus, any prediction (or estimation) should include a "reasonable" range in the values of relevant parameters to illustrate the uncertainty involved in the transport analysis.

ROLE OF SIMULATION

The words "model" and "simulation" have been used frequently in a variety of contexts in the preceding discussion. Simulation, or the application of models, is perhaps the most powerful tool available to the hydrologist for analyzing and increasing his or her understanding of the

flow system and transport mechanisms. Different approaches to simulation are an integral part of, and prove to be of great value in, all phases of an investigation involving ground-water flow or transport.

A number of "models" that exhibit differing levels of complexity are available to the investigator for application to ground-water flow problems, either with or without solute transport. For discussion, these models are grouped into two general categories: (1) analytical solutions for relevant boundary-value problems, and (2) computer codes that provide a numerical solution to the governing (partial) differential equation and associated boundary and initial conditions that define a given problem.

The first class of models, formal closed form mathematical solutions to relevant boundary-value problems, simulate systems that are highly idealized and generally simple relative to the usual complexity of natural systems. For example, in these systems the external geometry is usually simple (squares, rectangles, and circles or three-dimensional equivalents), and the flow medium is at least homogeneous, if not isotropic and homogeneous, so that the properties of the flow medium are easily specified. In view of this inherent simplicity, the similitude between the system represented in the mathematical solution and the natural system is never exact and is often rather poor. However, valuable qualitative insight into the real system can be gained through relatively easy experimentation with similar hypothetical systems. In general, however, considerable care is required to relate one or more of the available mathematical solutions to the natural system under study.

Boundary conditions are a key feature to consider in selecting a mathematical solution and in evaluating the degree of correspondence between the two systems. The value of applying analytical solutions to a field situation often lies in using them to define limiting cases and then comparing the results of the analytical solution with field data. For example, an analytical solution might represent advective and dispersive transport of a conservative solute in a highly idealized flow field. By judicious selection of the parameters for several cases, the results from a series of solutions to this hypothetical problem may bracket the distribution of a conservative constituent in the field problem. If this bracketing does not occur, something is occurring in the natural system that requires further explanation. Some of the available analytical solutions for problems in solute transport are given by Bear (1972), Bear (1979), Freeze and Cherry (1979), and Javandel and others (1984).

The second general category of models, computer codes that solve the governing differential equations numerically, represent the most flexible and powerful means of simulating systems involving solute transport, in that they are able to consider explicitly complex systems and problems. These models also represent the most powerful tool available to assist the hydrologist in increasing his or her understanding of the flow system and the mechanisms of solute transport.

A highly simplified flow diagram representing the general process of developing a transport model is shown in figure 12. This diagram emphasizes two major aspects of this complex process. First, the development of the

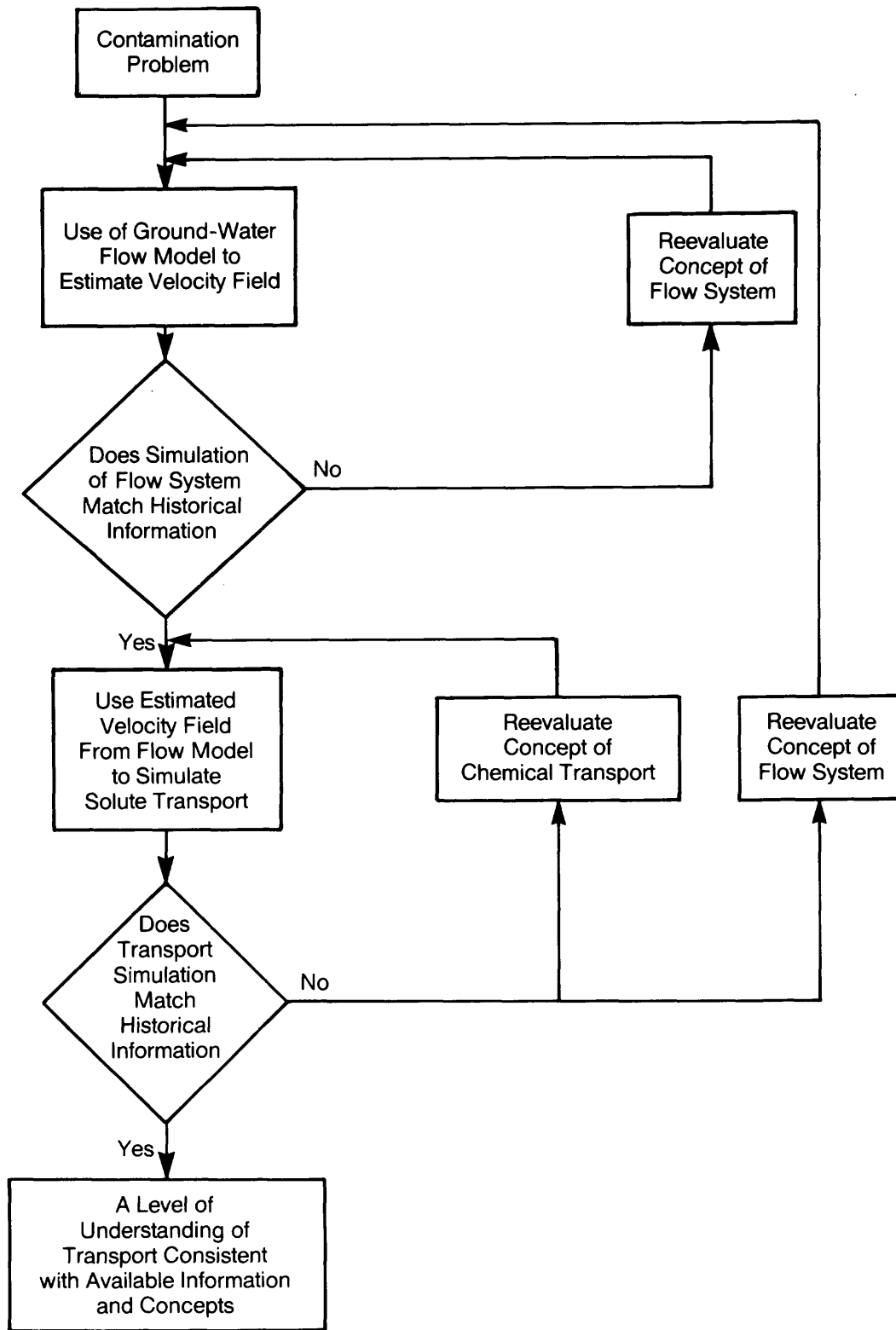


Figure 12. Role of simulation in the analysis of solute-transport problems.

transport model occurs in two phases for constant fluid density problems-- (1) initially, the development of the ground-water flow model alone and (2) subsequently, the development of the coupled ground-water flow model and solute-transport model. Second, as indicated by the feedback loops in figure 12, a critical comparison and evaluation of model results and field data is a continuing part of this process of developing a solute-transport model. At no point in this process can the investigator ignore the possibility that basic concepts regarding either the flow system or mechanisms of solute transport may need to be modified or completely changed. This recursive process of continuing critical evaluation at each small step is the basis for successful simulation and increased understanding of the ongoing physical, chemical, and microbiological processes.

From another point of view, the extensive capability of these numerical models is also their main potential weakness. Many simulations using these models are necessarily complex, and frequently are based on poorly defined, complex physical systems. Furthermore, such simulations use parameters that vary in three-dimensions and must be estimated from inadequate field data. This complexity in conjunction with the large uncertainty in the value of many of the field parameters gives ample opportunity for the hydrologist attempting to apply these models to misinterpret the results of the model simulations. This situation underscores the need for the investigator to continuously apply and study models with differing levels of complexity at the same time. Analytical solutions and even simple hand calculations should be applied wherever possible in conjunction with numerical simulations. Finally, a sensitivity analysis of the various parameters, and perhaps boundary conditions, at all stages of model complexity will invariably increase the hydrologist's insight into the physical system under study. (For an example of such sensitivity analysis, see LeBlanc, 1984b.)

A considerable and ever-increasing number of computer codes dealing with solute-transport problems is available. These "models" may be classified in general terms by the numerical approach used to solve the differential equation(s) and the complexity or specific type of problem the code is designed to solve. The most common numerical approaches to this problem are the finite difference, finite element, random walk, and the method of characteristics. Model complexity is generally measured in terms of the number of dimensions the code can handle (one, two, or three), whether or not the code considers explicitly the density (and/or viscosity) of the flowing fluid, and the complexity of the chemical reactions that can be incorporated into the numerical model. Numerical models are most useful when accompanied by complete documentation of the theory and a users guide. Some widely used numerical transport codes include Konikow and Bredehoeft (1978), Prickett and others (1981) and Voss (1985). In addition, a good "general-purpose" numerical ground-water flow model that can be used to estimate pathlines (the curve described by a particle during its motion) is that developed by McDonald and Harbaugh (1984).

Simulation is a very powerful tool for analysis, in that it accounts for all or most of the physical and chemical processes simultaneously, as in nature. Thus, simulation attempts to integrate all components of the transport system. However, an important adjunct to these mathematical and numerical

simulations are simple calculations that evaluate single components of the complex system to give insight into individual processes and to check the soundness and understanding gained from the complex models. Three simple hand calculations were enumerated in the preceding discussion: 1) water-budget calculations for the entire ground-water system and for the local area near the contamination site; 2) calculation of average linear velocities, travel times and distances; and 3) estimates of the mass of key chemical constituents in the plume.

In addition, plotting a given chemical constituent in plan or vertical cross section may result in a spatial distribution that appears physically unreasonable. Sometimes, the difficulty lies with the chemical data themselves. A number of simple checks can determine whether the results of a chemical analysis are at least consistent. One of the simplest of these checks is to determine whether, or how well, the anion and cation equivalents balance. Undoubtedly, additional hand calculations specific to a field problem can be employed as an easy means of gaining understanding of the specific problem.

The preceding discussion is an attempt to convey the central role of simulation, which may proceed in parallel at different levels of complexity, as a guide to stimulate thinking and assist the investigator in analyzing the ground-water solute-transport system under study. The process of investigation consists, in part, of continuing comparisons between field data and results of various simulations, followed by a critical evaluation of similarities and differences that result from these comparisons. This approach leads to a better understanding of the system and processes involved. As noted previously, only after an adequate level of understanding has been reached can estimates (or predictions) of future conditions and movement of solutes be undertaken; and such "predictions" must include an explicit statement regarding their range of uncertainty.

SUMMARY AND CONCLUSIONS

The U.S. Geological Survey has undertaken and will continue to undertake studies of the movement of solutes in ground water from point sources near the land surface. These studies involve a level of complexity that requires intensive and costly investigation. This report outlines a systematic approach to such investigations that is based on a recursive process which leads to a continually increasing level of understanding of the ground-water system and relevant physical processes of solute transport.

The approach uses a preliminary analysis prior to collection of new data to focus on the technical problems to be addressed and to direct the initial collection of new data if warranted. The field investigation (collection of new data) progresses in stages that use the new knowledge and understanding gained from the preceding data collection to aid in further data collection as the study proceeds.

A major premise of the approach is that the foundation of any analysis is a detailed quantitative definition of (1) the ground-water flow field in three dimensions, and (2) the distribution of solutes in the contaminant plume in three dimensions at one point in time, or preferably at more than one point in time. Simulation offers a means of quantifying the essential features of the ground-water flow field, and is an important tool for analysis. However, the scale of analysis for solute-transport studies is usually much finer than the scale of analysis for ground-water flow alone. Hence, an increase in detail of the velocity field is needed to provide for accurate calculations of pathlines in three-dimensional heterogeneous ground-water systems.

Solute-transport studies are interdisciplinary and involve considerable uncertainty. The framework presented is neither complete nor perfect and focuses primarily on the physical mechanisms. However, it does link the various important project components together indicating their important individual aspects. The role of simulation as an "integrating" factor that helps to increase our understanding of the complex interaction of all the system components is a key element in this framework. However, due to the uncertainty associated with most studies of this type, simulation is regarded primarily as a tool for gaining insight and understanding rather than for predictive purposes.

REFERENCES CITED

- Anderson, M. P., 1984, Movement of contaminants in groundwater: Groundwater transport-advection and dispersion: in Groundwater Contamination, Studies in Geophysics, National Academy Press, p. 37-45.
- Baedecker, M. J., and Back, W., 1979, Hydrogeological processes and chemical reactions at a landfill: Ground Water, v. 17, no. 5, p. 429-437.
- Baedecker, M. J., and Apgar, M. A., 1984, Hydrogeochemical studies at a landfill in Delaware: in Groundwater Contamination, Studies in Geophysics, National Academy Press, p. 127-138.
- Bear, J., 1972, Dynamics of fluids in porous media: American Elsevier, New York, 764 p.
- Bear, J. 1979, Hydraulics of groundwater: McGraw-Hill Book Company, New York, 569 p.
- Bredehoeft, J. D., and Pinder, G. F., 1973, Mass transport in flowing groundwater: Water Resources Research, v. 9, no. 1, p. 194-210.
- Buxton, H. T., and Reilly, T. E., 1987, A technique for analysis of groundwater systems at regional and subregional scales applied on Long Island, New York: in Selected papers in the hydrologic sciences 1986: U.S. Geological Survey Water-Supply Paper 2310, p. 129-142.
- Cherry, J. A. (Guest-Editor), 1983, Migration of contaminants in groundwater at a landfill: A case study: Journal of Hydrology, Special Issue, v. 63, no. 1/2, 197 p.
- Cherry, J. A., Gillham, R. W., and Barker, J. F., 1984, Contaminants in groundwater: in Groundwater Contamination, Studies in Geophysics, National Academy Press, p. 46-64.
- Claassen, H. C., 1982, Guidelines and techniques for obtaining water samples that accurately represent the water chemistry of an aquifer: U.S. Geological Survey Open-File Report 82-1024, 49 p.
- Franke, O. L., Reilly, T. E., and Bennett, G. D., 1987, Definition of boundary and initial conditions in the analysis of saturated ground-water flow systems--an introduction: Techniques of Water-Resources Investigations of the U.S. Geological Survey, Book 3, Chapter B5, 15 p.
- Freeze, R. A., and Cherry, J. A., 1979, Groundwater: Prentice-Hall Inc., Englewood Cliffs, N. J., 604 p.
- Gelhar, L. W., and Axness, C. L., 1983, Three-dimensional stochastic analysis of macrodispersion in aquifers: Water Resources Research, v. 19, no. 1, p. 161-180.

- Gelhar, L. W., Mantoglou, A., Welty, C., and Rehfeldt, K. R., 1985, A review of field-scale physical solute transport processes in saturated and unsaturated porous media: Electric Power Research Institute, EPRI EA-4190, 116 p.
- Gillham, R. W., and Cherry, J. A., 1982, Contaminant migration in saturated unconsolidated geologic deposits: in Recent trends in hydrogeology, Special Paper (Geological Society of America) 189, p. 31-62.
- Gillham, R. W., Robin, M. J. L., Barker, J. F., and Cherry, J. A., 1983, Groundwater monitoring and sample bias: American Petroleum Institute Publication 4367, 206p.
- Gillham, R. W., Robin, M. J. L., Barker, J. F., and Cherry, J. A., 1985, Field evaluation of well flushing procedures: American Petroleum Institute Publication 4405, 109p.
- Javandel, I., Doughty, C., and Tsang, C. F., 1984, Groundwater transport: Handbook of mathematical models, American Geophysical Union, Water Resources Monograph 10, 228p.
- Kimmel, Grant E., and Braids, Olin C., 1980, Leachate plumes in ground water from Babylon and Islip landfills, Long Island, New York: U.S. Geological Survey Professional Paper 1085, 38 p.
- Konikow, L. F., 1977, Modeling chloride movement in the alluvial aquifer at the Rocky Mountain Arsenal, Colorado: U.S. Geological Survey Water-Supply Paper 2044, 43 p.
- Konikow, L. F., 1981, Role of numerical simulation in analysis of groundwater quality problems: The Science of the Total Environment, v. 21, p. 299-312.
- Konikow, L. F., and Bredehoeft, J. D., 1978, Computer model of two-dimensional solute transport and dispersion in ground water: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 7, Chapter C2, 90 p.
- Konikow, L. F., and Grove, D. B., 1977, Derivation of equations describing solute transport and dispersion in ground water: U.S. Geological Survey Water-Resources Investigations 77-19, 30 p.
- Ku, Henry F. H., Katz, B. G., Sulam, D. J., and Krulikas, R. K., 1978, Scavenging of chromium and cadmium by aquifer material-South Farmingdale-Massapequa area, Long Island, New York: Ground Water, v. 16, no. 2, p. 112-118.
- LeBlanc, D. R., 1984a, Sewage plume in a sand and gravel aquifer, Cape Cod, Massachusetts: U.S. Geological Survey Water-Supply Paper 2218, 28 p.

- LeBlanc, D. R., 1984b, Digital modeling of solute transport in a plume of sewage-contaminated ground water: *in* Movement and fate of solutes in a plume of sewage-contaminated ground water, Cape Cod, Massachusetts: U.S. Geological Survey Toxic Waste Ground-Water Contamination Program: U.S. Geological Survey Open-File Report 84-457, p. 11-45.
- Lewis, F. M., Voss, C. L., and Rubin, J., 1986, Numerical simulation of advective-dispersive multisolite transport with sorption, ion exchange and equilibrium chemistry: U.S. Geological Survey Water-Resources Investigations Report 86-4022, 165 p.
- McDonald, M. G., and Harbaugh, A. W., 1984, A modular three-dimensional finite-difference ground-water flow model: U.S. Geological Survey Open-File Report 83-875, 528 p.
- Mercado, A., 1967, The spreading pattern of injected water in a permeability stratified aquifer: *in* Proceedings of the International Association of Scientific Hydrology Symposium, Haifa, Publication No. 72, p. 23-36.
- Mercado, A., 1984, A note on micro and macrodispersion: *Ground Water*, v. 22, no. 6, p. 790-791.
- Nicholson, R. V., Cherry, J. A., and Reardon, E. J., 1983, Migration of contaminants in groundwater at a landfill--a case study, 6. *Hydrogeochemistry: Journal of Hydrology*, v. 63, no. 1/2, p. 131-176.
- Perlmutter, N. M. and Lieber, Maxim, 1970, Dispersal of plating wastes and sewage contaminants in ground water and surface water, South Farmingdale-Massapequa area, Nassau County, New York: U.S. Geological Survey Water-Supply Paper 1879-G, 67 p.
- Pinder, G. F., 1984, Groundwater contaminant transport modeling: *Environmental Science and Technology*, v. 18, no. 4, p. 108A-114A.
- Plummer, L. N., Parkhurst, D. L., and Thorstenson, D. C., 1983, Development of reaction models for ground-water systems: *Geochimica et Cosmochimica Acta*, v. 47, no. 4, p. 665-685.
- Prickett, T. A., Naymik, T. G., and Lonquist, C. G., 1981, A "random-walk" solute transport model for selected ground-water quality evaluations: *Bulletin 65, State of Illinois, Illinois State Water Survey, Champaign, Illinois*, 103 p.
- Robertson, J. B., 1974, Digital modeling of radioactive and chemical waste transport in the Snake River Plain Aquifer at the National Reactor Testing Station, Idaho: U.S. Geological Survey Open-File Report IDO-22054, Waste Management TID-4500, 41 p.
- Rubin, Jacob, 1983, Transport of reacting solutes in porous media: relation between mathematical nature of problem formulation and chemical nature of reactions: *Water Resources Research*, v. 19, no. 5, p. 1231-1252.

- Saffman, P. G., 1959, A theory of dispersion in a porous medium: *Journal of Fluid Mechanics*, v. 6, p. 321-349.
- Scalf, M. R., McNabb, J. F., Dunlap, W. J., Cosby, R. L., and Fryberger, J., 1981, *Manual of ground-water sampling procedures*: National Water Well Association, 93 p.
- Skibitzke, H. E., and Robinson, G. M., 1963, Dispersion in ground water flowing through heterogeneous materials: U.S. Geological Survey Professional Paper 386-B, 3 p.
- United States Environmental Protection Agency, 1986, EPA Ground-Water Research Programs: EPA/600/8-86/004, EPA Office of Research and Development, 41 p.
- Voss, C. I., 1985, A finite-element simulation model for saturated-unsaturated, fluid-density-dependent ground-water flow with energy transport or chemically-reactive single-species solute transport: U.S. Geological Survey Water-Resources Investigations Report 84-4369, 409 p.
- Warrick, A. W., Biggar, J. W., and Nielsen, D. R., 1971, Simultaneous solute and water transfer for an unsaturated soil: *Water Resources Research*, v. 7, no. 5, p. 1216-1225.
- Yaron, B., Dagan, G., and Goldshmid, J. (eds.), 1984, *Pollutants in porous media--The unsaturated zone between soil surface and groundwater*: Springer-Verlag, Berlin, 296 p.