

APPLICABILITY OF MATHEMATICAL MODELS OF GROUND-WATER
FLOW SYSTEMS TO HYDROGEOCHEMICAL EXPLORATION

by

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PREFACE

This paper constitutes a response to a request by Dr. Rolland R. Reid, Director of the Idaho Bureau of Mines and Geology, to bring together the results of recent research on the regional flow of ground water which are pertinent to geochemical exploration for certain types of mineral deposits. The use of mathematical models as a tool for interpreting ground-water flow patterns is a well accepted technique in hydrogeology. However, few, if any, of the results of hydrogeological studies have been presented in a form which emphasizes their applicability to economic geology. While this paper comprises no new research in the field of hydrogeology, it presents information to which many economic geologists have not been exposed. It is hoped that the approach taken will provide a new basis for interpreting hydrogeochemical anomalies and perhaps a better understanding of the origin of certain types of ore deposits.

APPLICABILITY OF MATHEMATICAL MODELS OF GROUND-WATER FLOW SYSTEMS TO HYDROGEOCHEMICAL EXPLORATION

ABSTRACT

The growing interest in the use of dynamic ground water as a prospecting tool has accentuated the need for a conceptual framework within which such studies can be placed. This paper summarizes the results of studies which have utilized mathematical models as a means of analyzing patterns of ground water flow. The flow systems depicted by these models provide insight into the source areas for geochemical anomalies observed in ground water. The procedure proposed consists of the identification of geochemically anomalous ground-water discharge zones by a basin-wide sampling program. The recharge areas from which the anomalous, discharging ground water emanates are determined by the construction of mathematical models of the ground-water flow system in the basin in which the discharge area occurs. The criteria on which the mathematical models are based must be determined by hydrogeologic investigation.

INTRODUCTION

The role played by dynamic ground water in the evolution of mineral deposits currently is receiving considerable attention, primarily as a consequence of liquid inclusions studies and studies of the dissolved solids and isotope content of ocean water, brines and precipitation.

Ground water has been investigated as a medium from transporting certain dissolved ions to zones of accumulation (ore deposits), and as a tool for indicating the location of existing ore bodies. Customarily, however, the ground water has not been viewed in the context of a basin-wide flow system. This paper discusses the applicability of certain mathematical techniques used in ground-water studies to the search for ore bodies. The associated mathematical models also lend themselves to the examination of the flow of ground water adjacent to zones of mineral accumulation.

GROUND WATER AS A TRANSPORTING AGENT

That ground water does in fact act as a transport medium for substantial concentrations of dissolved minerals has been well documented. Included among the more recent studies which provide data on specific ions transported by ground water are White (1968), Seaber (1965), Maderak (1964), Clayton et al. (1966), de Geoffroy et al. (1967), Helgeson (1968), Price and Ragland, (1968), and Skinner et al. (1967). The high concentration of a given ion in ground water may be a consequence of the exposure of the ground water to rocks consisting of a high percentage of a soluble compound of that ion, or a consequence of extended exposure to many rocks containing only disseminated quantities of soluble compounds of the ion. Regardless of source of ions, the above studies verify that ground water is a transport agent and that the ions dissolved in ground water reflect the rock types through which the water has moved, as well as the length of the flow path along which the water has traveled and the length of time the water has been exposed to the rock. The latter two factors make essential a basin-wide sampling program, so that true anomalies can be distinguished from background concentrations which also may be high.

FACTORS AFFECTING THE UTILIZATION OF GROUND-WATER FLOW SYSTEMS IN MINERAL EXPLORATION

Exploration for large, buried ore bodies by analysis of ground-water flow systems depends on the ability of ground water to dissolve ions and act as a transport medium, on an understanding of the flow system, and on the detectability limits of the elements contributed to ground water by primary halos of ore bodies which contain compounds that are soluble under the physical and chemical conditions present within the halo. According to Kennedy (1956) primary halos in one district contain lead and zinc in concentrations 50 to 100 times greater than those in surrounding country rock. Kennedy (1956) also notes that primary halos in some districts may extend considerable distances away from commercially valuable mineralized zones. De Geoffroy et al. (1967) note that a carbonate environment and humid, temperate climates are particularly appropriate for the dissolution by ground water of cations such as Pb, Zn, and Cu from primary halos. The excess of bicarbonate over calcium and magnesium caused by dissolved CO₂ buffers the carbonate-bicarbonate-carbon dioxide equilibrium within a pH range of about 6.5 to 8.1, making the carbonate the most stable soluble form for Fe, Zn, Pb, and Cu. Given sufficient oxygen in ground water, the sulfides of these cations in the halo oxidize to sulfate and hydrolyze to the carbonate, which goes into solution in the moving ground water.

Detection and analysis of the concentration of ions in solution in ground water must be accomplished before or soon after the water is discharged at the ground surface; factors such as the release of carbon dioxide cause changes in pH which initiate precipitation of zinc carbonate or other compounds. Other processes such as adsorption of zinc ions on suspended particles in the surface water body (Jacobs, 1953) also may cause changes in the quality of ground water as it reaches the surface. Consequently, evidence of the passage of ground water through a primary halo may not be available if sample collection and analysis are not carried out soon after discharge.

The most efficient utilization of ground-water flow systems as a prospecting tool

in a relatively unexplored area, requires the withdrawal of samples from zones of ground-water discharge, i.e., locations at the surface toward which ground water moves and toward which dissolved ions are transported. These are the zones where samples can be most easily collected and where maximum information about the hydrogeologic and hydrochemical environment is most readily available. Surficial indicators of discharge zones include growths of hydrophytes (marsh grasses, cattails) and phreatophytes (willows, cottonwoods), wet seeps, springs, perennial streams, and occasionally saline deposits.

A more recently developed tool for locating discharge zones is infrared imagery, i.e., utilization of the electromagnetic spectrum between the wave lengths of .72 and 1,000 microns (Robinove, 1965). Use of infrared imagery for identification of ground water discharge areas depends on the fact that the radiation emitted by an object is a function of its temperature and its emissivity. Ground water often approaches the ground surface at a temperature different from that of its surroundings, consequently it produces an infrared anomaly. Buettner and Kern (1965) present a discussion of methods of determining the emissivity of various surfaces.

Infrared photography and radiometry are the two techniques for detecting and presenting infrared images. Radiometry is generally conceded to be most successful but considerably more difficult and expensive to operate (Lepley and Palmer, 1967). A method for computation of surface temperatures by use of radiometers is presented by Lenschow and Dutton (1964).

Examples of the application of infrared imagery to the identification of ground-water discharge zones have been presented by Lepley and Palmer (1967), Fischer *et al.* (1966) and Skibitske and Brown (1965). Each of these investigations dealt in part with locating submarine ground-water discharge zones off the coast of certain Hawaiian islands. The method proved successful in that environment. The location of ground-water discharge zones on land needs further study, however, Lenschow and Dutton (1964) present evidence that the technique is feasible. The technique has been shown to be ideal for locating high temperature ground-water discharge zones as hot springs.

Sources of Samples

After the ground-water discharge zones in a basin of interest have been delineated, samples can be obtained from a number of sources therein. Springs represent the least expensive and most direct route to ground water; maximum advantage should be taken of all springs present. Only the most recently discharged water should be collected in order to avoid the post-discharge chemical changes mentioned earlier. Other ground-water sampling points include seeps and shallow wells, preferably uncased, which may already exist or may be drilled, augered or dug. A third alternative is effluent stream sampling; however, as will be shown later, stream waters represent a mixture of ground waters from a variety of locations within a basin; consequently, interpretation of the geochemistry of stream waters can be difficult. Soils and phreatophytes are also possible sampling media. However, in discharge zones, soils and plants will contain concentrations of ions that have accumulated over long periods of ground-water discharge; an apparent anomaly may be simply a product of time.

Selection of Anomalous Discharge Zones

The concentration of an ion or ions which denotes a hydrogeochemically anomalous ground-water discharge zone depends on several factors. The concentrations of a particular ion must be determined for all discharge zones within a region before the concentration which constitutes an anomaly can be designated. The background concentration can vary significantly from one geologic province to another for a variety of hydrologic and geologic reasons (White, 1968; Williams, 1968). During the analysis of spring samples in Southwest Wisconsin, de Geoffroy *et al.* (1967) considered anomalous any concentration of zinc above the 75th percentile concentration for samples analyzed in a given area. The value of the 75th percentile concentration for that particular area is .27 ppm. In many locations a concentration of .27 ppm would not be anomalous and would fall below the 75th percentile concentration. Reasons for this inconsistency subsequently will be discussed. A ground-water discharge zone can be designated as hydrogeochemically anomalous only after the basin-wide sampling program has been carried out.

DETERMINATION OF LOCATION OF ORE BODIES ON BASIS OF FLOW SYSTEMS AND GEOCHEMICALLY ANOMALOUS GROUND WATER

Subsequent to the location and chemical analysis of the ground-water discharge zones in an area under investigation, the location of the ore body producing anomalous concentrations of dissolved metals must be determined. Specifically, the flow path followed by the geochemically anomalous particles of ground water must be interpreted. Given sufficient hydrologic data and a sufficient knowledge of the geology in the ground-water basin, it would be possible to construct 2-dimensional, empirical flow nets from which flow directions could be interpreted. Such data, however, are seldom available. consequently it becomes advantageous to utilize whatever geological and hydrological data are available, in combination with a theoretical model for the examination of the flow patterns within the ground-water basin.

It can be shown that the flow of fluids and their constituents in a porous medium is a function of the distribution of potential energy, ϕ , within the medium (Hubbert, 1956). Hubbert (1940, p. 798) defines the fluid potential, ϕ , at a given point as, "the amount of work required to transport a unit mass of fluid from an arbitrarily chosen standard state to the state at the point under consideration." In most treatments of ground-water motion the potential, ϕ , at a given point is expressed as

$$\phi = gz + \int_{p_0}^p \frac{dp}{\rho} \quad (1)$$

where: ϕ = fluid potential (L^2/T^2)
 g = acceleration due to gravity (L/T^2)
 z = elevation above a standard datum (L)
 p = pressure at the given point (M/LT^2)
 p_0 = pressure at a point of reference (M/LT^2)
 ρ = fluid density (M/L^3)

Equation (1) assumes that fluid density is a function of pressure along. If fluid

density, ρ , is not dependent on pressure then ρ can be taken outside the integral and treated as a constant. In reality, the concentration of total dissolved solids in the fluid may be sufficiently great that ρ is a function of salinity. However, the value of ϕ can be adjusted for this case by converting any potential affected by salinity to a fresh water potential, or vice versa. For an example of such a treatment, see Cooper *et al.* (1964). Fluid potential within a porous medium may also be influenced by temperature, electro-osmotic potential and chemico-osmotic potential. These latter three factors, however, are customarily neglected since their effects are usually small relative to the effect of elevation and pressure (van Everdingen, 1968).

For purposes of regional flow analysis, the ratio of the change in elevation of the water table with time to the thickness of saturated porous medium through which flow occurs in a hydrologic basin is usually small. Consequently, a reasonable interpretation of regional ground-water flow patterns can be developed by assuming that the water table or potential surface remains steady (Freeze and Witherspoon, 1966). That is, the fluid potential at any point on the water table is assumed not to vary with time. Because the distribution of potential throughout the porous medium is a function of the potential at the water table (the upper boundary) this assumption requires that the potential at each point in the porous medium be constant. Under such a steady state condition the Laplace differential equation can be utilized to determine approximately the distribution of potential and the resultant flow pattern within an isotropic, saturated porous medium under investigation. For two-dimensional flow this equation states:

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial z^2} = 0$$

Where x and z are mutually perpendicular axes and ϕ is as defined earlier. In order to obtain the distribution of potential within a given isotropic, homogeneous, porous medium, the Laplace equation must be solved subject to the boundary conditions for that particular ground-water basin.

As an illustrative example, consider Figure 1a. Assume that geochemically anomalous water has been observed in one or more springs, wells, or seeps at point p just east of the tributary stream. We wish to identify the possible paths followed by the ground water discharging at point p in order to define the areas where the chemically anomalous ground water may have entered the system.

Figure 1b illustrates an approximation of the configuration of the water table along section A-B, the ground-water divides at each end of the section, and the lower flow boundary which occurs at a depth where permeability becomes so low as to be negligible. The latter condition may occur above a shale layer or above basement rock. Toth (1963) determined the flow pattern for such cases in the following manner. Toth approximated a cross section such as that in Figure 1b with a model like the one shown in Figure 2. He assumed that the component of potential gradient perpendicular to the plane of the cross section is negligible, because slopes of valley flanks are ordinarily much greater than the slope parallel to a stream. Therefore, application of the Laplace equation to Figure 2 should provide the ground-water flow pattern for this particular flow system geometry. In the model, the configuration of the water

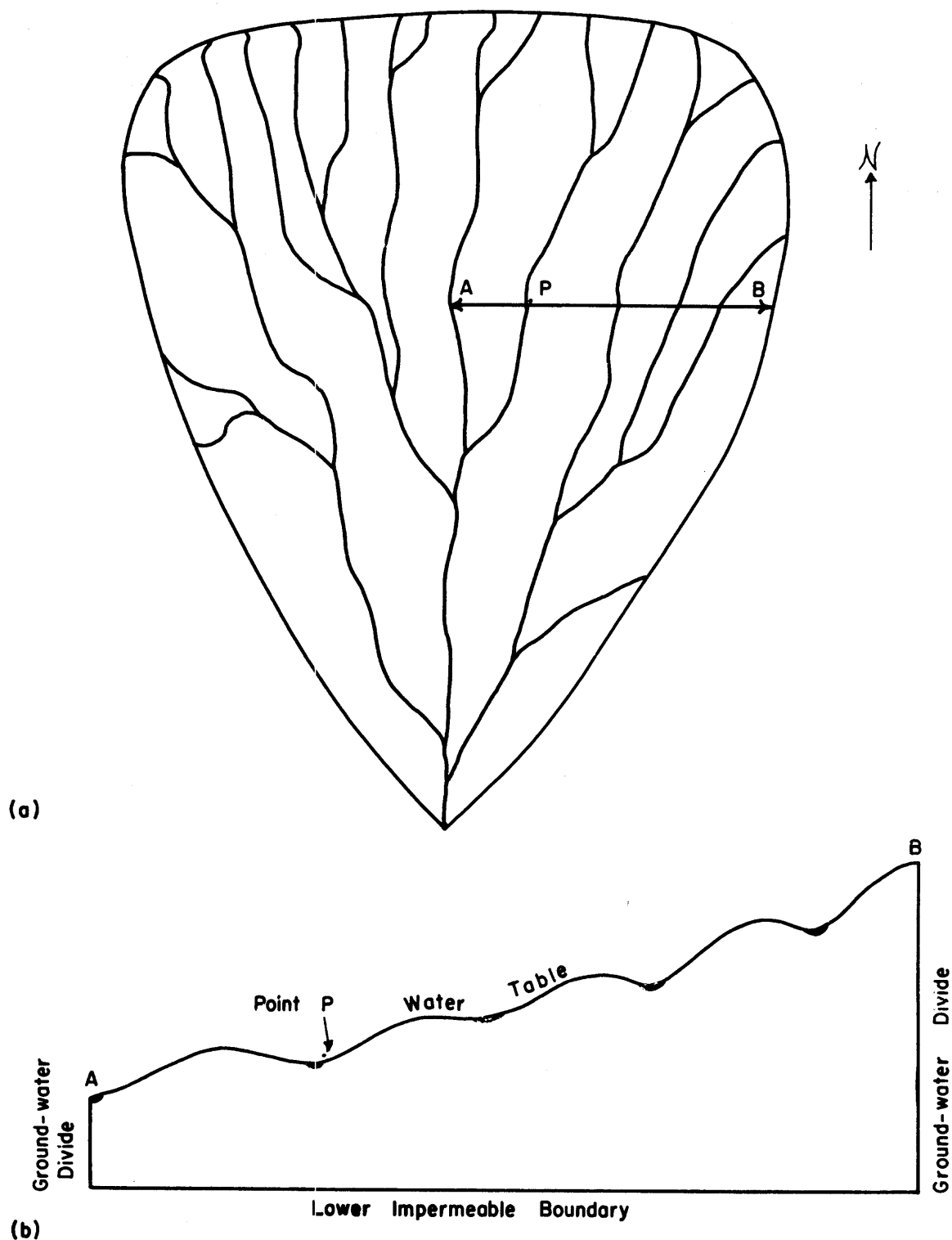


Figure 1. a.) Plan view of a representative ground-water basin wherein the ground water-flow pattern is desired along section A-B on which is located a point P.
 b.) Cross section showing approximate configuration of water table and right, left, and lower boundary of flow system along line A-B.

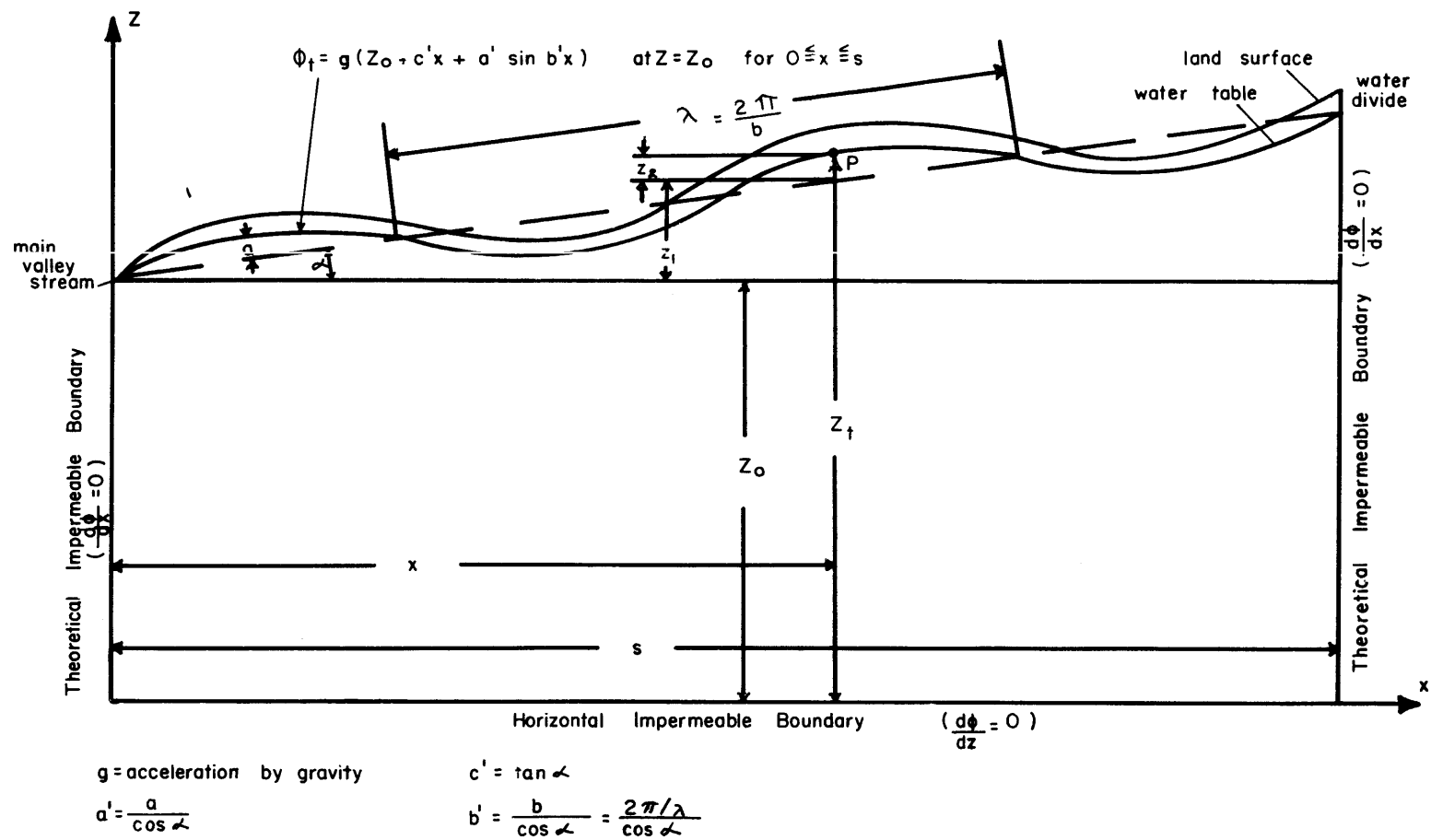


Figure 2. Geometrical configuration for mathematical model of approximate ground-water flow along section A-B in Figure 1. (modified after Toth, 1962)

table is assumed to be a sine wave sloping at an angle α from the horizontal. Other characteristics of the sine wave, such as amplitude and wave length, are identified in the diagram. The amplitude a represents local relief; the wave length, λ , represents distance between tributary divides or tributary streams; consequently λ defines the number of tributary streams along a cross section of any given length. Also included in Figure 2 is the mathematical expression for the boundary conditions subject to which the LaPlace equation must be solved in order to obtain the distribution of potential within the system. Because analytical solutions to the LaPlace equation for irregularly shaped spaces are not available, it must be assumed that the potential at the water table occurs along the horizontal line $z \leq z_0$ for $0 \leq x \leq s$. Therefore, this particular model is valid only for regional slopes of less than about 3 degrees. For values of α above 3 degrees a significant error is introduced. More recently developed numerical methods which will be discussed later eliminate this restriction.

Toth (1963) solved the LaPlace equation subject to the aforementioned boundary conditions and plotted the resulting potential distributions and flow patterns for several combinations of values of a (local relief), z_0 (thickness of porous medium through which flow occurs) and α (angle of regional slope). Toth's model indicates that 3 general types of flow patterns may occur in a porous medium bounded by a geometry such as that shown in Figures 1 and 2. Toth applied the terms local, intermediate and regional to these flow systems, all of which are illustrated in Figure 3. Given a sufficiently high regional slope α , a sufficiently thick isotropic section through which flow occurs z_0 , or sufficiently low local relief a , all three types of systems will occur. The significance of each of the three types of systems to the general quality of ground water has been discussed by Williams (1968). Meyboom (1967) concluded that variations in water quality in the Moose Mountain area of Saskatchewan can be correlated with local and intermediate flow systems.

If the values of local relief, thickness of section through which flow occurs, and regional slope in Figure 3 approximate conditions in the prototype shown in Figure 1, then one would conclude that the geochemically anomalous ground water at point p could have entered the system in one of two places: The ground-water mound to the immediate right of point p, or the mound beneath the second highest divide in the basin. In spite of the fact that most of the water discharging at point p traveled through the local flow system, the small proportion of water needed to produce the anomaly may have traveled through the intermediate system. The recharge areas for both these systems would be checked further for the source of the anomaly observed at point p.

Because the values of a (local relief), z_0 (thickness of porous medium through which flow occurs), and α (angle of regional slopes) influence the possible sources of ground water for our geochemical anomaly at point p in Figure 1, the effect of each variable on flow merits discussion. The effect of these variables on the origin of the geochemically anomalous ground water is illustrated in Figures 4, 5, and 6. In Figure 4 all variables other than z_0 are held constant. z_0 is 1000 feet and 5000 feet in Figure 4a and 4b, respectively. The effect of a thin saturated section is to limit the source of the chemically anomalous water at point p to the ground-water mound immediately to the right of point p. In the thicker section (Figure 4b) point p may receive ground water from the potential high immediately to the right or from the potential high beneath the second highest divide in the basin.

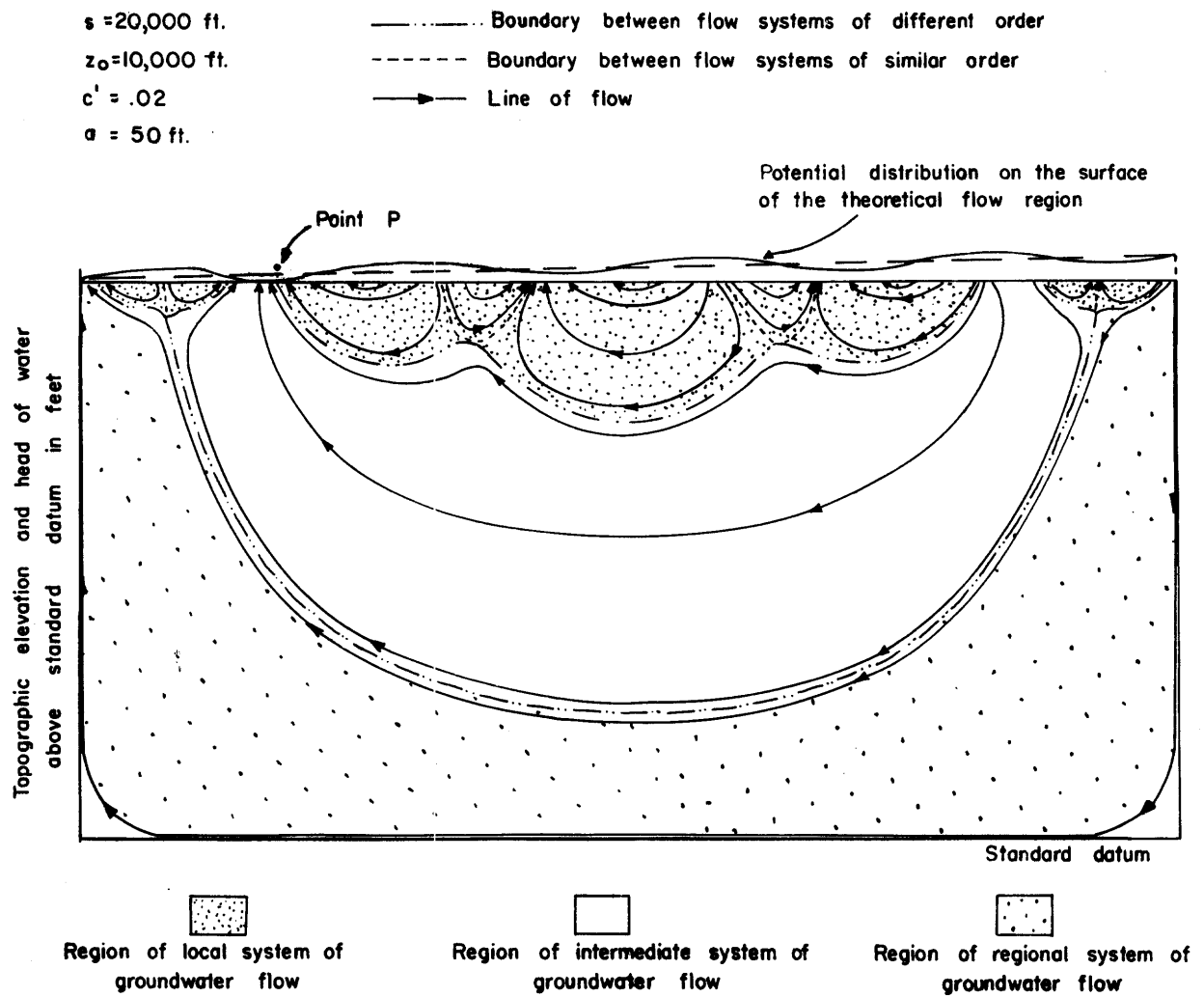


Figure 3. Theoretical flow patterns and boundaries between different flow systems.
 (Modified after Toth, 1963)

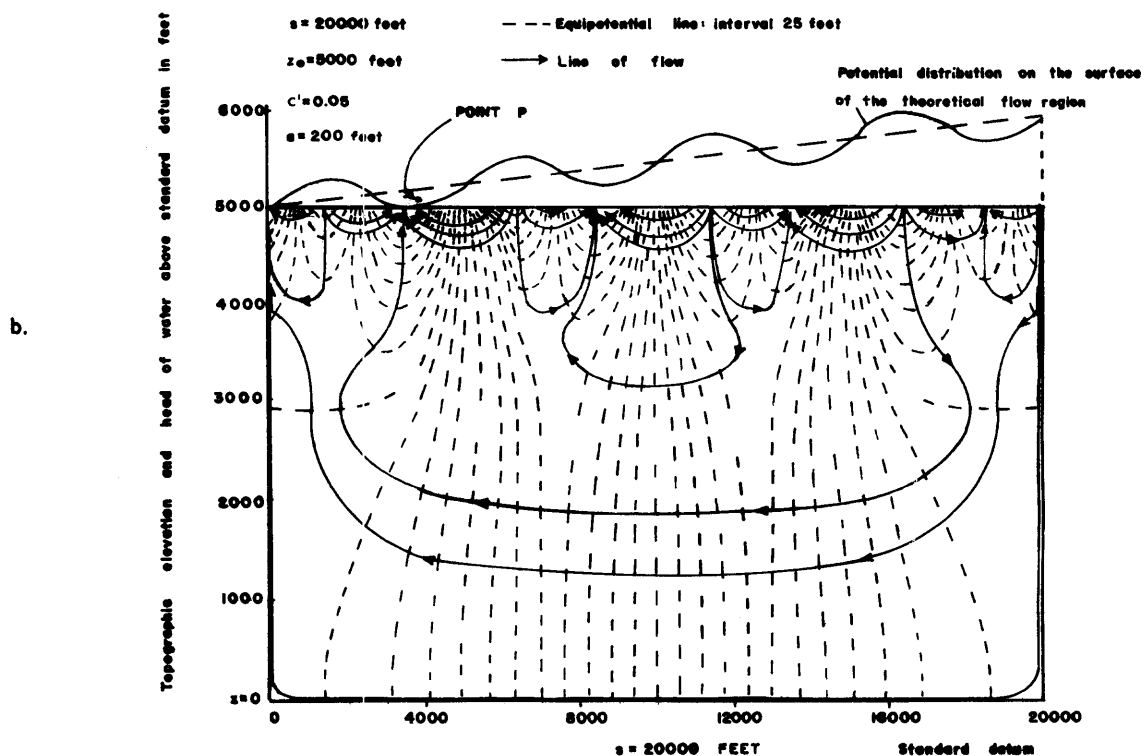
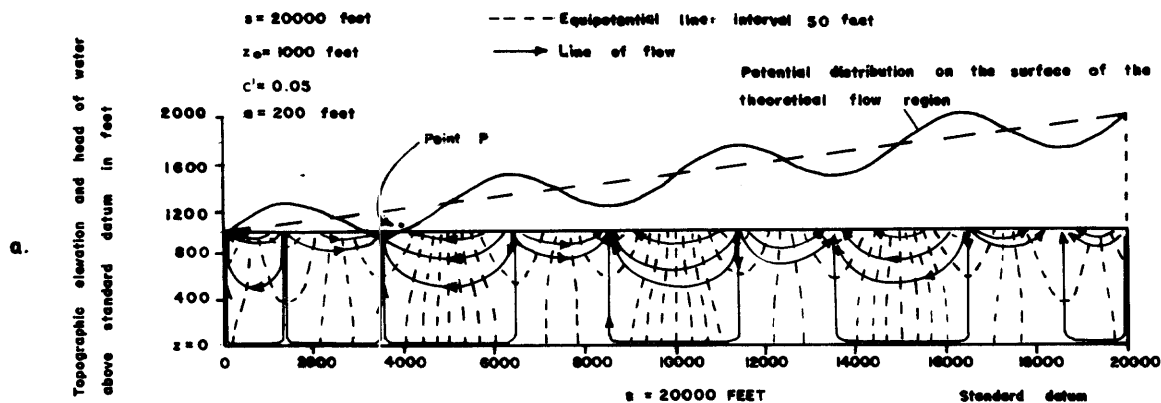


Figure 4. Cross sections illustrating the effect of thickness of section through which flow occurs on the source of water at point P. (modified after Toth, 1962)

The effect of regional slope on the possible sources of ground water discharging at point p is illustrated in Figure 5. In the figure, the larger the value of c^1 (where $c^1 = \tan a$) the greater the regional slope. In Figure 5a, $c^1 = .02$; in Figure 5b, $c^1 = .05$. In each of the cases illustrated, point p receives ground water only from the ground-water mound immediately to the right of the main stream. It should be noted, however, that a regional flow system is produced by the greater slope in Figure 5b; if point p had been adjacent to the main stream in the basin our sample could have contained water from two locations in the basin.

The effect of local relief (a value) on the sources of ground water discharging at point p is illustrated in Figure 6. In Figure 6a, the value of a is 50 feet; whereas, in Figure 6b, a is 200 feet. In both cases the geochemically anomalous ground water at point p could have entered the system only via the ground-water mound immediately to the right of point p; here also, however, if the geochemical anomaly had been observed in the ground water adjacent to the main stream in the basin instead of at point p, the source might also have been the ground-water mound beneath the highest divide in the basin.

These 4 figures (3, 4, 5, and 6) illustrate the necessity for modeling any given hydrologic basin before final conclusions are drawn regarding the origin of geochemically anomalous ground water at points within that basin. Where the assumptions of isotropy and homogeneity are met in the field and where regional slopes are less than about 3° , the method of Toth should be applicable.

Freeze and Witherspoon (1966) have derived an analytical solution to the LaPlace equation subject to a more complicated set of geologic conditions than those assumed by Toth. They obtained a solution for the basin cross section illustrated in Figure 7. The section, through which flow occurs, contains three horizontal strata, each with uniform permeabilities of 1, 10, and 1, from uppermost to lowermost, respectively. The water table is represented by a series of short, straight-line segments rather than by a sine curve. Details of the cross section and of the mathematical expression of the boundary conditions are included in Freeze and Witherspoon (1966). The flow lines in Figure 7 are for the water table configuration shown and for the basin depth indicated. Basin depth and relief are expressed as a proportion of s , the basin width. For layered cases, if quantity of flow is not desired, then only the ratio of different permeabilities is critical; the ratio and not absolute values determine flow patterns. The flow paths for this particular layering and water table configuration illustrate that the effect of a subsurface permeable layer within a basin is to transmit ground water directly to the main discharge point (main stream) within the basin. A geochemical anomaly observed in the lowest order discharge zone in this basin would be traceable only to the ground-water mounds adjacent to that discharge zone. Sources of geochemically anomalous ground water in the discharge zone of the main stream in this basin, on the other hand, may include the recharge portions of most of the tributary basins. If a basin is isotropic and homogeneous (not layered) most of the ground water is likely to be transported through local flow systems; in inhomogeneous basins, such as the one in Figure 7, much of the ground water may be transported by a high permeability layer. The effect on geochemical sample interpretation can be tremendous.

Although the boundary conditions in Figure 7 are more complex than those in

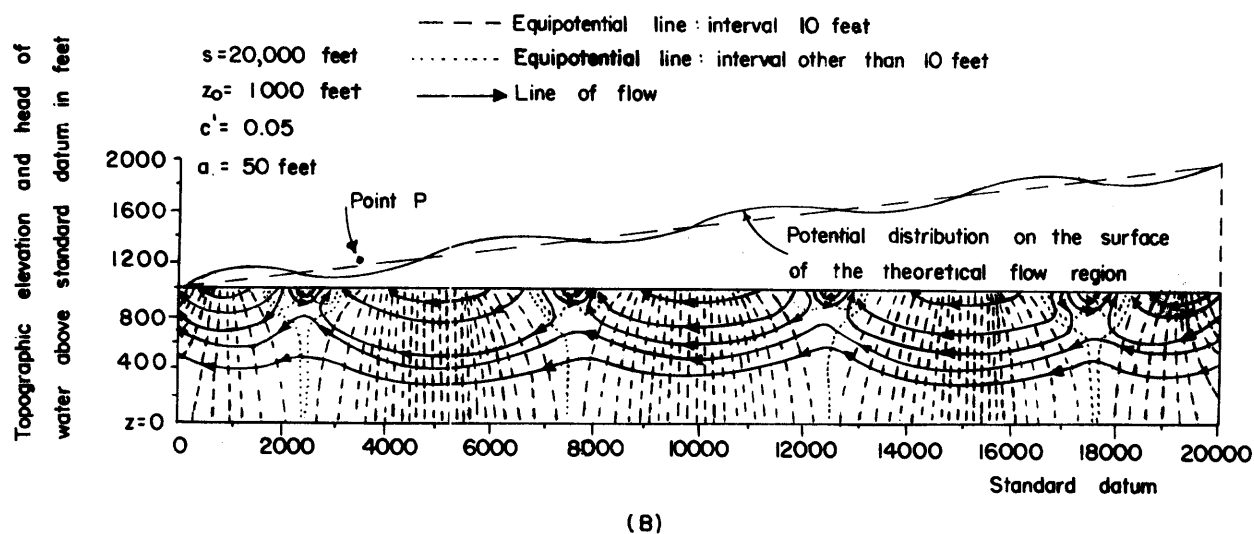
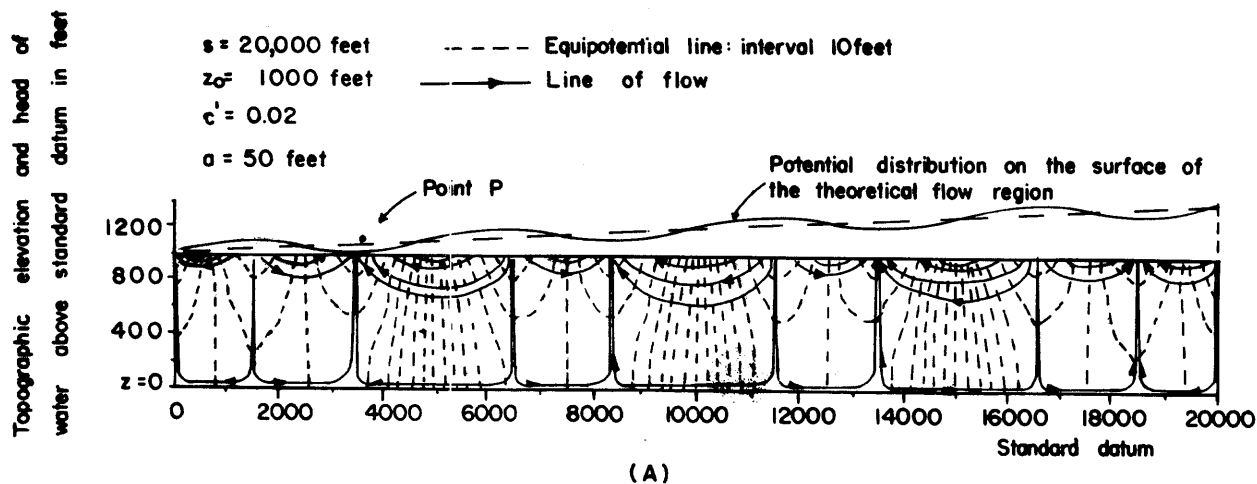
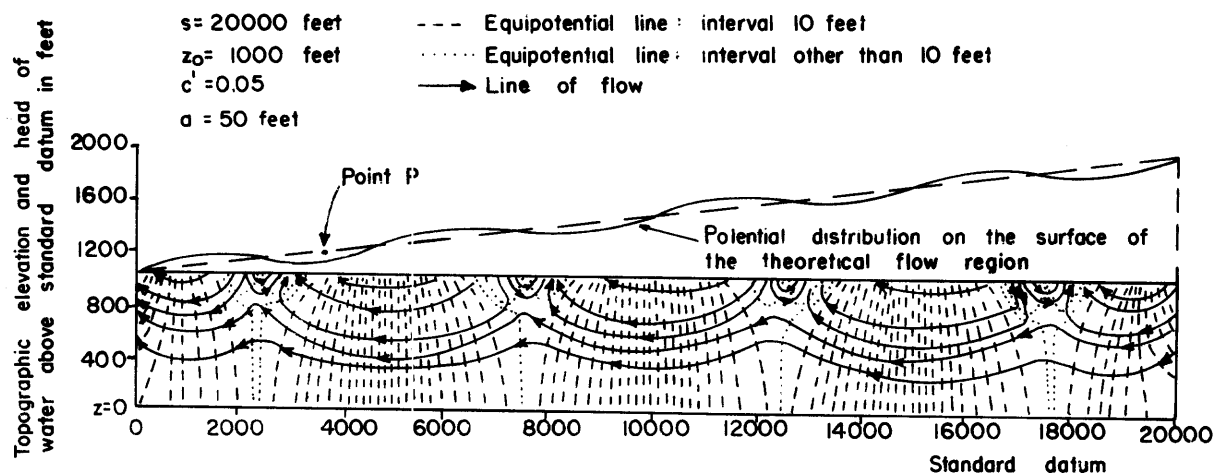
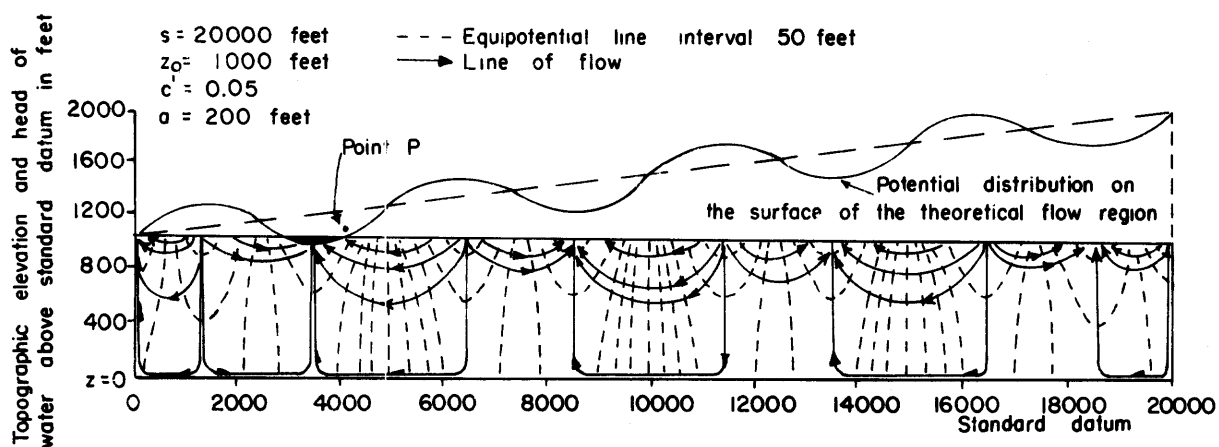


Figure 5. Cross sections illustrating the effect of low regional slope (a) and higher regional slope (b) on the origin of ground water discharging at points within the basin. (Modified after Toth, 1963)



(A)



(B)

Figure 6. Cross sections illustrating the effect of low local relief (a) and higher local relief (b) on the origin of ground water discharging at points within the basin. (Modified after Toth, 1963)

Figures 3, 4, 5, and 6, the solution is still limited to regional slopes of $\leq 3^\circ$. Solutions to the LaPlace equation are not available for that portion of the model between the water table and the horizontal line at the elevation of the main stream in the basin.

Freeze and Witherspoon's (1966) analytical solution to the LaPlace equation for the model shown in Figure 7 is for a generalized water table; other configurations are possible but a different solution results. The generalized solution has been programmed in Fortran IV language. Data describing geometry and properties of a particular basin to be approximated by the model can be inserted into the program.

For cases of more complicated geometry and layering and for high regional slopes or anisotropic conditions, utilization of the LaPlace equation for flow system interpretation and determination of sources of geochemically anomalous ground water becomes impractical or impossible. However, numerical solutions to either the LaPlace equation or the 2-dimensional Richards' equation (Richards, 1931) using the finite difference or finite element technique and a digital computer in combination with a plotter permits the determination of ground-water flow patterns for more complicated cases. Richards' equation,

$$\frac{\partial}{\partial x} \left[K(x, z) \frac{\partial h}{\partial x} \right] + \frac{\partial}{\partial z} \left[K(x, z) \frac{\partial h}{\partial z} \right] = 0 \quad (2)$$

expresses permeability, K , as a function of directions parallel to the x and z axes, thereby permitting the examination of the effect of anisotropy on the 2-dimensional flow pattern. Head, h , which has units of length, is used as the expression of potential and is defined as

$$h = \frac{\phi}{g}$$

where g is acceleration due to gravity; it is treated as a constant. Numerical solutions to equation (2) can be obtained for a variety of combinations of flow system boundary geometry and geology, provided that a reasonable estimate of the relative permeabilities of the different strata is available. Freeze (1966, 1969) and Freeze and Witherspoon (1966, 1967, 1968) described the utilization of the finite difference technique for obtaining solutions. In addition, Freeze (1966, 1969) presents details of the computer programs involved. Kealy and Williams (1970) discuss the use of the finite element technique.

In addition to permitting the examination of the effect of anisotropy and complex stratification, numerical solutions to Richards' equation can be obtained even for irregularly shaped areas; therefore, the assumption that the potential distribution along the water table occurs along a horizontal line of elevation equal to that of the main stream in the basin is not necessary. The potential distribution between this horizontal line and the water table is provided in the numerical solution; in other words numerical solutions are not restricted to regional slopes of less than 3° .

Figure 8 is a plot of a numerical solution to the LaPlace equation which illustrates the potential distribution produced by a horizontal, permeable layer located in the center of the section through which flow occurs. Only a portion of the flow-lines are

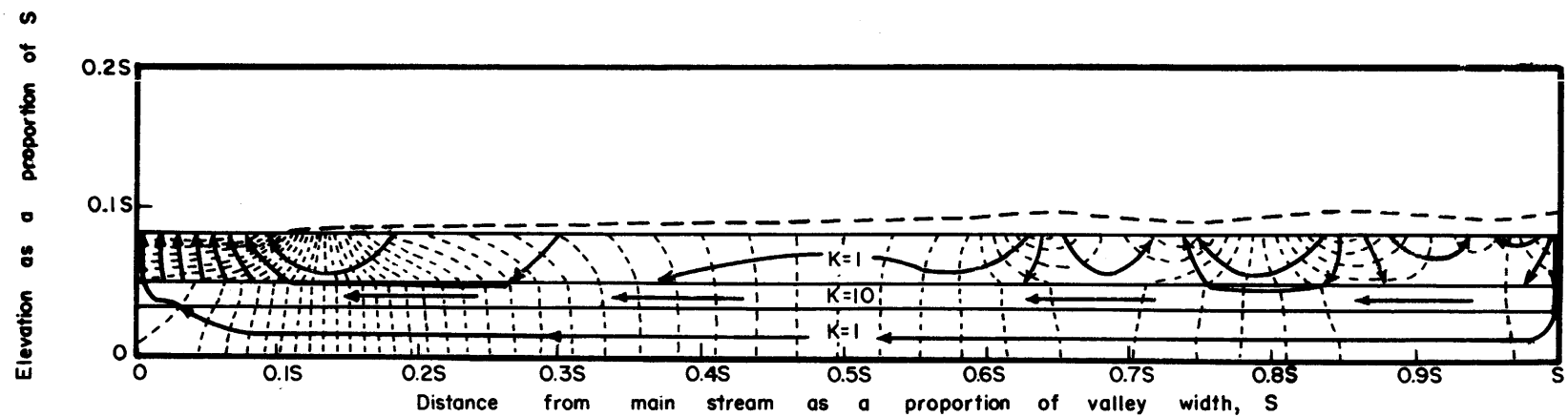


Figure 7. Cross section showing effect of stratification on the sources of ground water discharging at various points within a basin (after Freeze and Witherspoon, 1966).

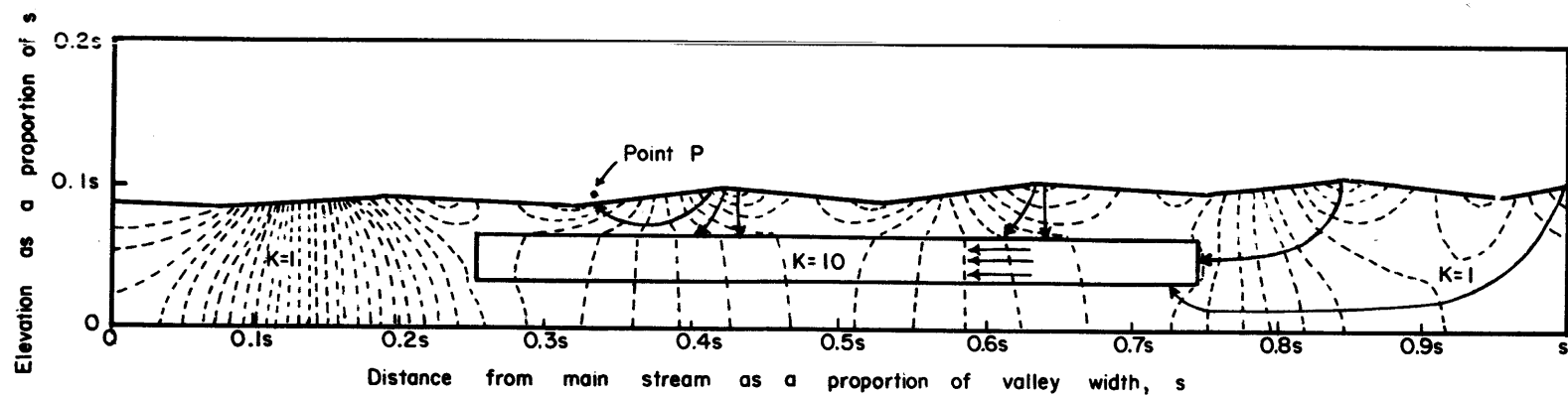


Figure 8. Cross section showing potential distribution resulting from the occurrence of a permeable rectangular stratum within a less permeable medium (modified after Freeze and Witherspoon, 1967)

shown. The model could be utilized to represent the section along the line A-B in Figure 1 if a permeable stratum such as the one shown in Figure 8 were known to occur similarly in the basin shown in Figure 1. The effect of the permeable layer is to permit the geochemically anomalous water at point p to have originated at any of the ground-water mounds up-gradient from point p. It is improbable that the anomalous water entered the system via the ground-water mound down-gradient from point p.

Figure 9 illustrates the importance of properly designating the location and orientation of permeable strata if their effect on sources of geochemically anomalous ground waters is to be defined. In Figure 9 the permeable stratum has dimensions identical to those of the stratum in Figure 8 but in Figure 9 the stratum is located in the upper half of the basin. The smaller topographic basins have been removed also in order to better illustrate the effect of the stratum on flow. According to the potential distribution in Figure 9 the permeable stratum divides the single topographic basin into two hydrologic basins. Because of the more permeable formation, ground water discharging at point P₁ and P₃ enters the system in the upper portion of the basin. Ground water discharging at point P₂ enters the system via the potential high immediately to the right of point P₂.

The geology illustrated in Figure 10 causes a similar effect on flow. The sloping shale or clay layer designated by K = 1 produces two hydrologic basins within the single topographic basin. As before, geochemically anomalous ground water discharging at points P₁ and P₃ enters the system near the highest point in the topographic basin. Ground water discharging at point P₂ may have entered the system only in the lower half of the basin.

The two configurations of strata in Figures 9 and 10 illustrate the importance of proper interpretation of hydrogeology during evaluation of the source of geochemically anomalous water in springs discharging from basin slopes. The effect of fault zones and layers which crop out on basin walls can be determined similarly if the hydraulic properties and the water table configuration within and adjacent to each layer can be estimated or measured.

Finite element or finite difference programs are adaptable to a variety of hydrogeologic relationships. Generally the availability of reliable hydrogeologic data will be limiting, rather than the ability of a mathematical model to handle the data.

Isolation of the effect of flow path length on the dissolved solids content of discharging ground water deserves further consideration. Previously cited studies show that concentration of dissolved solids can be expected to increase as flow path length increases. This observation suggests that ground water discharging from an intermediate or regional flow system may contain high concentrations of a dissolved ion even when no ore body containing that ion is present. That is, the concentration of some ions may be high simply because the discharging ground water was exposed to large volumes of rock containing disseminate quantities of a soluble mineral containing that ion. The ability to recognize this effect rests on a basin-wide sampling program which carefully identifies background concentrations throughout the basin. Fortunately the effect of long flow path on the concentration of an ion in ground water usually will not be unique to any single flow section; therefore, high concentrations caused by long flow paths may be reflected as background concentrations.

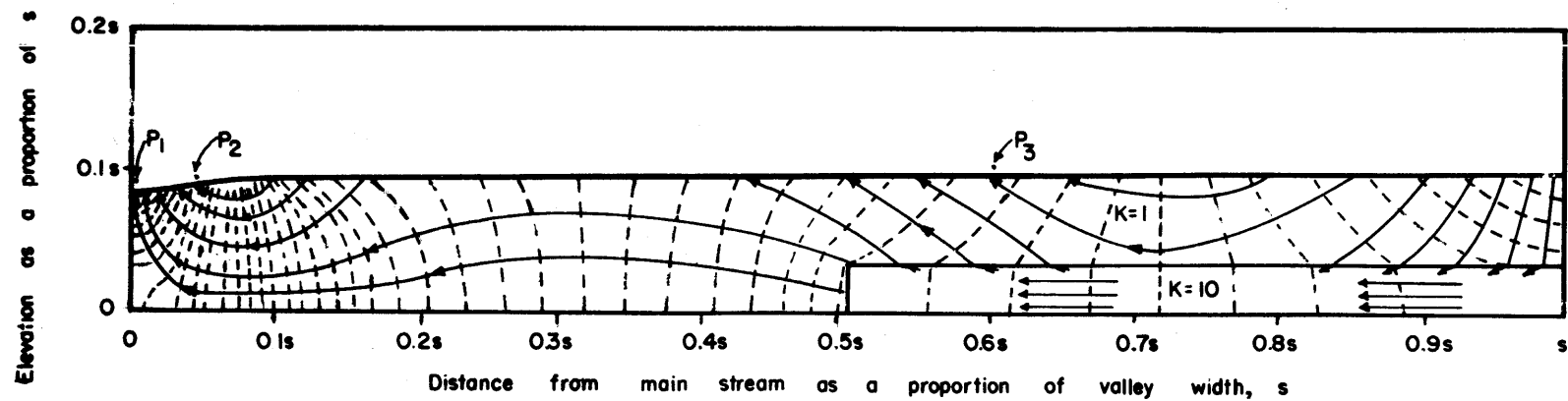


Figure 9. Cross section illustrating the effect of a confined, permeable, partial stratum on the sources of water discharging at the points indicated (modified after Freeze and Witherspoon, 1967)

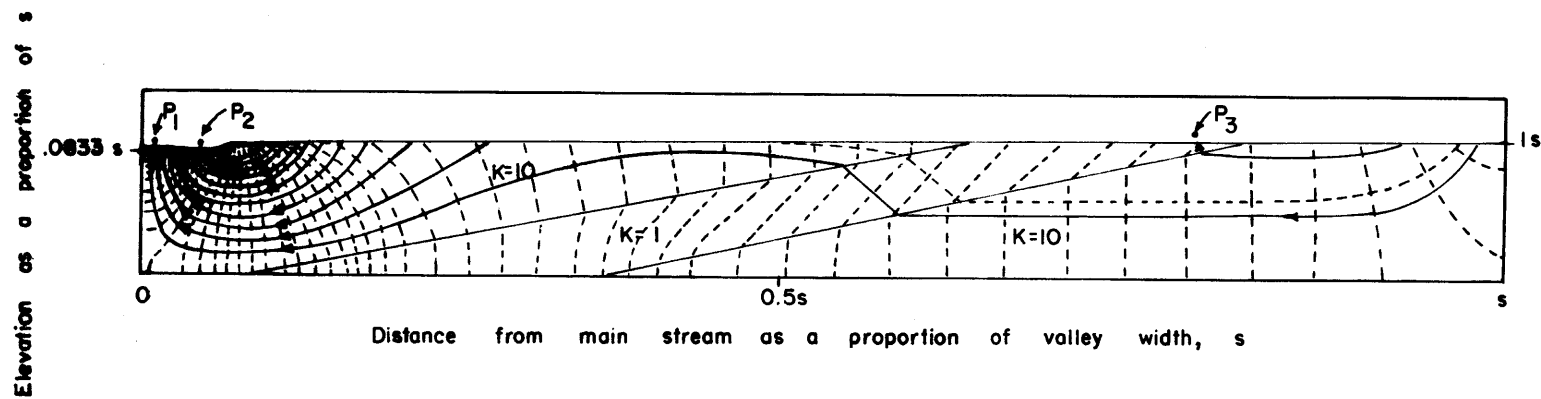


Figure 10. Cross section showing effect of a sloping, low-permeability layer on sources of ground water discharging at various points within the basin (modified after Freeze and Witherspoon, 1968)

With the flow systems depicted in Figures 4 through 10 in mind it is possible to comment further upon the use of stream and soil samples for geochemical analysis. Inspection of Figure 4 for instance reveals that some of the water in the main stream was derived from at least two ground-water recharge zones in the section. Similar sources exist on the opposite side of the basin. Because the flow system presented in Figure 4 is two-dimensional, an infinite number of such sections are located between any point along the main stream and the headwater of the stream. Therefore, geochemically anomalous water observed at any given point in the main stream may have derived from base flow which entered through many ground-water flow systems. Furthermore, anomalous base flow may be diluted and masked out by surface runoff after entry into the stream. If a geochemically anomalous stream is encountered, however, an effort should be made to find a sharp change in the concentration of the ion of interest. A sharp change in concentration along the stream's course may denote the entry of anomalous base flow. Care should be taken to collect samples only when the water in the stream is base flow. Other sources of streamflow are not likely to produce geochemical anomalies and they are likely to dilute anomalous base flow to the levels below detection limits. Fewer problems are likely to be encountered in low order tributaries where sources of surface and ground water are more limited.

Ground-water discharge zones customarily occupy bands of varying width adjacent to a stream. In these zones discharge occurs by evapotranspiration. Resulting problems to be anticipated with soil sampling in such areas have been described previously. In summary, ions may accumulate in the soils in those areas over a long period of time, thereby producing misleading anomalies. Vegetation in discharge zones may contain pseudo-anomalies for similar reasons.

Evidence supporting the validity of the use of ground water as a prospecting tool is included in the work of de Geoffroy et al. (1967). In that study the investigators examined ground water discharging from springs in the Upper Mississippi Valley lead-zinc district. Springs in five first-order basins were sampled and their waters analyzed for pH, zinc and iron. Because the basins were first-order, ground water discharging from the springs could have entered each system only via the potential high adjacent to each spring. The possibility of an anomaly being produced by an ore body located beneath a recharge area outside the basin from which the samples came was thereby precluded. Each basin was further subdivided according to geologic parameters. All fold axes were drawn on a topographic map and the area between each pair of fold axes assigned to a section. Areas of investigation were defined as the intersection of the hydrologic and geologic sets. Data from springs were grouped according to area of investigation and the formation from which each spring discharged noted. It was assumed that spring water discharging from a given formation had not "mingled" with water from other formations. Statistical techniques were then utilized to interpret mineralization within areas and within formations. The effect of geology on the source of anomalous ground waters discharging from springs was thereby determined without actually constructing the mathematical models of the flow systems. Field investigations subsequently confirmed most of the anomalies produced by analysis of spring samples. If basins of order greater than 1 had been present, additional work would have been necessary.

SUMMARY

Studies cited herein have demonstrated that ground-water flow systems are transport agents for dissolved solids. These dissolved materials normally are transported to the discharge areas of the flow system. There the discharged solids may be deposited or removed by surface water.

Given sufficient hydrogeologic data, mathematical models of steady state ground-water flow systems can be used to interpret the results of hydrogeochemical studies used in exploration for ore deposits. Analysis of ground-water flow systems produced by the mathematical models suggests that the following principles should be applied:

1. For purposes of hydrogeochemical exploration, maximum emphasis should be placed on ground-water samples collected from discharge areas of low order (1st or 2nd) tributary basins. In discharge areas samples may be collected from springs, seeps, or shallow drillholes. Discharge areas may be identified by permanent seeps, springs and streams, by the presence of hydrophytes and phreatophytes, or by infrared techniques.
2. Samples of ground water should be collected during the dry part of the year when discharging water is most likely to derive from the true ground-water flow system and not from interflow. Ephemeral springs and seeps should be avoided. Ephemeral discharge zones usually will not support the growth of hydrophytes or phreatophytes; consequently their absence may be a criterion for the identification of such zones.
3. In higher order tributaries maximum weight should be placed on ground-water samples collected from recharge areas. Drillholes will usually be required for sample collection. Ground water discharging into or adjacent to high order streams may derive from two or more recharge areas.
4. Soil samples for geochemical analysis should be restricted to ground-water recharge areas. Geochemical anomalies in soil samples from ground-water discharge areas may be the product of long term discharge and evapotranspiration of ground water containing only background concentrations of the anomalous ion.
5. Stream samples may be useful in the identification of cross sections along which ground water should be sampled. An abrupt change in concentration of a given dissolved ion along a stream course may indicate the entry of anomalous ground water into the stream. Care should be taken to sample streams when they are receiving only base flow. That is, streams should not be sampled when they are receiving melting snow, surface runoff or interflow. These latter sources of water may mask out anomalies contained in base flow. Stream hydrographs, if available, can be utilized to identify periods when the flow of the stream is essentially baseflow. If hydrographs are not available, then selection of sampling period will have to be based on experience with the hydrology of the area.

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