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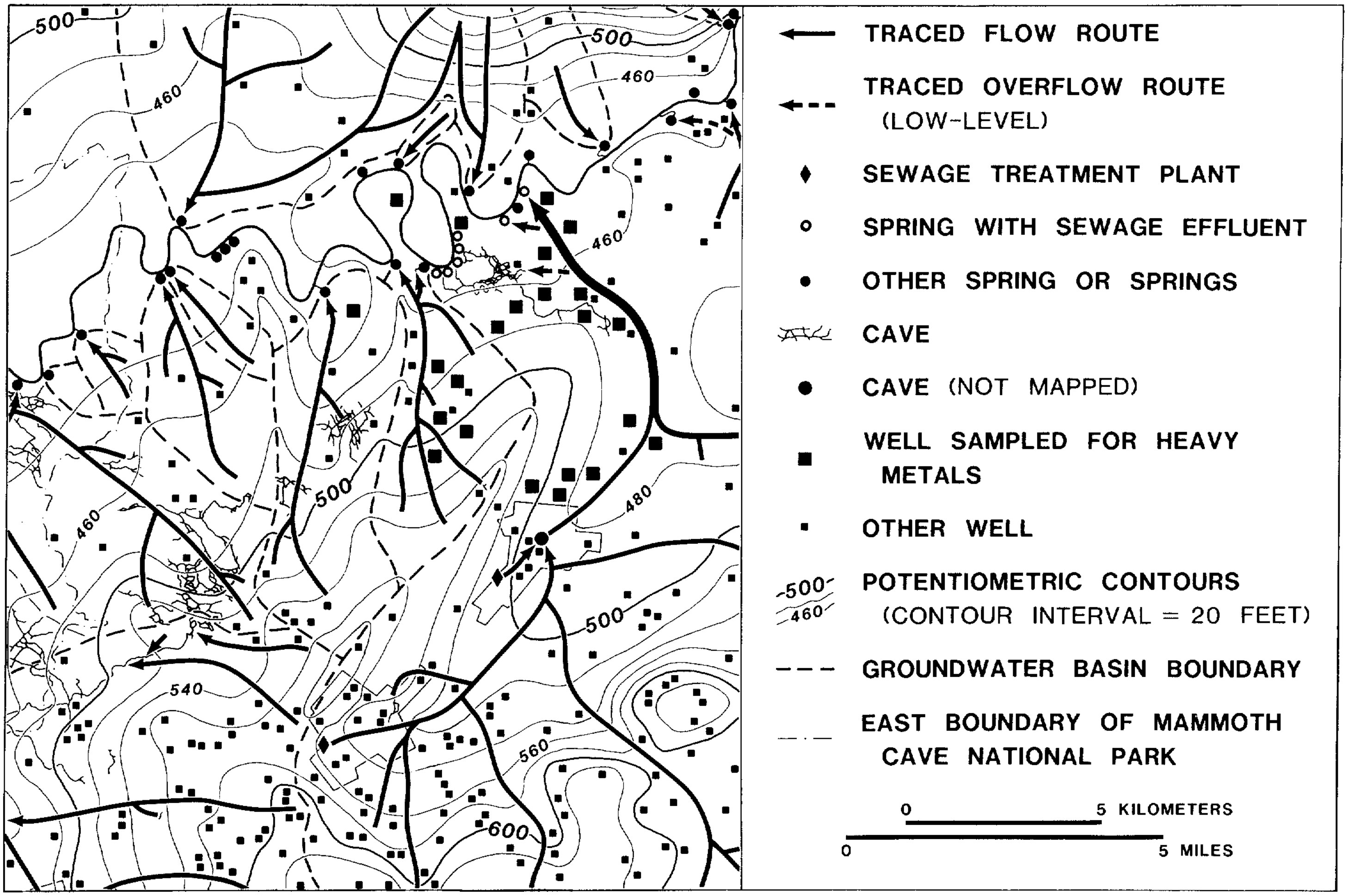
APPLICATION OF DYE-TRACING TECHNIQUES FOR DETERMINING SOLUTE-TRANSPORT CHARACTERISTICS OF GROUND WATER IN KARST TERRANES



COVER: Ground-water flow routes and pollutant dispersal in the Horse Cave and Cave City area, Kentucky, just east of Mammoth Cave National Park. Dye-tracing and mapping of the potentiometric surface (the water table) has made it possible to determine: 1) the boundaries of ground-water basins, 2) the flow-routing of sewage effluent discharged into the aquifer, 3) the flow-routing of other of pollutants that might be discharged into the aquifer anywhere else in the map area, and 4) the recharge area of springs. Reliable monitoring for pollutants here and in most karst terranes can only be done at springs, wells drilled to intercept known cave streams, wells known to become turbid after heavy rains, and wells drilled on photo-lineaments -- but only if each site proposed for monitoring has been shown by dye-tracing to drain from the site to be monitored. (reproduced from: Quinlan, James F., Special problems of groundwater monitoring in karst terranes, in Neilsen, David M., and Quinlan, James, F., eds., Symposium on Standards Development for Groundwater and Vadose Zone Monitoring Investigations. American Society for Testing and Materials, Special Technical Paper, 1988. (in press)

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION IV
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Application Of Dye-Tracing Techniques For Determining Solute-Transport Characteristics Of Ground Water In Karst Terranes

Prepared By

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Approximately 20% of the United States is underlain by karst aquifers. This approximation includes roughly 50% of both Kentucky and Tennessee, substantial portions of northern Georgia and Alabama, and parts of other Region IV states. The prevalence of karst aquifers in the southeast, the common use of karst aquifers as drinking water sources and the vulnerability of these aquifers to contamination highlighted the need to provide a mechanism to assist in ground-water management and protection in karst terranes. In an attempt to meet this need, the U.S. Environmental Protection Agency (EPA) - Region IV and the Kentucky District of the U.S. Geological Survey (USGS), have been cooperating to document the application of dye tracing techniques and concepts to ground-water protection in karst aquifers. I am pleased to announce that these efforts have resulted in the preparation of this manual, entitled, “Application Of Dye-Tracing Techniques For Determining Solute-Transport Characteristics Of Ground Water In Karst Terranes.” The information presented herein should be viewed as another analytical “tool” to assist in the management and protection of karst water supplies.

Joe R. Franzmathes for
Greer C. Tidwell
Regional Administrator

SEP 27 1988
Date

APPLICATION OF DYE-TRACING TECHNIQUES FOR DETERMINING SOLUTE-TRANSPORT CHARACTERISTICS OF GROUND WATER IN KARST TERRANES

by

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FOREWORD

The dawning of the “Age of Environmental Awareness” has been accompanied by great advances in the study of karst hydrology -- its methodology, results, and understanding. This manual is another of those advances. It describes a clever application to subsurface streams of empirical techniques for study of surface streams. It makes possible a good approximation of the time of travel, peak concentration, and flow duration of harmful contaminants accidentally spilled into many karst aquifers and flowing to a spring or well, and it does so for various discharge conditions. As such, these techniques for analysis and interpretation of dye-recovery curves are powerful, useful tools for the protection of water supplies. These techniques are an important complement to those essential for delineation of wellheads and springheads. For karst terranes characterized by conduit-flow, such delineation can only be done by dye-tracing, preferably guided by inferences from good potentiometric maps.

Interpretation of dye-recovery curves can yield much information about the nature of groundwater flow in a karst aquifer and the structure of its conduit system, as shown in this manual, by Maloszewski and Zuber (1985), Zuber (1986), Gaspar (1987), Smart (1988), and other investigators. Similarly, much can be learned from interpretation of flood-discharge hydrography of springs, as shown by Wilcock (1968), Brown (1972), Sara (1977), Podobnik (1987), White (1988, p. 183-186), Meiman _et al._ (1988), and others.

An unstated, implicit assumption made by the authors of this manual in their analysis of dye-recovery curves is that flow is from a single input to a single output. This is a reasonable assumption in many karst terranes, but there are five other significant types of karst networks, those with:

1. One or more additional unknown inputs;
2. One or more additional unknown outputs;
3. Both one or more additional unknown inputs and outputs;
4. Distributary flow to multiple outlets;
5. Cutarounds and braided passages. (A cutaround is a passage bifurcation in which flow diverges from and then converges to the main conduit. The flow routes rejoin one another, but one of them is longer and/or less hydraulically efficient than the other. Where convergence occurs, a second pulse, lagging behind the initial pulse, is formed in the main conduit.)

The first three types of karst network are illustrated and discussed by Brown and Ford (1971), Brown (1972), and Gaspar (1987). If flow in an aquifer is through the first type, predictions based on the procedures recommended in this manual will be accurate. If flow is through the second or third types, the accuracy of the predictions will tend to be inversely proportional to the amount of dye diverted to unknown discharge points. Distributary flow is a subtype of the second and third types of network; it is common in karsts of the Midwestern United States.

Flow through cutarounds and braided passages induces bimodality and polymodality in dye-recovery curves, as illustrated and discussed by Gaspar (1987) and Smart (1988). If such curves depart significantly from those for a relatively simple system like that described in this manual, the accuracy of predictions in the fifth type of network will be inversely proportional to the time between the maxima and will also be affected by the number of maxima and the extent to which they are similar to the greatest maximum.

Another factor that influences the shape of a dye-recovery curve is the extent to which tracer penetrates the bedrock matrix deeply enough to be influenced by adjacent fractures (Maloszewski and Zuber, 1985; Zuber, 1986). Such penetration is strongly influenced by the porosity of the matrix and is inversely proportional to the flow velocity; matrix penetration by tracer can affect both the duration of a test and the shape of its dye-recovery curve.

A karst aquifer may or may not lend itself to the dye-recovery analysis proposed in this manual. But one will not find out -- or determine the type of karst network present -- until and unless dye-tests are run and interpreted. Results of the dye-recovery analysis are vital for wellhead and springhead protection, especially if flow is through a relatively simple conduit system like that studied by the authors.

It was the intention of the authors to only briefly summarize a few principles and descriptions of karst hydrology and geomorphology; more would be beyond the intended scope of this manual. For a fuller discussion of these topics the reader is referred to the recent excellent textbook by White (1988). Similarly, and although there are much data and unique information on dye-tracing in this manual, the reader desiring a comprehensive how-to (and how-not-to) handbook on various dye-tracing techniques and instrumentation is referred to the enchiridion by Aley <u>et al.</u> (1989) .

Flow velocities in karst aquifers may be tens of thousands to many millions of times faster than flow in granular aquifers. Therefore, it would be prudent for managers of water supplies in karst terranes to have the recharge areas for their springs and wells delineated and to have dye-recovery analysis done for the sites most susceptible to accidental spills of harmful contaminants. They should do so before it is too late. Although dye-injection immediately after a spill can sometimes be used to monitor the probable arrival time of pollutants, the tracing necessary for applying the dye-recovery analysis described in this manual can only be done <u>before</u> the spill occurs.

Dye-tracing, like neurosurgery, can be done by anyone. But when either is needed, it is judicious and most cost-efficient to have it done by experienced professionals, those who have already made the numerous mistakes associated with learning or those who have trained under the tutelage of an expert and learned to avoid numerous procedural errors that could have economically and physically fatal consequences.

The analytical technique for dye-recovery analysis described in this manual is best applied to systems similar to the relatively simple but common one studied by the authors. Accordingly, their approach should be widely applicable. When combined with basin delineation by dye-tracing, the two techniques represent the best pre-spill hydrologic preparations available for spill-response in karst terranes. Their technique is a significant advance in the evaluation of karst aquifers. Use of it and testing of it is encouraged and recommended.

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APPLICATION OF DYE-TRACING TECHNIQUES FOR DETERMINING SOLUTE-TRANSPORT CHARACTERISTICS OF GROUND WATER IN KARST TERRANES

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ILLUSTRATIONS

TABLES

Factors for Converting Inch-Pound Units to International System of Units (SI)

The inch-pound units used in this report may be converted to metric (International System) units by the following factors:

Multiply inch-pound units	By	To obtain metric unit
inch (in.)	25.4	millimeter (mm)
feet (ft)	0.3048	meters (m)
mile (mi)	1.609	kilometer (km)
square mile (mi^2)	2.590	square kilometer (km^2)
gallon per minute (gal/rein)	0.06309	liters per second (L/s)
million gallons per day (Mgal/d)	0.04381	cubic meter per second (m^3/s)
	3,785	cubic meter per day (m^3/d)
foot per second (ft/s)	0.305	meter per second (m/s)
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
foot squared per second (ft^2/s)	0.09290	meter squared per second (m^2/s)
micromhos per centimeter at 25° Celsius (µmhos/cm at 25° C)	1,000	microsiemens per centimeter at 25° Celsius (µS/cm at 25° C)

Temperature in degrees Fahrenheit (°F) can be converted to degrees Celsius (°C) as follows:

°C - (°F - 32)/1.8

Sea Level: In this report "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)--a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called "Sea Level Datum of 1929."

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ABSTRACT

Some of the most serious incidents of ground-water contamination, nationwide, have been reported in karst terranes. Karst terranes are characterized by sinkholes; karst windows; springs; caves; and losing, sinking, gaining, and underground streams. These karst features are environmentally significant because they are commonly directly connected to the ground-water system. If these ground-water systems are used as a drinking water source, their environmental significance is increased. Sinkholes are especially significant because they can funnel surface runoff to the ground-water system. Thus, any pollutant carried by surface runoff across a karst terrane has the potential for rapid transport to the ground-water system.

Because of the extreme vulnerability of karst ground-water systems to contamination, water-management and protection agencies need an understanding of the occurrence of ground water, including the extent of the recharge areas for specific karst aquifers, a knowledge of the inherent vulnerabilities of the systems, and an understanding of the characteristics of pollutant transport within the systems. To provide water managers (those responsible for providing and managing water supplies) and protection agencies (those responsible for regulating water supplies and water quality) with a tool for the management and protection of their karst water resources, the U.S. Geological Survey in cooperation with Region IV of the U.S. Environmental Protection Agency has prepared this manual to illustrate the application of dye-tracing results and the related predictive techniques that could be used for the protection of ground-water supplies in karst terrane. This manual will also be useful for State and local agencies responsible for implementing Wellhead Protection Programs pursuant to the Safe Drinking Water Act as amended in 1986.

This manual includes a brief review of karst hydrogeology, summarizes dye-tracing concepts and selected techniques, lists sources for equipment and materials, and includes an extensive list of references for more detailed information on karst hydrogeology and on various aspects of dye tracing in karst terrane. Both qualitative and quantitative dye-tracing techniques are described and quantitative analyses and interpretation of dye-trace data are demonstrated.

Qualitative dye tracing with various fluorescent dyes and passive dye detectors, consisting of activated coconut charcoal or surgical cotton, can be used to identify point-to-point connections between points of ground-water recharge, such as sinkholes, sinking streams, and karst windows and discharge points, such as water-supply springs and wells, Results of qualitative tracing can be used to confirm the direction of ground-water flow inferred

from water-level contour maps, and to help delineate the recharge area draining to a spring or well. Qualitative dye tracing is, generally, the first step in the collection and interpretation of quantitative dye trace data.

Quantitative dye tracing usually requires automatic samplers, discharge measurements at the ground-water resurgence, and fluorometric or spectrofluorometric analysis to quantify passage of the dye cloud. These results can be used to determine solute-transport characteristics such as traveltime for arrival of the leading edge of the dye cloud, peak dye concentration, trailing edge, and persistence of the dye cloud at the discharge point, which may be a spring or well used for public water supply.

Repeated quantitative dye traces between the same recharge and discharge points, under different flow conditions, can be used to develop predictive relations between ground-water discharge, apparent ground-water flow velocity, and solute-transport characteristics. Normalized peak-solute concentration, mean traveltime, and standard deviation of time of travel can be used to produce a composite, dimensionless recovery curve that is used to simulate solute-transport characteristics for selected discharges. Using this curve and previously developed predictive relations, a water manager can estimate the arrival time, peak concentration, and persistence of a soluble conservative contaminant at a supply spring or well, on the basis of discharge and the quantity of spilled contaminant.

1. INTRODUCTION

1.1 Background

The primary objective of the manager of a public water-supply system is to provide the consumer with a safe, dependable supply of drinking water. In large areas of many states, ground water is the exclusive or primary source of drinking water. Often, disinfection is the only treatment used to meet applicable public drinking-water standards. However, reports of ground-water contamination nationwide, combined with increasing dependence on ground water, have led to a growing awareness of the potential for degradation of this valuable source of drinking water.

Almost all ground water is vulnerable to contamination, whether the contamination is caused by natural geologic or hydrologic conditions or by man's activities. Karst ground-water supplies are particularly vulnerable to contamination because of the relatively direct connection to surface activities and the rapid transport of surface runoff and contaminants to karst ground-water systems. The potential for contamination of karst ground-water systems from man-made sources is particularly great where urban areas and major transportation corridors are built in the recharge areas of karst aquifers.

Karst terrane is characterized by surface and subsurface features, such as sinkholes; karst windows; springs; caves; and losing, sinking, gaining and underground streams. Sinkholes are environmentally significant land forms because they can provide a direct path for surface runoff to recharge karst aquifers. They commonly lead directly to the aquifer system through pipe-like openings in residuum and bedrock. Some sinkholes may also act as collection and retention basins for surface runoff. Thus, depending upon the size of the area draining to the sinkhole and the nature of the subsurface openings, relatively large quantities of water may enter the aquifer system in a short period of time. Where sinkholes occur, any pollutant carried by surface runoff has the potential for rapid transport to ground water.

Public water-supplies in karst terranes may be more vulnerable to detrimental effect than nonkarst, ground-water supplies. Because of the variability of soil cover and the likelihood of overlying soils being shallow or absent in karst areas, the potential exists for little or no enhancement of water quality before surface water is recharged to the aquifer system. Also , pollutant traveltime in a karst aquifer can be rapid, on the order of miles per day in contrast to feet per year in most non-karst aquifers. Therefore, the managers of a water supply derived from ground water in a karst terrane need to have a detailed understanding of the extent of the aquifer recharge area, a knowledge of the inherent vulnerabilities of the aquifer, and an understanding of how pollutants move through the system. Accordingly, specialized qualitative techniques are required to delineate the recharge areas of karst aquifer and to identify continuity between potential recharge and discharge points of aquifers. In addition, predictive techniques are needed in order that the water-supply manager can effectively respond to the presence of contaminants in the karst aquifer.

In response to the widespread need for the protection of vulnerable ground-water supplies, Congress enacted the 1986 Amendments to the Safe Drinking Water Act. Prior to 1986, the Federal statutes available to the U.S. Environmental Protection Agency (EPA), although designed for more general purposes, provided substantial protection for ground water (U.S. Environmental Protection Agency, 1984, p. 23). These statutes are designed to protect ground water by focusing on controlling specific contaminants or sources of contamination. However, with the enactment of the 1986 Amendments to the Safe Drinking Water Act, there is for the first time a Federal statutory goal for the protection of ground water as reflected by the establishment of the Wellhead Protection Program. This goal represents a significant change in the roles and relations of Federal, state, and local governments with regard to ground-water protection.

The Wellhead Protection Program (Section 1428 of the Safe Drinking Water Act) is a state program designed to prevent contamination of public water-supply wells and well fields that may adversely affect human health. Although springs that supply public drinking water were not specifically mentioned in the statute, it has been interpreted by the EPA that the protection of public water-supply springs should be included in the program.

The Act requires states to develop programs to protect the wellhead protection area of all public water-supply systems from contaminants that may have any adverse effects on the health of humans. A wellhead protection area is defined by statute as the surface or subsurface areas surrounding wellfields through which contaminants are reasonably likely to move toward and reach such wells or wellfields.

The Act specifies that the following elements be incorporated into state programs:

> A description of the duties and responsibilities of state and local agencies charged with the protection of public water-supplies:
>
> Determination of wellhead protection areas for each public water-supply well.
>
> Identification of all potential man-made sources within each wellhead protection area.
>
> As appropriate, technical assistance; financial assistance; implementation of control measures; and education, training, and demonstration projects to protect the wellhead areas.
>
> Contingency plans for alternative water supplies in case of contamination.
>
> Siting considerations for all new wells.
>
> Procedures for public participation.

States electing to develop a Wellhead Protection Program need to submit their program proposal to the EPA by June 1989 and the program needs to be implemented within two years of approval. The EPA has established a policy that states shall have considerable flexibility in carrying out the program.

Guidance available from the EPA to states in developing their programs include “Guidance for Applicants for State Wellhead Protection Program Assistance Funds Under the Safe Drinking Water Act” (U.S. Environmental Protection Agency, 1987a) and “Guidelines for Delineation of Wellhead Protection Areas” (U.S. Environmental Protection Agency, 1987b).

Recognizing the occurrence of water supplies in karst aquifers of the southeastern United States, the U.S. Geological Survey in cooperation with Region IV of the Environmental Protection Agency, prepared this manual to assist Federal, State, and local agencies in ground-water management and protection in karst terranes to support the Wellhead Protection Program. The manual demonstrates the application of dye-tracing concepts and techniques for determining solute-transport characteristics of ground water in karst terranes and illustrates the development of predictive techniques for ground-water protection.

With the serious potential for ground-water contamination and the need to identify the areas most likely to drain directly to karst ground-water systems, numerous investigations by state and Federal agencies, university researchers, and environmental consulting firms have been conducted to better define the hydraulic nature of these systems, Some objectives of these investigations include, but are not limited to, the location and classification of sinkholes most susceptible to surface runoff; the identification of point-to-point hydrologic connections by dye traces between selected sinkholes, losing and sinking streams, and public water-supply springs and wells; and the definition of the relation between precipitation, storm-water drainageways, streams, sinkhole drainage, ground-water movement, and downgradient springs and wells.

Information gained from these studies has been helpful to local, state, and Federal water supply management and protection agencies and researchers in their efforts to develop aquifer and well-head protection plans. The results have been useful for developing land-use controls around sinkholes whose drainage has been traced to public water-supply springs or wells. Recent studies have demonstrated the use of predictive techniques for estimating solute transport in karst terranes.

1.2 Purpose and Scope

The purposes of this manual are to provide a review of the hydrogeology of karst terranes, summarize concepts and techniques for dye tracing, and describe and demonstrate the application of dye-trace data to determine solute-transport characteristics of ground-water in karst terranes. The manual was prepared in support of the Wellhead Protection Program pursuant to the 1986 Amendments to the Safe Drinking Water Act.

The dye-tracing procedures and the analysis and application of dye-trace data provided in this manual were used to determine ground-water flow characteristics in the Elizabethtown area, Kentucky (Mull, Smoot, and Liebermann, 1988). In general, these techniques may be used in other karst areas with similar hydrologic characteristics. The quantitative analyses of dye-recovery data and the development of prediction capabilities are most useful in areas where ground-water flow occurs primarily in conduits that drain to a spring or springs where discharge can be measured.

1.3 Acknowledmnents

The authors are grateful to James F. Quinlan of the U.S. National Park Service; and Ronald J. Mikulak of the EPA, and Robert E. Faye and John K, Carmichael of the U.S. Geological Survey; each of whom performed a technical review of the manual. Their constructive criticism was beneficial to the technical content and accuracy of the manual.

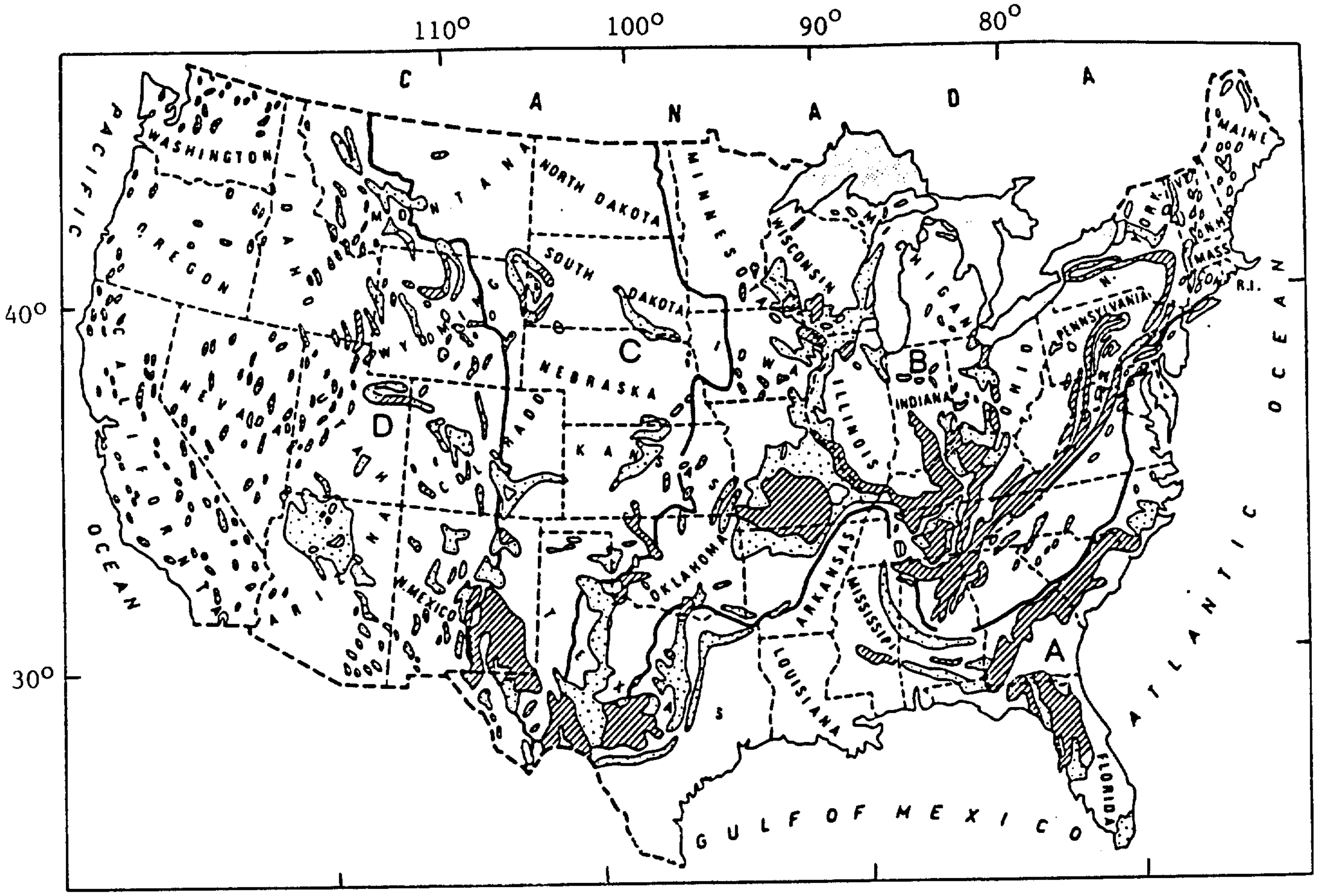
The authors are also grateful to the City of Elizabethtown, which provided much of the dye-trace data used in this manual, for its cooperative support of a dye-trace investigation by the U.S. Geological Survey.

2. HYDROGEOLOGY OF KARST TERRANE

Karst is an internationally used word for terranes with characteristic hydrology and landforms. Most karst terranes are underlain by limestone or dolomite, but some are underlain by gypsum, halite, or other relatively soluble rocks in which the topography is chiefly formed by the removal of rock by dissolution. As a result of the rock volubility and other geological processes operating through time, karst terranes are characterized by unique topographic and subsurface features, These include sinkholes; karst windows; springs; caves; and losing, sinking, gaining, and underground streams, but in some terranes one or more of these features may be dominant. The hydrology of aquifers underlying karst terranes is markedly different from that of most granular or fractured-rock aquifers because of the abundance, size, and integration of solutionally enlarged openings in karst aquifers.

There are many different geologic settings and hydrologic conditions that influence the development and hydrology of karst terranes. For the purposes of this manual, many important aspects of the hydrogeology of karst terrane can be mentioned only briefly, A comprehensive guide to the hydrogeology of karst terranes and its literature has been published by White (1988). It and other references cited herein will direct the reader to more complete discussions of various aspects of the hydrogeology of karst terranes,

According to Davies and LeGrand (1972), about 15 percent of the conterminous United States, consists of limestone, gypsum, and other soluble rock at or near the land surface (fig. 1), Karst terranes are particularly well developed in the following areas: (1) Tertiary Coastal Plain of Georgia and Florida, (2) Paleozoic belt of the Appalachian Mountains stretching from Pennsylvania to Alabama, (3) nearly flat-lying Paleozoic rocks of Alabama, Tennessee, Kentucky, Ohio, Indiana, Illinois, Wisconsin, Minnesota, Arkansas and Missouri, (4) nearly flat-lying Cretaceus carbonate rocks in Texas, (5) nearly flat-lying Permian rocks of New Mexico, and (6) the Paleozoic belt of folded rocks in South Dakota, Wyoming, and Montana (LeGrand, Stringfield, and LaMoreaux, 1976). Much of the subsurface of the Coastal Plain in South Carolina and Alabama is a karst aquifer, but there is minimal surface expression of typical karst features. Most of the karst areas are underlain by carbonate rocks that have varying amounts of fractures. The fractures usually are enlarged by solution where they are in the zone of ground-water circulation. The enlargement of the fractures is controlled, in part, by geologic structure and lithology.



(from W.E. Davis, in Komatina, 1975, figure 7, p. 23)

EXPLANATION

A = Atlantic and Gulf Coastal Plain regions
B = East-central region
C = Great Plains region
D = Western mountain region

▨ Karst areas

⁙ Carbonate and other soluble rock at or near the surface

0 200 400 600 MILES
0 200 400 600 KILOMETERS

Figure 1.--Distribution of karst areas in relation to carbonate and other soluble rock in the conterminous United States.

There are five key elements necessary for a ground-water basin to develop in carbonate rocks. It must have: (1) an area of intake or recharge, (2) a system of interconnected conduits that transmit water, (3) a discharge point, (4) rainfall, and (5) relief. If any one of these elements is missing, the rock mass is hydrologically inert and likely cannot function as a ground-water basin.

Ground-water recharge occurs as infiltration through unconsolidated material overlying bedrock or as direct inflow from sinking streams and open swallets. Infiltrated water moves vertically until it intercepts relatively horizontal conduits that have been enlarged by the solutional and erosive action of flowing water. Springs are the discharge points of the ground-water basin and usually are located at or near the regional base level or where insoluble rocks or structural barriers such as faults, impede the solutional development of conduits,

Adequate rainfall is necessary for the solution of limestone to take place. Karst development tends to be absent if precipitation is less than 10-12 inches per year. Maximum karstification occurs in regions of heavy precipitation and in regions with marked seasons of heavy precipitation and drought (Sweeting, 1973, p. 6).

The development of ground-water basins requires vertical and horizontal circulation of ground-water. Such development is enhanced if available relief places the soluble rock above the regional base level.

The presence of solutionally enlarged fractures presents unique problems for water managers in karst terrane because of the velocity of ground-water flow and the possibility that relatively little water-quality enhancement occurs while the water is in transit within the karst aquifers. Ground-water velocities in conduits may be as high as 7,500 feet per hour (ft/hr) where the potentiometric gradient is as steep as 1:4 (Ford, 1967). Under fairly typical ground-water gradients of 0.5 to 100 feet per mile (ft/mi), velocities range from 30 ft/hr during base flow to 1,300 ft/hr during flood flow within the same conduit (Quinlan and others, 1983, p.11). Under such conditions, pollutants can impact water quality more than 10 miles away in just a week during base flow (Vandike, 1982) and much sooner during flood flow.

Where fractures within a bedrock aquifer are well developed and ground-water flow is convergent to major springs via well developed conduits, the aquifer is considered to be mature. Mature carbonate aquifers are generally developed beneath mature karst terrane, having well-developed sinkholes that collect and drain surface runoff directly into the subsurface conduit system. Streams can also drain to the subsurface through swallets developed in the stream bed or disappear into a swallet at the end of a valley.

In maturely karstified terranes, springs in a given area generally have similar flow and water-quality characteristics. Spring discharge is normally flashy, responding rapidly to rainfall. Flow is turbulent and turbidity, discharge, and temperature are highly variable. Also, hardness is usually low but highly variable. Springs with these characteristics are the outlets for conduit-flow systems (Schuster and White, 1971, 1972) that usually drain a discrete ground-water basin. Flow in a conduit system is similar to flow in a surface stream in that both are convergent through a system of tributaries and both receive diffuse (non-concentrated) flow through the adjacent bedrock or sediment.

If the aquifer is less mature, water moves through small bedrock openings that have undergone only limited solutional enlargement. Flow velocities are low and ground water may require months to travel a few tens of feet through the carbonate bedrock (Freidrich, 1981; Freidrich and Smart, 1981). Discharge from springs fed by slow-moving water in less mature karst is non-flashy, relatively uniform, and responds slowly to storms. Flow is usually laminar, turbidity is very low, and water temperature is very near the mean annual surface-water temperature. Springs with these characteristics are typical of ground-water outlets from diffuse-flow systems (Schuster and White, 1971, 1972).

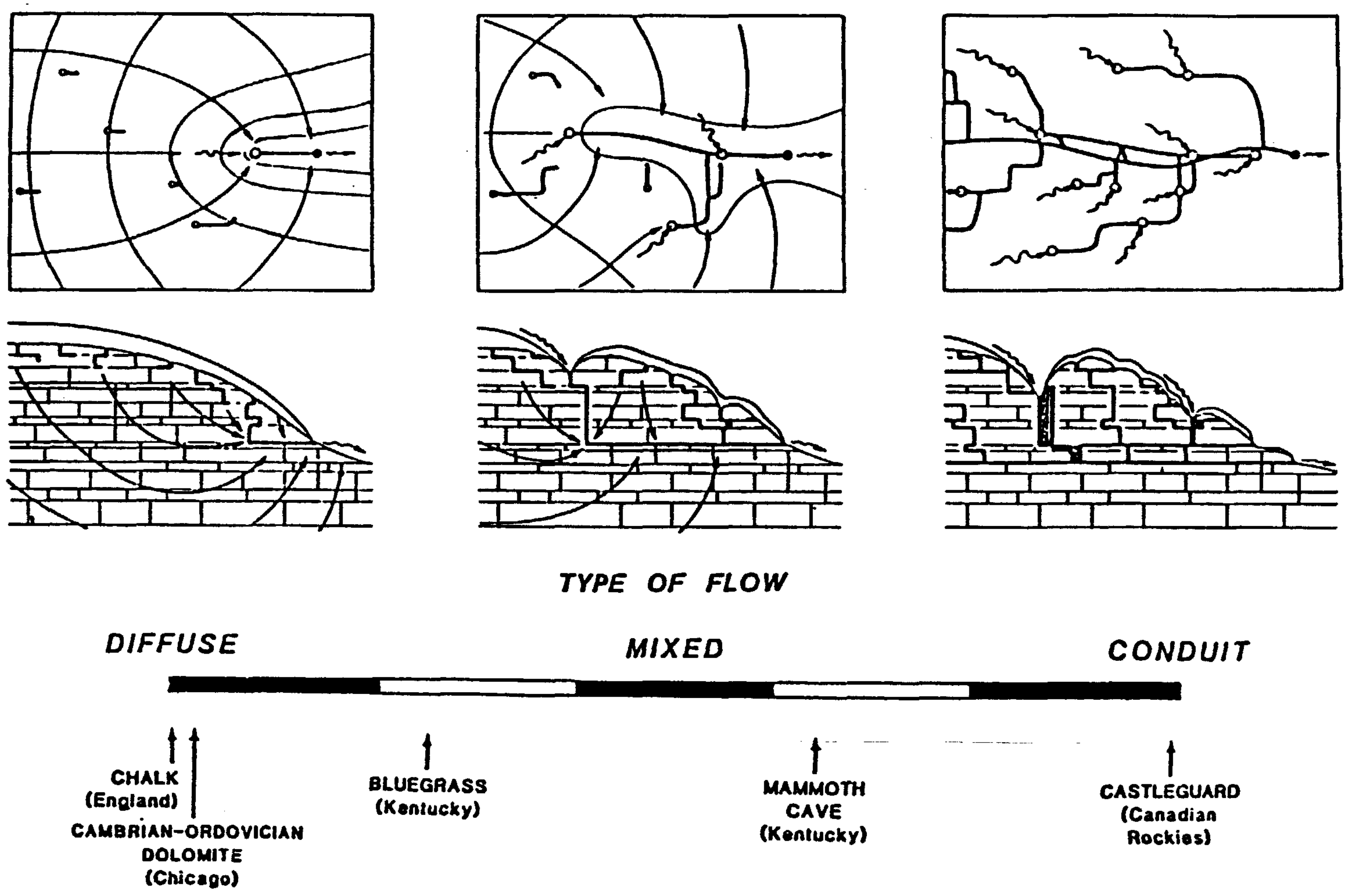
Quinlan and Ewers (1985) propose that the major portion of ground-water movement in a diffuse-flow (less mature karst) system is also through a tributary network of conduits. Only in the headwaters of a ground-water basin and adjacent to a conduit is flow actually diffuse. Their inspections in quarries and caves show that the smallest microscopic solutional enlargements of bedding planes and joints function as tributary conduits. They also propose that conduit and diffuse flow in carbonate aquifers are end members of a flow continuum (fig. 2). Although most carbonate aquifers are characterized by both types of flow, as discussed in detail by Atkinson (1977), generally, one type of flow predominates. Smart and Hobbs (1986) state that flow in massive carbonate aquifers tends to be either predominately diffuse or predominately conduit, depending on the degree of solutional development.

2.1 Karst Features

The most noticeable and direct evidence of karstification is the landforms that are unique to karst regions. Most karst landforms are the direct consequence of dissolution of soluble carbonate bedrock and are characteristic of areas having vertical and horizontal underground drainage, Although some karst landforms, such as sinkholes, may develop within a relatively thick zone of unconsolidated regolith overlying bedrock, it is the presence of solutionally enlarged openings in bedrock that ultimately controls the development of such features. Karst features include sinkholes; karst windows; springs; caves; and losing, gaining, sinking, and underground streams. These features are discussed in detail by White (1988), Jennings (1985), Milanovic (1981), and Sweeting (1973). The following discussion is limited to karst features that are most related to the ground-water system, primarily those that collect and discharge into, store and transmit, or discharge water from the ground-water system.

2.1.1 Sinkholes

The term sinkhole has been used to identify a variety of topographic depressions resulting from a number of geologic and man-induced processes. In geologic research, the term doline is synonymous with sinkhole and has become standard in the literature. However, Beck (1984, p. IX), cautions against the use of the term sinkhole to describe depressions caused by mine collapse or other man-induced activities which are not caused by karst processes,



(adapted from Quinlan and Ewers, 1985, figures 4-5, p. 107-108)

The open circles indicate sinkholes that are water inputs. Blackened circles are springs. Wavy lines are surface streams. Heavy black lines are cave passages. Flow lines and equipotential lines are shown for diffuse flow and mixed flow, but the concept of such lines is not applicable in a purely conduit system.

Figure 2.--Diffuse, mixed, and conduit flow in a hypothetical ground water basin, showing the sequence of its evolution.

Therefore, as used in this manual, the term sinkhole refers to an area of localized land surface subsidence, or collapse, due to karst processes which result in closed depressions (Monroe, 1970 and Sweeting, 1973, p. 45).

Sinkholes are depressions that can provide a direct path for surface runoff to drain to the subsurface. They can occur singly or in groups in close proximity to each other. In size, diameter is usually greater than depth, and average sinkholes range from a few feet to hundreds of feet in depth and to several thousand feet in diameter (Sweeting, 1973, p. 44). Sinkholes are generally circular or oval in plan view but have a wide variety of forms such as dish or bowl shaped, conical, and cylindrical (Jennings, 1985, p. 106), Increasing size is usually accompanied by increasing complexity of form. Sinkholes frequently develop preferentially along joints in the underlying bedrock. This often results in sinkholes which have a distinct long dimension which corresponds with local joint patterns.

The number of sinkholes generally depends on the nature of the land surface and the depth of karstification. In general, plains tend to have a large number of sinkholes of small size, and hilly terranes tend to have fewer sinkholes but of larger size, On steep slopes, sinkholes are uncommon, but if found they are likely the result of collapse of cave roofs rather than gradual subsidence of surficial materials (Milanovic, 1981, p. 60).

Several natural processes contribute to the formation of sinkholes including solution, cave-roof collapse, and subsidence. Sinkholes are generally formed by the collapse or migration of surface material into the subsurface that results in the typical funnel-shaped depressions. In general, there are two types of collapse that form sinkholes: (1) slumping of surface material (regolith collapse) into solutionally enlarged openings in limestone bedrock and (2) collapse of carbonate (limestone) cave roofs. Sinkholes caused by the collapse of cave roofs may be either shallow or deep-seated and may develop suddenly when the cave roof can no longer support itself above the underlying cave passage. Although dramatic and at times damaging, this process is considered by some investigators to be the least common cause of collapse sinkholes.

Sinkholes can also form as a result of man’s activities which tend to accelerate natural processes. Such induced sinkholes are caused primarily by ground-water withdrawals and diversion or impoundment of surface water which accelerates the downward migration of unconsolidated deposits into solutionally enlarged openings in bedrock (Newton, 1987). Induced sinkholes may provide convenient sites for dye injection and monitoring similar to natural sinkholes. However, care must be used because the area around these sites can be much less stable than in the vicinity of natural sinkholes.

There are numerous systems for the classification of sinkholes based on characteristics as varied as their processes of formation, size and orientation, and relation to surface runoff and the water table. The classification system proposed for use in this manual is based on the relative ability of the sinkhole to transmit water to the subsurface. This system emphasizes the interrelation between sinkholes and the ground-water system and especially the potential for sinkholes to funnel surface runoff directly into the subsurface. The system was used by Mull, Smoot, and Liebermann (1988) to identify those sinkholes with the greatest potential for contaminating the ground water in the Elizabethtown area, Kentucky. The criteria for sinkhole classification are based on the material in which the sinkhole is developed (sedimentary rock) and the presence or absence of drain holes (swallets). These criteria yield four types of sinkholes:

(1) sinkholes developed in unconsolidated material overlying bedrock with no bedrock exposed in the depression, but with well developed, open swallets that empties into bedrock,

(2) sinkholes that have bedrock exposed in the depression and a well developed swallet that empties-into bedrock,

(3) sinkholes or depressions in which the bottom is covered or plugged with sediment and in which bedrock is not exposed, and

(4) sinkholes in which bedrock is exposed but the bottom is covered or plugged with sediment.

Sinkholes of types 1 and 2, having a well-developed, open drain or swallet, are thought-to have the greatest potential for polluting ground water because the open drain is usually connected to subsurface openings that lead directly to the ground-water system. Thus, there is no potential for enhancement of water quality by processes such as filtration, as may be the case if water percolates through soil or other unconsolidated material at the bottom of types 3 and 4 sinkholes that do not have open swallets. Because of the open drains, types 1 and 2 sinkholes offer the most direct method for injecting tracers (dye) into the ground-water flow system because the tracers can be added to water draining directly to the subsurface through the open swallet.

Although types 3 and 4 sinkholes may be hydraulically connected to the aquifer system, the potential for pollution is generally less than from sinkholes with open drains because the percolation of water through sediments may provide some enhancement of quality before the water reaches the aquifer. Types 3 and 4 sinkholes can also be used as dye injection points during tracer tests, but the quantity and type of dye used must reflect the fact that the dye must first percolate through the soil plug before reaching the subsurface flow system. Also, dye traveltimes from types 3 and 4 sinkholes are difficult to predict because of the time required for water and dye to percolate through the soil plug,

The nature of the swallet and the hydraulic characteristics of the underlying aquifer will, in part, control the rate and quantity of water draining from the sinkhole. Pending or sinkhole flooding can occur in types 1 and 2 sinkholes if runoff exceeds the drainage capacity of the swallet or if the subsurface system of conduits which receives sinkhole drainage is blocked. Drainage from sinkholes is also controlled by the nature of sediment and debris washed into the swallet. Heavy sediment loads, such as are common from freshly disturbed construction or cultivated sites, coupled with large debris, can partially obstruct or plug the swallet resulting in the pending of water in the sinkhole. Soil and debris plugs can be temporary and be flushed open with subsequent heavy runoff. Mull and Lyverse (1984, p. 17) reported several instances following periods of rapid runoff in which water collected in and overflowed sinkholes because the drain was partially plugged. In some cases, water ponded in a sinkhole having a plugged swallet may overflow the sinkhole and flow to other sinkhole swallets or surface streams. However, depending on the shape and size of the sinkhole and the nature of the area draining to it, the ponded water may not drain to an adjacent sinkhole or surface stream but may remain in the drainage basin of the sinkhole and eventually drain to the subsurface through the swallet.

Because virtually all surface runoff that is collected by sinkholes is eventually funneled directly into the ground-water system, drainage through sinkholes can seriously impact water supplies developed from underlying carbonate aquifers. Thus, it is imperative that water managers identify those sinkholes and sinkhole areas that recharge a particular karst water-supply spring or well in order to develop adequate ground-water protection procedures. Such procedures can be preventive, such as the application of land-use restrictions around selected sinkholes, or reactive, such as the determination of traveltimes and other aquifer flow characteristics developed from quantitative dye tracing.

Sinkholes are often the most ubiquitous evidence of karstification. Although some authors consider the absence of sinkholes sufficient evidence to classify an area as non-karst, Dalgleish and Alexander (1984) point out that in some areas of the Midwest more than 60 percent of the existing sinkholes are not shown on 7 l/2-minute (1:24,000) topographic maps. Also, Quinlan and Ewers (1985) state that karst cannot be defined solely in terms of the presence or absence of sinkholes, As a genaralization, almost any terrane underlain by near-surface carbonate rocks has some degree of karst and can, therefore, exhibit water supply and protection problems that are characteristic of classic karst terranes.

2.1.2 Karst Windows

A karst window is a landform that has features of both springs and sinkholes. It is a depression with a stream flowing across its floor: it may be an unroofed part of a cave. Thrailkill (1985, p. 39) adds the criteria that karst windows are deep sinkholes in which major subsurface flow surfaces and that the streamflow is near the level of major subsurface flow.

Most karst-window streams issue as a spring at one end of the sinkhole, flow across its floor, and sink into the subsurface through a swallet. The length of the surface flow varies from what may appear to be a pool in the bottom of a sinkhole to a stream several hundred feet long (Thrailkill, 1985, p. 39), As with a sinkhole that drains to the subsurface, the karst window may flood and overflow its depression if the openings draining to the subsurface become blocked or if the subsurface conduits receiving that drainage are filled. Karst windows are hydrologically significant because the exposed streams provide a direct path to the subsurface for any contaminant deposited in or near the sinkhole. Also, they serve as convenient ground-water sampling and monitoring points.

2.1.3 Losing, Sinking, Gaining, and Underground Streams, and Blind Valleys

Underground streams are common in karst terranes and, in contrast to ground water in granular aquifers, exhibit many characteristics of surface streams. Losing streams have streambeds above the water table and recharge the underlying karst aquifers. Losing streams may lose all or part of their flow to the ground-water system at points or intervals along their course through openings in bedrock that intersect the streambed or as seepage through alluvium overlying bedrock. Losses of flow can also occur through well developed swallets in the streambed that occur singly or as a group of sinkpoints developed over a particular part of the aquifer. Streams may gain flow in one reach but lose in another reach depending on local geologic and hydrologic conditions. A losing stream may be perennial or intermittent and may either gain or lose at different times of the year depending on the seasonal fluctuations of the water table. Although difficult to quantify, recharge to the aquifer by losing streams may constitute a major portion of the total ground-water recharge in some areas.

Some sink points in streams in karst terrane behave in a way that are unique to streams with major connections to the karst ground-water system. During time of flood, they may discharge ground water rather than receive water from the stream. This happens because the conduit or cave system fed by the stream also receives water from other underground feeders, and during flood events the total flow underground cannot pass through conduit constrictions and backs up to the point where it issues from a former sinkpoint. The French word “estavelle” is the commonly used term for such points of reversing flow (Jennings, 1985 p. 46). The term is also applied to sinkholes that alternately receive or discharge water and are not necessarily located in a streambed (Milanovic, 1981 p, 102). Estavelles may serve a dual purpose for the water manager; as a sinkpoint for potential contaminants or dye injection point during periods of low flow and a water-quality monitoring or dye-recovery point during periods of high flow.

The authors distinguish losing streams from sinking streams on the basis of the quantity of streamflow that drains underground and the presence of a swallet through which water drains underground. Losing streams are those that lose part or all of their flow by seepage. In contrast, sinking streams are those that terminate and usually drain underground through one or more well developed swallets, usually at the end of a valley.

A valley that ends suddenly at the point where its stream disappears underground is termed a blind valley (Monroe, 1970). Some blind valleys have no present-day streams and are suggestive of an earlier stage of karstification. Thrailkill (1985, p. 40) uses the term “paleovalleys” to describe valleys that contain no active surface stream channel. Paleovalleys usually contain a series of sinkholes in their bottoms, and apparently formed when their surface streams were diverted underground at several points. Eventually all stream flow was underground except possibly during high discharge events.

Relatively large sinking streams are commonly called “lost rivers” because they drain underground through caves of relatively large size and issue from caves as relatively large springs. A well known lost river occurs in Bowling Green, Kentucky where flow in a major conduit surfaces at the Lost River Blue Hole, flows on the surface for about 400 feet, and sinks into the large entrance to Lost′ River Cave. The underground river flows beneath the City of Bowling Green, eventually resurfacing at the Lost River Rise, a straight-line distance of about 2.8 miles. From this point, the river flows on the surface to the Barren River, the major base level stream of the area (Crawford, 1981).

The subsurface course of a lost river is described as an underground stream. A cave stream is another example of an underground stream. Flow patterns of underground streams do not always obey topographic drainage patterns as do surface streams, Using qualitative dye traces in the Bowling Green, Kentucky, area, Able (1986, p. 37) demonstrated that two adjacent valleys with separate surface streams, transferred ground water beneath their topographic drainage divide through underground streams.

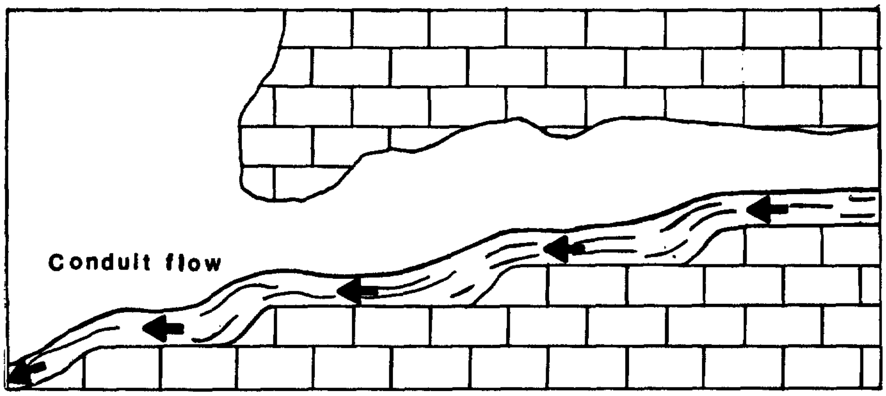
Because water in losing, sinking, and underground streams is subject to contamination from the surface, the contaminants may be transported directly into the ground-water system. Thus, it is important to identify these features in areas where karst aquifers are the source of public water supplies.

Gaining streams occur where the streambed descends to an altitude low enough to intersect the zone of saturation. Such streams may be gaining from headwaters to their mouth or for only a short distance. Because stream flow in a gaining stream is mainly ground-water discharge, the water quality of the stream can be affected. Thus identification of the area draining to gaining streams is needed, especially where gaining streams are used for public water supplies.

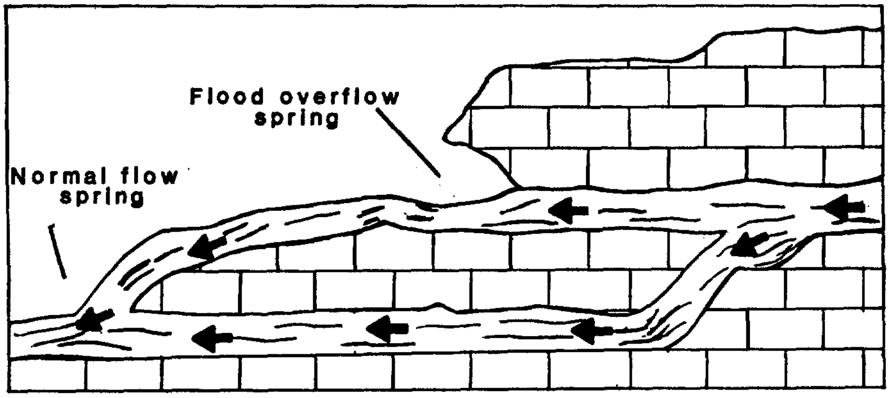
2.1.4 Karst Springs

A karst spring is a natural point of discharge from a karst ground-water aquifer. Discharge from a karst spring may issue from openings ranging in size from less than an inch to many feet in diameter. Water may either flow out under gravity or rise under pressure to form seeps or surface streams. The discharge openings may be visible, or invisible where covered by unconsolidated material or submerged below the surface of a lake or stream. Different discharge points within the same system can be active during different flow conditions. Some of the more common types of karst springs are shown in figure 3.

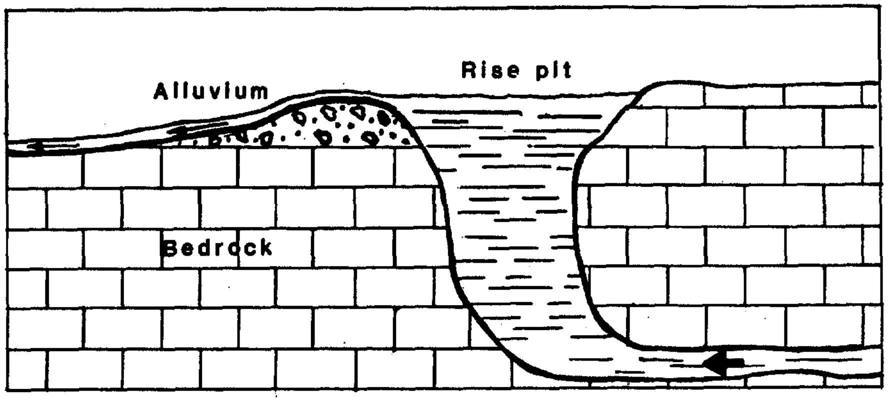
A karst spring may occur at local or regional base levels or at a point where the land surface intersects the water table or water-bearing cavities. Underlying impervious bedrock can cause springs at the interface of the karst aquifer and the bedrock. Springs can occur either in valley bottoms or at sharp breaks in slope. Karst springs may occur at any point where impermeable rock or structural features, such as faults, impedes ground-water flow and thus restricts the formation of conduits in the soluble bedrock. Karst springs can occur high, along valley sides, without obvious topographic or geologic cause. This may be caused by rapid down cutting of the main valley which has exceeded the downward development of solutionally enlarged openings sufficient to lower the karst spring outlets to the local base level (Jennings, 1985 p. 50).



CONDUIT SPRING



FLOOD OVERFLOW SPRING



RISE PIT SPRING

(modified from Jennings, 1985, figure 15, p. 47)

Figure 3.--Common types of karst springs.

A karst spring is generally the principal discharge point for a karst ground-water basin, A particular karst spring may discharge from a master conduit and represent drainage from a system of integrated conduits that converge to that conduit (convergent flow) or be one of a group of springs (terminal distributaries) that function much like the delta of a surface stream in which ground water is dispersed to many springs from a tributary system of conduits (distributary flow) (Quinlan, Saunders, and Ewers, 1978). Quinlan and Ewers (1985) state that terminal distributaries and their related springs are a common feature of carbonate aquifers. Quinlan and Rowe (1977) discuss a distributary system of Hidden River Cave, Kentucky in which 46 springs at 16 locations in a 5-mile reach of river, discharge water to the Green River,

Because karst springs are usually the principal discharge points for drainage from an entire ground-water basin, they represent the most likely and convenient points to monitor the recovery of dye injected upgradient from the springs. Thus, it is mandatory that all springs that may drain a particular injection point, be located and monitored during dye tracing.

2.2 Occurrence and Movement of Ground Water

Ground water in karst terrane occurs in both unconsolidated sediment and bedrock that may comprise a complex interrelated aquifer system. The nature of ground-water movement in karst terrane varies considerably from place to place depending on the nature of the aquifer system.

Ground water in the unconsolidated surficial material overlying bedrock is generally thought to occur in intergranular (primary) openings and thus, to behave according to the theories of ground-water movement in porous media. Although this is generally true, there is evidence that concentrated flow also occurs in enlarged openings (macropores) in the unconsolidated material (Bevan and Germann, 1982, p. 1311). Quinlan and Aley (1987) state that concentrated flow in macropores (root channels, cracks or fissures, animal burrows, and textural transitions) is commonly several orders of magnitude more rapid than in the adjacent unconsolidated sediment. Mull, Smoot, and Liebermann (1988) report the presence of pipe-like openings and numerous conduits in the unconsolidated material overlying bedrock in the Elizabethtown area, Kentucky. Many of these conduits contained water, in some cases, as much as 40 feet above bedrock. This indicates that, in places, there is a conduit system in the unconsolidated material that can collect and funnel water to water bearing conduits in the underlying bedrock. Because of this conduit system, potential ground-water contaminants placed on the surface or in depressions such as sinkholes, can enter the ground-water flow system fairly quickly, despite the fact that the thickness of unconsolidated, surficial material may be 50 feet or more.

The occurrence and movement of ground water in bedrock underlying karst terrane is quite different from that underlying non-karst terrane, primarily because of the presence of conduits that permit relatively rapid transmission of ground water. The predominant rock types in most karst terrane are limestone and dolomite. These rocks may be relatively impervious except where fractures and bedding planes have been enlarged by circulating ground water. The circulating water dissolves carbonate bedrock and enlarges the openings.

The enlarged openings may be vertical or horizontal and range in size from a fraction of an inch to tens of feet, such as at Mammoth Cave, Kentucky. As mentioned earlier, ground-water flow in a mature karst aquifer is primarily through conduits and can be described by pipe and channel flow equations (Gale, 1984). Components of ground-water flow in a mature karst aquifer are shown by the generalized block diagram (Gunn, 1985) in figure 4.

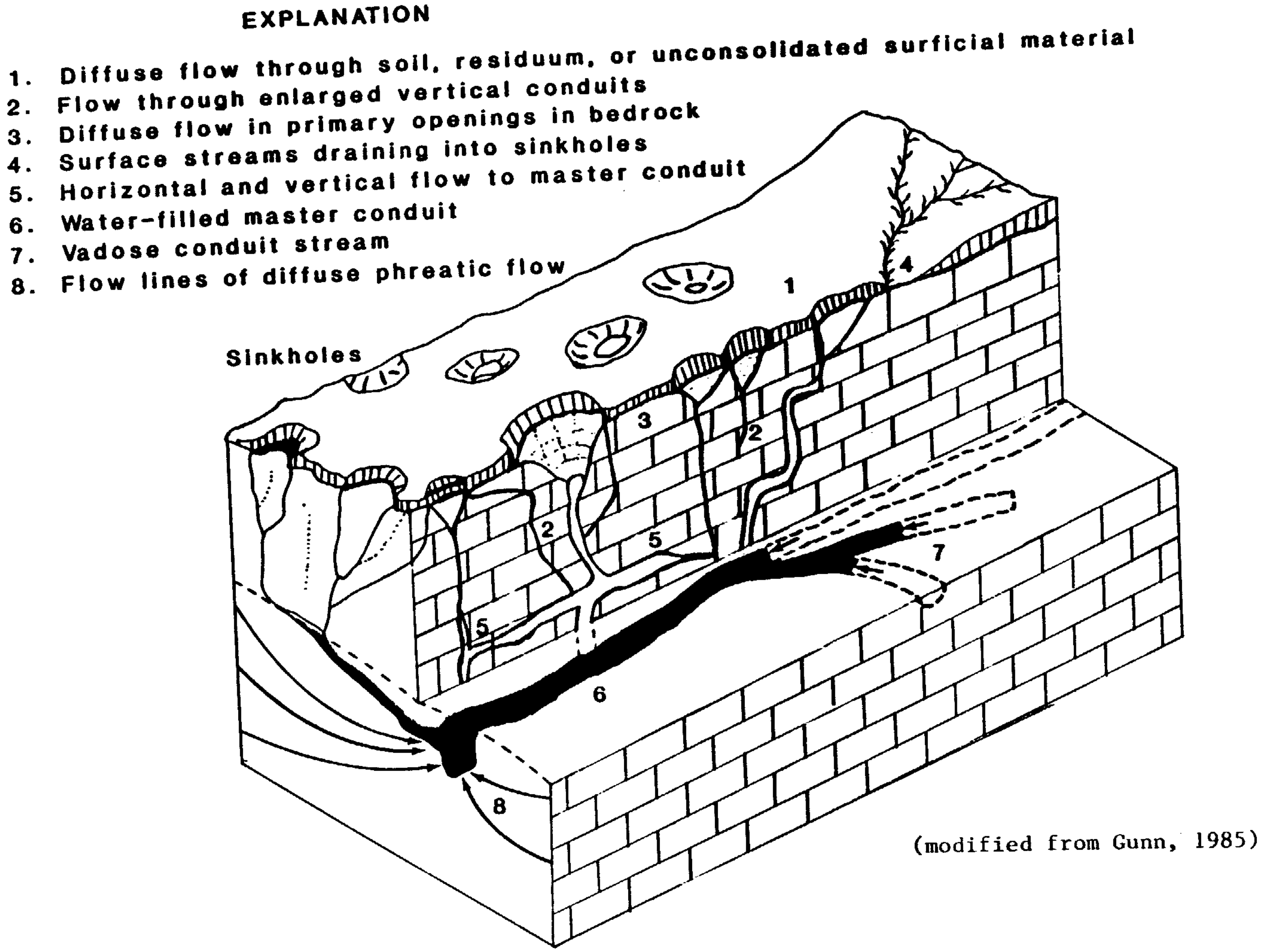
Ground water in karst terrane, as in other terranes, moves in response to hydraulic gradients from points of recharge to points of discharge. The horizontal gradient of the ground-water surface, the general shape of the water table, and the general direction of movement can be determined from a water-level contour or potentiometric map. The contours are based on the altitude of the water level in wells, springs, and streams. The general direction of ground-water movement can be estimated by drawing flow lines perpendicular to the water-level contours. Results from dye traces can also be used to confirm the direction of ground-water movement shown by the water-level contour map.

The rate of ground-water movement is also important to the understanding and solution of many ground-water problems in karst terrane, especially to those related to contamination of the ground-water system in karst terranes. Results of dye tracing can define the rate of ground-water movement and the fact that the rate is not constant, but varies with hydrologic conditions.

Karst aquifers have been classified into three types based on the nature of ground-water flow (White, 1969, 1988, p. 171). Each type contains subvarieties and variations. The classification system applies mainly to karst regions with low and gentle relief and is intended to establish some useful criteria for determining the nature of the underground-flow system from observable geologic characteristics. The following discussion of the three types of karst aquifers is adapted from Fetter (1980), Milanovic (1981), and White (1969).

(1) Diffuse-flow karst aquifers. Diffuse-flow aquifers commonly develop in dolomitic rocks or shaly limestones where the solutional activity of moving ground water has been retarded by lithologic factors. Water movement is laminar, along joints and bedding planes that have been only slightly enlarged by solution. Ground-water flow is usually not concentrated in certain zones in the aquifer and, if present, caves are limited in size and not interconnected. Discharge from the aquifer occurs through many small springs and seeps, The water table is well defined and can rise well above the regional base level. Typical karst landforms are absent or poorly developed. An example of a diffuse-flow aquifer is the dolomite aquifer in Silurian rocks of the Dupage County-Chicago Region of Illinois (Zeizel and others, 1962).

(2) Free-flow karst aquifers. Free-flow or conduit-flow aquifers are developed in thick and massive soluble rocks where ground-water flow is concentrated in a well-defined and integrated system of enlarged conduits which behave hydraulically as a system of pipes. Flow velocities are similar to surface streams and are often turbulent. The regional discharge may occur through a single large spring. Because of the rapid drainage, the water table can be virtually flat



(modified from Gunn, 1985)

Figure 4.--Components of ground-water flow in a mature karsted aquifer.

for miles, with only a slight elevation above the regional base level. Water levels in the conduit network and spring discharge respond rapidly to recharge events, and during periods of heavy precipitation the spring hydrography may resemble the flood peak of a surface stream. Examples of this type of aquifer may be found in the Missouri and Arkansas Ozarks, southern Indiana, and central Kentucky.

(3) Confined-flow karst aquifers. Confined-flow karst aquifers contain beds of low hydraulic conductivity, caused by stratigraphic or structural conditions, that control the rate and direction of ground-water flow. Flow in karst aquifers bounded by such confining beds can occur at great depths in solution openings that are much deeper than in free-flow aquifers. The flow is not concentrated in master conduits but occurs in a system of relatively dense solution joints that form characteristic network caves. The Floridan aquifer (Stringfeld, 1966) is an example of a confined-flow karst aquifer.

In summary, two types of ground-water flow generally occur in karst terrane, diffuse (slow, laminar flow) and conduit (rapid, turbulent flow). Diffuse flow occurs predominantly in primary openings, whereas conduit flow occurs mostly in secondary openings that range from a fraction of an inch to tens of feet. Water that moves through conduits can enter the subsurface through discrete points, such as sinkholes or sinking streams. Flow in a diffuse-flow aquifer can be concentrated into discrete conduits in the subsurface. The hydrologic significance of conduit flow is the rapid transmission of water through the aquifer. For further discussions on the classification and subdivision of karst aquifers see Thrailkill (1986), Smart and Hobbs (1986), and White (1977, 1988).

2.3 Vulnerability of Karst Aquifers to Contamination

As previously stated, ground water in karst terrane can be extremely vulnerable to contamination. This vulnerability varies according to the nature of the contaminant, karst features, occurrence of ground water in karst terrane, the degree of contact of infiltrating water with the soil zone, and the opportunity for transported pollutants to enter the aquifer system.

In general, water quality can be considered in terms of physical, chemical, and biological characteristics. Contaminants of concern are generally of a chemical or biological nature. The chemical contaminants that may be transported in a karst ground-water flow system can be classified as inorganic or organic, dissolved or suspended (particulate), or volatile. Contaminants may originate from a variety of land-use activities, such as agriculture, mining, construction, urban stormwater and spills, and waste and wastewater management practices, such as municipal or industrial wastewater discharges, septic tank leachate, and landfill leachate. Crawford (1982) has identified many of these contaminants and contaminant sources in the Lost River drainage basin near Bowling Green, Kentucky. Leaking underground storage tanks and industrial discharges have entered the cave system beneath Bowling Green, causing explosive fumes to rise into homes and other buildings.

Dissolved contaminants in conduit-flow aquifers can be readily transported under all types of flow conditions. Examples include many industrial organic compounds, herbicides, nutrients, and trace metals.

Constituents associated with suspended matter generally require more energy (generated by high velocities and turbulence) for transport. The energy required for transport is related to the density, size, and shape of the suspended particles. Contaminants could include sediment with attached insecticides, nutrients, and heavy metals, Contaminants associated with suspended material can also be mechanically filtered out in diffuse-flow conditions by the small pore openings in the aquifer matrix. In contrast, in the large, well-developed solutional openings in some karst aquifers, it is common for large-sized sediment and other particulate material with associated contaminants to be readily transported, These contaminants may enter the aquifer from a sinking stream or sinkhole, move rapidly through the conduit system, and exit at a spring or well.

Biological contaminants such as viruses, bacteria, and other microorganisms, as well as larger organisms, may be readily transported in a karst aquifer in much the same manner as chemical contaminants. They may or may not be associated with other suspended matter. The larger organisms and organism/suspended matter aggregates generally require large openings and high velocities for ground-water transport similar to those that typify ground-water movement in karst terranes.

Almost all water that reaches a ground-water flow system percolates through a soil zone. The soil zone can significantly enhance the quality of percolating water by filtration, various physical and chemical reactions (solution, precipitation, oxidation-reduction, ion exchange, adsorption-desorption, and acid-base reactions), microbiological transformation, and other physical, chemical, or biological processes. However, in karst terrane, the infiltrating water may have little or no contact with the soil zone and, thus, limited opportunity for quality enhancement before entering the ground-water system.

Although sinkholes with plugged drains may be hydraulically connected to the aquifer system, the potential for pollution is generally less than from those with open drains. Because water infiltrates through sediments in the bottom of the sinkhole, some water-quality enhancement can occur.

As described previously in this manual, the development of solutionally enlarged openings in soluble bedrock below the soil zone and other unconsolidated material is generally the first phase of sinkhole development. The growth and interconnection of these openings provide the subsurface drainage system for the infiltration and transport of unconsolidated material from the surface and results in sinkhole formation. It is this same network of subsurface openings that provides avenues for rapid movement of contaminants to ground water. Because ground water in karst aquifers moves mainly through open conduits, it typically moves much faster than in other aquifers and may be on the order of miles per day. Therefore, any contaminant entering the ground-water system, such as one carried by surface runoff, has the potential for rapid transport and distribution within the system.

3. DYE TRACING CONCEPTS, MATERIALS, AND TECHNIQUES

3.1 Introduction

Given the unique characteristics of karst ground-water systems, the management of a water supply using such an aquifer is difficult. The water-supply manager needs to fully understand the aquifer's geographic extent and hydraulic characteristics in order that a safe, reliable supply of water can be provided to the consumer. Specialized, site-specific predictive techniques based on qualitative and quantitative dye tracing can be used to develop appropriate plans to react to events and actions, which may jeopardize the safety of the water source.

The practice of tracing ground-water flow by adding distinctive substances to water draining underground and monitoring the downgradient resurgence of that water has long been a useful tool for hydrologic investigations. Given the hydrology of karst terranes, dye tracing is generally the most practical and satisfactory method to provide information for the management and protection of karst aquifers. Information from properly conducted dye traces can identify point-to-point connections between discrete recharge areas and discharge points such as springs or wells. In addition, analysis of dye-recovery data can provide critical management information, such as time of travel, peak concentration, and persistence of potential contaminants.

One of the earliest reported water-tracing experiments took place almost 2,000 years ago when chaff was thrown into Ram Crater Lake in order to identify springs at the headwaters of the Jordan River (Mazor, 1976). Throughout the development of tracer techniques, the materials used for tracers have been limited only by the creativity of the experimenters and in recent years have included such diverse items as computer-card chips, dog biscuits, plastic pellets, oranges, and food coloring. Accidental or intentional dumping of distinctive substances has often served to identify point-to-point connections between various sinkholes and springs or wells, For example, Quinlan and Rowe (1977, p. 9) reported the dumping of an estimated 340 tons of whey into a sinkhole that contaminated water from public-supply wells at Smiths Grove, Kentucky, about 5 miles away. Also, Aley and Fletcher (1976) reported that water from a sinkhole was traced to a nearby high school in Tennessee when revenue agents dumped 2,000 gallons of illegal whiskey into the sinkhole, Mull, Smoot, and Liebermann (1988), reported that drainage from a salt-storage yard that flows into a cave near Elizabethtown, Kentucky was traced to an unused spring about 1.4 miles away.

In all cases mentioned above, the primary objective of water tracing was successfully, but perhaps unintentionally, accomplished, The subsurface connection between a specific recharge point and a discharge point located some distance away was identified, Dye tracing to identify point-to-point connections is generally known as qualitative dye tracing and may use visual observation or a passive detector and visual observation to detect dye at a discharge point. Time of travel and flow velocity may generally be determined through qualitative dye tracing. However, if more precise hydrologic information, such as time of travel and ground-water flow velocity, or potential contaminant transport characteristics, such as persistence, dispersion rates, and concentration are needed, then quantitative dye tracing using discharge measurements and precise measurements of the dye concentrations in the water are required.

Many reports give detailed information on the theory and techniques of qualitative and quantitative dye tracing. In particular, the manuals by Aley and Fletcher (1976) and Quinlan (1987a), provide detailed discussions of criteria for dye selection and qualitative dye tracing techniques. Smart and Laidlaw (1977) provide a primary reference on properties of dyes used for tracing. Basic information on quantitative aspects of dye tracing of surface waters are presented by Wilson, Cobb, and Kilpatrick (1986), Hubbard and others (1982), Kilpatrick and Cobb (1985). Techniques for tracing ground waters are discussed by Jones (1984). Dye-tracing techniques that may be described as semi-quantitative are discussed by Duley (1986) and Spangler, Byrd, and Thrailkill (1984).

The distinguishing characteristic of semi-quantitative tracing is instrumental analysis of various elutants or detectors to confirm the recovery of a particular dye used for tracing. The use of filter fluorometers or scanning spectrofluorometers can identify dye concentrations well below the limits of visual detection. Semi-quantitative tracing is not discussed in this manual because the equipment and procedures used in this method are similar to those of qualitative and quantitative tracing which are described in detail in the following sections.

Investigators need to contact appropriate state water-supply and ground-water protection program and health department offices concerning state policies on dye tracing and to coordinate and inform these offices of tracing activities. This will serve to determine if other dye traces have been conducted in the same area. Discussion with other investigators may prevent wasted effort and expense due to confusing or erroneous results caused by simultaneous use of the same tracer or the recovery of dye from an otherwise unknown tracer test.

3.1.1 Dye Characteristics and Nomenclature

Perhaps the most widely used tracers in karst terrane are fluorescent dyes. These dyes are commonly used because they are readily available, are generally the most practical and convenient tracers, and they all, to some degree, are absorbed on activated coconut charcoal or unbleached cotton. Fluorescent dyes are generally superior to non-fluorescent dyes because they can be detected at concentrations ranging from one to three orders of magnitude less than those required for visual detection of non-fluorescent dyes. Thus, traces with fluorescent dyes usually can be completed without the aesthetically unpleasant probability of discoloring a private or public water supply .

Because tracing karst ground-water flow frequently involves either private or public water supplies, the problem of toxicity of the tracers must be considered. There is a relatively large amount of information available on the toxicity of the most commonly used tracers. Smart (1984) presents a review of the toxicity of 12 fluorescent dyes used for water tracing that includes the tracers discussed in this manual, namely, rhodamine WT, optical brighteners, Direct Yellow 96, and fluorescein. As reported by Smart, three dyes present minimal carcinogenic and mutagenic hazard: Tinopal CBS-X (brightener), fluorescein, and rhodamine WT. Douglas and others (1983) reported that rhodamine WT is non-carcinogenic but found a small but statistically significant dose-related, mutagenic effect. However, they concluded that the use of rhodamine WT does not appear to represent a major genotoxic hazard. Steinheimer and Johnson (1986) have shown that, under customary dye-study practices in surface waters, the possible formation of carcinogenic nitrosamines from the use of rhodamine WT should not constitute an environmental hazard. In ground water which may be enriched with nitrite, nitrosamines could form, but high-nitrite concentrations in ground water are uncommon (Hem, 1985, p. 124-126). Therefore, the possible formation of nitrosamines from rhodamine WT is not likely to be a problem. Quinlan (1987b) points out that numerous investigators (Anliker and Muller, 1975; Lyman and others, 1975; Ganz and others, 1975; Burg and others, 1977; and Smart, 1984) have found optical brighteners to be non-toxic, non-carcinogenic, and non-mutagenic and therefore safe for use as a tracer. It should be pointed out that one dye, rhodamine B, that was earlier approved by the EPA for use as a tracer in potable water (Cotruvo, 1980) is now not recommended because impurities within it are known to be carcinogenic and possibly mutagenic (Smart, 1984).

Because most dyes are available under many commercial names, the Colour Index (CI) Generic Name or Constitution Number of a dye needs to be used to avoid confusion and the possible use of inappropriate dyes. Positive dye identification is especially needed if dye properties and results of dye tracing are being discussed. The standard industrial reference to dyes is the Colour Index (SDC & AATC, 1971-1982) which describes about 38,000 dyes and pigments. Concise guides to dye nomenclature can be found in Giles (1974), Abrahart (1968), and especially the paper by Smart and Laidlaw (1977). In addition, useful discussions on dye nomenclature and the problems arising from multiplicity of names for the same dye are presented by Quinlan (1987b and 1986b) and Quinlan and Smart (1977). The problems of dye nomenclature are reduced if only one or two dyes are used. However, knowledge of dye nomenclature and classification is essential in order to select multiple dyes with similar characteristics or obtain a replacement if the original dye is no longer available.

3.1.2 Fluorescent Tracers

Although many different fluorescent dyes are used as ground-water tracers, present usage is centered on four: rhodamine WT (CI Acid Red 388), fluorescein (CI Acid Yellow 73), optical brighteners, and Direct Yellow 96. In general, rhodamine WT is not used for qualitative tracing because of the difficulty of visually distinguishing the pink color of the dye from that of other organic compounds that can easily be sorbed by activated coconut charcoal. Characteristics of the fluorescent dyes discussed in this manual are presented in table 1.

Although there are two dyes called fluorescein, and both are labeled CI Acid Yellow 73, only one is water-soluble. The water soluble sodium salt of fluorescein ($C_{20}H_{12}O_5$) is sodium fluorescein ($C_{20}H_{10}O_5Na_2$) and is commonly used for water tracing. The European name for sodium fluorescein is uranine. However, the conventional usage in the United States and England is simply fluorescein, which is followed in this manual.

Table 1.--Characteristics of commonly used tracer dyes

Tracer and color index	Passive detector	Detection (elutriant)	Detectable concentrations	Advantages	Disadvantages	Remarks
Sodium fluorescein CI Acid Yellow 73	Activated coconut charcoal 6-14 mesh	Ethyl alcohol and 5 percent KOH or fluorometric analysis of water samples.	0.1 micrograms per liter, dependent on background levels and fluctuation.	1. Does not require constant monitoring or fluorometric analysis. 2. Inexpensive.	1. Dye is photochemically unstable. 2. Moderate sorption on clay. 3. pH-sensitive.	Most common dye used in karst terrane.
Rhodamine WT CI Acid Red 388	Activated coconut charcoal 6-14 mesh	1-Propanol and NH_4OH, or ethyl alcohol, 5 percent KOH and water, or fluorometric analysis of water samples.	0.01 micrograms per liter, with fluorometer.	1. Dye is photochemically stable. 2. Dye may be used In low pH waters.	1. May require fluorometric analysis. 2. Moderate clay sorption. 3. Difficult to distinguish during qualitative tracing.	Not recommended for qualitative tracing. Ideal for quantitative tracing.
Optical brighteners CI Fluorescent brightener 28	Unbleached cotton	Visual examination of detectors under UV light or fluorometric analysis.	Dependent on background levels, but generally at least 0.1 micrograms per liter.	1. Inexpensive. 2. No coloring of water.	1. Background readings may limit use. 2. Adsorbed onto some organics.	Nay be used simultaneously with a green and orange dye that sorb onto activated coconut charcoal.
Direct Yellow DY 96	Unbleached cotton	Visual examination of detectors under UV light or fluorometric analysis.	1.0 micrograms per liter, on cotton.	1. No natural background. 2. Good stability and low sorption. 3. No coloring of water in usual concentrations.	1. Moderate cost. 2. Sensitive to PH.	Has been used extensively in Kentucky.

Table modified from Jones, 1984.

SDC SOC and AATCC Color Index.

[2]**Very** Very dilute dye solutions are concentrated upon the detector over a period of time.

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Fluorescein has been widely used for ground-water tracing in karst terrane since the late 1800's (Aley and Fletcher, 1976). It is presently one of the most widely used water-tracers in karst areas in the United States (Quinlan, 1986a) because of its safety, availability, and its ready adsorption onto activated coconut charcoal. Fluorescein is a reddish-brown powder that turns vivid yellow-green in water, is photochemically unstable, and loses fluorescence in water with pH less than 5.5.

Optical brighteners and CI Direct Yellow 96 are suitable for dye tracing because they are detectable in low concentrations, are non-toxic, have low affinity for adsorption onto clays, and are readily adsorbed on undyed surgical cotton used to recover dye in passive detectors. Optical brighteners are, however, widely used in laundry detergents and soaps for enhancing fabric colors and are thus a common constituent of domestic wastewater. For this reason, the effectiveness of optical brighteners for water tracing may be limited in areas where effluent from septic systems is present. Because, the presence of optical brighteners indicates the presence of laundry wastewaters, they can be used as indicators of sewage in various ground-water resurgences. If relatively high levels of optical brighteners are present as background, the choice and amount of brightener used for tracing can be affected. The background levels of optical brighteners can easily be determined by placing undyed cotton detectors in ground-water resurgences and testing for fluorescence before tracer dyes are injected. This background check needs to be done before the use of any dye.

CI Direct Yellow 96, because of its distinctive yellow fluorescence, is ideal for water tracing in areas where background levels of optical brighteners are present. Unlike optical brighteners, CI Direct Yellow 96 does not undergo significant photochemical decay. CI Direct Yellow 96 is a powder that needs to be mixed thoroughly with water before injection into the ground-water system and, like optical brighteners, is readily adsorbed onto undyed cotton detectors. Optical brighteners and CI Direct Yellow 96 have been used with a great deal of success for water tracing in several karst areas. For example, Quinlan and Rowe (1977), Thrailkill and others (1982), and Spangler, Bird, and Thrailkill (1984) have reported successful tracing with optical brighteners and CI Direct Yellow 96 in the Mammoth Cave and Inner Blue Grass regions in Kentucky.

3.2 Qualitative Dye Tracing

3.2.1 Introduction

Although one primary purpose of this manual is to present procedures and techniques for quantitative dye tracing, the results of qualitative dye tracing are usually needed to design and implement the more labor intensive quantitative phase of dye tracing. In particular, qualitative dye tracing can delineate the boundaries of a ground-water basin and identify point-to-point connections between input and recovery points allowing special attention to be given to those points with the highest potential for contaminating the ground-water system. In some cases, a qualitative dye trace may provide adequate information to satisfy the needs of the water-supply manager. For example, if a particular spring, used as a water-supply source, is shown to be the resurgence of drainage from sinkholes, compatible land-use practices around these sinkholes may adequately protect the water supply. If, however, qualitative dye tracing shows inputs from several widespread source areas, then land-use controls alone may not be effective and quantitative dye trace data and analysis may be required to more effectively manage and protect the ground-water resource.

Qualitative dye tracing involves the tagging of a discrete sample of water with an appropriate tracer and monitoring the arrival of that tracer-laden water at various ground-water resurgences. The arrival of the dye may be observed visually or the dye may be recovered by passive detectors and identified by various chemical or instrumental analyses that reveal its presence.

The following discussion describes the procedures and equipment used for qualitative dye tracing by many investigators, but is based, primarily, on those used in the Mammoth Cave area by Quinlan (1981). As Quinlan (1987a) states, the procedures and techniques summarized here are not the only successful techniques for dye tracing in karst terrane, but he and many investigators, including the authors, have found that these techniques consistently give reliable results.

3.2.2 Selecting Dye for Injection

Selecting a particular dye for water tracing in karst terrane is based on factors such as quality of the water draining underground, nature of the background concentrations of potential tracers such as optical brighteners, character of the injection point, availability and cost of a particular dye, and the availability or complexity of equipment needed to detect the dye. Dye-selection criteria and the advantages and disadvantages of the four most commonly used dyes are discussed below and summarized in table 1, Although rhodamine WT is not generally considered for qualitative dye tracing because of the difficulty of detection without the use of a spectrofluorometer or a filter flourometer, rhodamine WT is included because it can be used for qualitative dye tracing under conditions of availability, convenience, or necessity.

Although not generally a problem in karst terrane, low pH water can seriously attenuate the fluorescence of fluorescein and Direct Yellow 96. The fluorescence of optical brighteners is much less affected by pH, thus these tracers can be used if the pH of the water being traced is 5.0 or less.

Quinlan (1987a) states that all tracer dyes tend to react with the environment through which they flow and that all four tracers discussed here are sorbed on to clays, although optical brighteners and CI Direct Yellow 96 are sorbed to a much lesser extent than fluorescein or rhodamine WT. He further states, that sorption usually precludes the use of fluorescein or rhodamine WT in granular aquifers. Thus, loss due to adsorption can influence the selection or quantity of a dye if the dye must drain through unconsolidated soil and residuum before reaching the bedrock-conduit system. In this case, an appropriate increase in the quantity of dye injected may be necessary.

The level of background fluorescence can effect the selection of a particular tracer. For example, if injection water contains a relatively high component of domestic sewage, fluorescence from optical brighteners, a common constituent of home-laundry products, may preclude the use of optical brighteners as tracers. CI Direct Yellow 96 can be used where there is a high background level of optical brighteners. Flourescein may also be present because of its use as a coloring agent in a number of home products such as shampoos, bathroom cleaners, and antifreeze. Either optical brighteners or fluorescein can be used if the background levels of that particular dye are determined to be sufficiently low and stable before the trace is begun. In fact, determination of background levels needs to be adopted as the first step in most traces because this provides a standard for comparison of the dye recovered.

Because some fluorescent dyes decay upon exposure to ultraviolet light, these dyes are less than ideal if the water being traced repeatedly sinks and rises and flows along the surface. Smart and Laidlaw (1977) report that the photochemical decay rates are very high for fluorescein, which rapidly loses its fluorescence under bright sunlight conditions. Quinlan (1987a) also reports that optical brighteners and fluorescein are very susceptible to photochemical decay, especially when in low concentrations, but this is only a problem if the detectors for recovering the dye are placed in direct sunlight. If the loss of fluorescein or optical brighteners due to photochemical decay is possible, CI Direct Yellow 96 may be used because it does not undergo any significant photochemical decay (Quinlan, 1987a).

An evaluation of cost and availability of a particular dye involves factors that can be unique to a particular user. Therefore, these factors are not discussed here. Also, the various methods and equipment required for the recovery of the tracers commonly used for qualitative tracing are discussed in detail in a later section and are listed in Table 1.

3.2.3 Selecting Quantity of Dye for Injection

Having selected a particular fluorescent dye, the next step is to select the optimum quantity of dye for injection. Except in unusual circumstances, where a highly visual appearance of the dye is desired, the quantity of dye to be injected is selected in order to provide a detectable amount of dye at the recovery point, but remain below visible levels. The quantity of fluorescent dye used for each injection is based generally, on estimated flow conditions and the straight-line distance of the trace. To some extent, the quantity of dye will vary depending on the nature of the injection point. For example, if the dye can be added to water draining directly into an open swallet, less dye will be required than if the dye must infiltrate through soil and unconsolidated material in the bottom of a plugged sinkhole. Dye studies conducted by the U.S. Geological Survey usually limit the maximum concentration of fluorescent dye at a water-user withdrawal point to 0.01 mg/L (Hubbard and others, 1982).

Selecting the optimum amount of dye for qualitative tracing is, to some extent, a matter of experience. The amounts may be adjusted depending on the initial results. Quinlan (1987a) suggests several rules of thumb as starting points for tracing under average conditions in the Central Kentucky karst and using various passive detectors for dye recovery. For qualitative traces under moderate-flow conditions to the average spring, he suggests one pound of fluorescein per straight-line mile of trace, up to a maximum of five pounds. For Direct Yellow 96 and optical brighteners in powder form, two pounds per straight-line mile of trace, and for some optical brighteners in liquid form, one gallon per straight-line mile, up to a maximum of four gallons is recommended. For initial traces in the Elizabethtown area, Kentucky (Mull, Smoot, and Liebermann, 1988), the above procedure was used for estimating the quantity of fluorescein dye for injection with satisfactory results. However, as knowledge of the flow system developed, the amount of fluorescein per each injection was reduced to about 1/2 pound per straight-line mile of trace. This amount proved adequate and likely could have been reduced further, once the conduit flow-path between the injection and recovery points was established.

Aley and Fletcher (1976) present a nomograph for selecting the quantity of fluorescein to be injected if the ground-water flow system under investigation consists primarily of conduit flow in solution channels or fracture zones. Their equation, shown here in the original units, is:

$$W_d = 1.478\sqrt{DQ/V}, \qquad \text{(eq. 1)}$$

where W_d - weight of fluorescein dye in kg to be injected;

D = straight-line distance in km from injection point to recovery point;

Q = discharge at the resurgence in cubic meters per second; and

V = estimated velocity of ground-water flow in meters per hour.

For this equation, the velocity of ground-water flow is the most difficult to estimate because it depends on the nature of the conduits and the hydrologic conditions at the time of the trace. Therefore, initial dye tracing needs to be attempted under medium base flow conditions for a study area. Subsequent traces under extreme flow conditions are needed to better define the flow variations and possible changes in flow paths under different flow conditions.

3.2.4 Dye-Handling Procedures

In order to simplify dye injection when using powder such as fluorescein, especially during windy conditions, the powder can be mixed with water before going to the field. An approximate ratio of 0.5 pound per gallon is suggested. The dye solution is poured into water draining directly into a swallet in order to lessen dye loss due to photochemical decay or absorption by organic debris at the surface. While mixing and injecting the dye, extreme care needs to be used to avoid contaminating clothing or the area around the injection point. The need for care in handling the dye before and during the injection can not be overstressed because of the possibility of contaminating the dye detectors or the area around the injection site. Such contamination can lead to a false positive trace and erroneous interpretations. To lessen the possibility of contamination, long-sleeve rubber or disposable, plastic gloves needs to be worn during all dye-handling operations. In addition, refer to other quality-control procedures described in section 3.4.

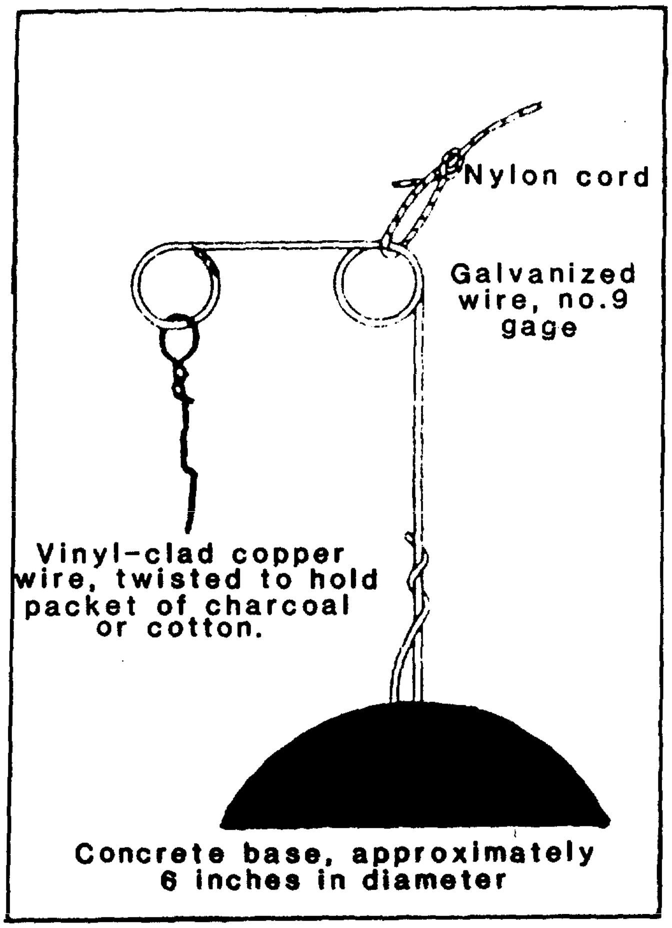
If a trace is required during dry-weather conditions, hauled water can be used to flush the dye into a particular injection point. Most investigators suggest the use of two tanks of water for dry weather dye injection. Successful dry-weather traces have been completed using 1,000 to 1,600 gallons of water per tank, (Mull, Smoot, and Liebermann, 1988, and Quinlan, 1987a). Jones (1984) suggests the use of at least 500 gallons of water for dye injection and about 100 gallons should be dumped before the dye is added. In general, the quantity of injected water seems to be less critical than the use of the two-tank method for injection. The swallet is dosed with water from the first tank but the dye is not injected until water from the second tank begins to drain underground. This provides initial wetting of conduit surfaces followed by a slug of water to flush the dye through the system. The success of this procedure depends on the length of the trace, the period of time the recovery site is monitored, and the nature of the conduits in relation to the quantity of water used for the injection.

3.2.5 Dye-Recovery Equipment and Procedures

In tests using fluorescein, the dye is recovered by passive dye-detectors consisting of packets of activated coconut charcoal suspended in all suspected ground-water resurgence points for a particular trace. In addition, detectors are placed in unlikely resurgences in order to define the background levels of fluorescence and to show the condition of the dye-recovery material in the absence of dye.

The dye-detectors, or “bugs,” consist of a bag or packet of activated coconut charcoal attached to a length of wire imbedded in a gum-drop shaped concrete anchor about 6 inches in diameter and 3 inches high (fig. 5). The anchor may be made by pouring concrete into plastic bowls lined with plastic film. A piece of 9-gage, galvanized wire, about 18 inches in length, is imbedded in the wet concrete. Some investigators prefer to use two wires, one for holding the bag of charcoal and the other for holding the swatch of cotton if optical brighteners are in use (Spangler, Byrd, Thrailkill, 1984). The bag for holding the activated coconut charcoal is fabricated from a folded 3 by 7 inch piece of aluminum, nylon, or fiberglass screening. Only activated coconut charcoal (6-14 mesh) is used for absorbing fluorescein. It is available from several scientific supply houses (table 2). Charcoal intended for water-treatment processes, aquariums, or home barbecue grills does not sorb the dye and is not acceptable for use as a detector. Because the coconut charcoal loses its sorptive ability upon exposure to the atmosphere, it must be stored in air-tight containers at all times. For this reason, the preferred procedure is to place the charcoal in the fiberglass packets while in the field at each site, Some investigators prefer to fabricate fiberglass or aluminum packets, complete with charcoal, before going to the field, This is acceptable provided the packets are properly stored and protected from dye contamination,

In order to maximize exposure to the dye, the gum-drop anchor is placed near the center of flow of the suspected dye-resurgence point. If flow velocities are sufficiently high to cause the loss of the anchor or detector, the anchor should be placed in the main stream but in an area of lower velocity such as a pool. In cases where the channel is too shallow for the anchor, a U-shaped wire pin may be driven into the channel bottom to hold the



(adapted from Quinlan, 1987a, figure 1, p. E-B)

Figure 5.--Anchor used to suspend dye detectors (bugs) in springs or streams.

Table 2.--Sources of materials and equipment for dye tracing

Item	Cost as of 8-02-87	Source
Fluoroscein (CI Acid Yellow 73)	814.50 per pound 75 percent (powder)	Chemcentral/Detroit 13395 Huron River Drive Romulus, MI 48174 (313) 941-4800
	$30 per pound 50 percent (powder)	Pylam Products Co. Inc. 1001 Stewart Avenue Garden City, NY 11530 (800) 645-6096
Direct Yellow 96 (Diphenyl Brilliant Flavine 7GFF)	**$14.71 per pound (powder)**	Ciba-Geigy Corp. Dyestuffs & chemical Div. P.O, Box 18300 Greensburg, NC 27419 (800) 334-9481
Rhodamine WT (CI Acid Red 388)	20% solution $10.83 per pound (9.92 pounds per gallon)	Crompton & Knowles Industrial Products Division P.O. Box 33188 Charlotte, NC 26233 (600) 438-4122
Phorwite l BBH 768 (CI F.B.A. 28)	**$5.90 per pound (powder)**	Mobay Chemical Corp. Dyes and Pigments Division Mobay Road Pittsburg, PA 15205 (600) 662-2927
Unbleached cotton pads Swiss Beauty Pads	$72.00 per case case of 3840	U.S. Cotton, Inc. P.O. Box 367 Saratoga, CA 95071 (406) 378-7752
Activated coconut charcoal 6-14 mesh	**$18.00** per pound	Fisher Scientific Co, 541 Creak Road Cincinatti, OH 45242 (513) 793-5100
Ultra-violet lamp, long-wave model 11-964-6	$176.00	Fisher Scientific Co. 541 Creak Road Cincinatti, OS 45242 (513) 793-5100
Filter fluorometer		Turner Designs 2247 Old Middle field Way Mountain View, CA 94043-2849 (415) 965-9800
model 10, 10-000	$5,502.00	
laboratory case 10-002	$ 431.00	
cuvette holder 10-303	$ 210.00	
rhodamine WT filter kit 10-04	**$** 314.00	
Automatic sampler		Instrumentation Specialties company P.O. Box 82531 Lincoln, NE 66501 (800) 226-4373 (402) 474-2233
model 2700 with 24 1000 mL glass bottles	**$2,170.00**	
N1Cad battery	$ 195.00	
battery charger	**$** 56.00	
A/C converter and battery charger	**$** 175.00	
vinyl auction line with strainer 25ft, x 3/8 in diameter	$ 64.00	
teflon auction line, 25ft, x 3/8 in diameter	$ 92.50	
stainless steel strainer	$ 65.00	

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packet in place. However, this technique tends to hold the packet on the bottom of the channel where it may be covered with sediment or damaged by bottom-dwelling organisms,

The anchor is secured to the bank with a small nylon cord. Use of a tan-colored cord lessens the chance of discovery and tampering. If the potential for vandalism is high, hide the anchor or place it in a location that is not easily accessible. In addition, a business card or note containing information about the investigations can be encased in plastic and attached to the anchor to help satisfy the curiosity of potential vandals.

In addition to discharge points such as streams and springs, detectors may also be suspended in toilet tanks in selected private homes served by a well or in the stream of water discharging from private or public supply wells. Toilet-tank placement of the detector is not acceptable if self-dispensing toilet bowl cleaners are used. In that case, the detector can be suspended in a container such as a 5-gallon bucket, and water from a garden hose directed to flow into the container. The container needs to be placed out of direct sunlight and located so that the wastewater does not create a nuisance. A flow rate of approximately 1 gallon per minute is adequate,

The packets are left in place from 1 to 5 days but are generally changed more often if turbidity levels are high. When retrieved, each packet is rinsed to remove accumulated sediment and trash, Each packet is then sealed in a lock-top plastic bag, labeled, and returned to the laboratory in a light-tight case. If the packets are not processed immediately, they should be dried and refrigerated in order to decrease bacterial action that could reduce fluorescence. Packets processed this way can be stored several weeks without adversely affecting the fluorescence of sorbed dye.

Before being removed from the fiberglass bag in the laboratory, the charcoal is rinsed with a jet of water to remove sediment which can interfere with the analysis. Some investigators prefer to test only about half of the charcoal and store the remainder in case there is need to confirm the results of the trace,

The presence of dye and, thus, a positive trace is determined by elutriating the exposed charcoal in an alcohol solution and visually checking for the characteristic yellow-green color above the charcoal. For rhodamine WT, charcoal is placed in a small jar or beaker and covered with about 30 mL of elutriant solution consisting of 38 percent ammonium hydroxide, 43 percent l-propanol, and 19 percent distilled water (Smart, 1972). For fluorescein, a saturated solution of about 5 percent potassium hydroxide is the most efficient elutriant (Quinlan, 1987a), This solution consists of 6 to 7 grams of potassium hydroxide dissolved in 100 mL of 70 percent isopropyl alcohol (rubbing alcohol). After the potassium hydroxide dissolves, the solution separates into a supersaturated solution and a saturated solution. The lighter saturated solution is decanted into the containers to cover the charcoal. Additional test solution can be made by adding potassium hydroxide or alcohol to the original solution so long as only the lighter, saturated part of the solution is used to elutriate the charcoal. However, Quinlan (1987a) reports that the potassium hydroxide and alcohol solution has a limited shelf-life and should not be used if more than a few days old. The ammonium hydroxide, l-propanol, and distilled water elutriant has a shelf-life of several months. Either elutriant can be used with the other dye, but each is most efficient for the dye indicated.

In strongly positive tests, the maximum color intensity develops almost immediately upon addition of the elutriant and then slowly decreases (Jones, 1984). Aley and Fletcher (1976) propose a system for qualitative assessment of fluorescein dye concentrations that lists dye elutriating periods ranging from 15 minutes up to 10 days. During the investigation in the Elizabethtown area, Kentucky, Mull, Smoot, and Liebermann (1988) adopted 4 hours as the maximum time for elutriation. In cases where the typical yellow-green color of fluorescein is not obvious, detection can be enhanced by focusing a beam of sunlight or light from a microscope lamp through the solution. Quinlan (1987a) states that the light-beaming technique increases the detectability of fluorescein so that concentrations as low as one part per billion may be seen.

Identification of a strongly positive test is generally obvious. However, weakly positive tests require special care and experience lest the presence of algae and organic matter, which can occur as background, be incorrectly interpreted as fluorescein. Persons unfamiliar with the color of dye elutriated from charcoal detectors need to prepare and elute laboratory test solutions of various dye concentrations before interpreting first-time dye traces. Dye identification can be confirmed by instrumental analysis of the elutriant, as described in section 3.3.5.

Optical brighteners and Direct Yellow 96 are recovered on swatches of undyed, surgical cotton suspended in the ground-water discharge in much the same manner as the charcoal packets. The cotton swatches are about 4 inches long, 2 inches wide, and 1 inch thick and are suspended from the anchored wire by a paper clip or appropriate cord, or enclosed in aluminum, nylon, or fiberglass packets similar to those used to hold the charcoal, Care needs to be exercised, however, because some surgical cotton is brightened. Also, the manufacturer may change production techniques at some time, and sell brightened instead of-unbrightened cotton. Therefore, the cotton being used for dye detectors needs to be checked for fluorescence or contamination before placement in the field.

The cotton swatches are rinsed to remove sediment and trash when they are recovered from the test site. Each cotton detector is placed in a carefully labeled, lock-top plastic bag for return to the laboratory. As with the packets of charcoal, the cotton may be stored in a freezer for several weeks without affecting the fluorescence. Because of the possible masking of fluorescence by sediment, the cotton needs to be thoroughly cleaned with a high-pressure jet of water before testing.

The presence of both optical brighteners and Direct Yellow 96 is confirmed by viewing the cotton detectors under long-wave length ultraviolet light. The fluorescence of these tracers is more visible if the exposed cotton is viewed with ultraviolet light under subdued lighting such as a darkened room or viewing box. Cotton that has adsorbed optical brighteners will characteristically fluoresce blue-white, while the fluorescence of Direct Yellow 96 is canary yellow. A positive trace is indicated only if the entire cotton mass fluoresces relatively evenly. Scattered specks of fluorescence on the cotton should not be interpreted as a positive dye recovery, Because different types of dye collectors and detection techniques are used to recover fluorescein and optical brighteners, multiple qualitative dye traces to the same recovery point may be performed simultaneously. For example, fluorescein can be placed in one injection point and recovered on activated coconut charcoal, while Direct Yellow 96 or an optical brightener could be placed into a second injection point and recovered on unbleached cotton suspended on the same anchor. If a fluorometer or spectrofluorometer is available, rhodamine WT might also be placed into a third injection point. As many as three separate injection points may be traced to one resurgence or discharge point during the same test.

3.3 Quantitative Dye Tracing

3.3.1 Introduction

As used in this manual, quantitative dye tracing consists of the injection of a known quantity of dye and the measurement of the concentration of dye over time, at a particular ground-water discharge point such as a spring or well. Determination of dye recovery requires measurement of both dye content and ground-water discharge. These measurements are made at each dye - resurgence site that was identified as being hydraulically connected to injection locations by previous qualitative tracer tests. Water samples are collected, usually with automatic samplers, during passage of the dye cloud and the dye content of each sample is measured with a properly calibrated fluorometer or spectrofluorometer. These data are plotted against time to produce a dye-recovery (time-concentration) or breakthrough curve. A typical dye-recovery curve is shown in figure 6.

Quantitative dye-tracing can be performed to determine potential contaminant transport characteristics, such as persistence, dispersion rates, and concentration. Quantitative dye tracer tests are generally more labor intensive and require more sophisticated equipment and techniques than qualitative dye tracing because the objective is to define dye concentration variations during passage of the dye cloud rather than simply to determine if the dye appeared at a particular spring or well.

The shape and magnitude of the dye-recovery curve is determined by: (1) the quantity of dye injected, (2) the characteristics of the dye, (3) discharge rate at the resurgence, (4) rate of dispersion of the dye, and (5) the cross-sectional mixing of the dye before arrival at the sampling point, The apparent shape of the dye-recovery curve can also be affected by the sampling interval. Analysis of the dye-recovery curve provides insight into the flow characteristics of the aquifer such as the effective time of travel between a swallet and the resurgence and the velocity of ground-water flow. Additional analysis of the recovery curve and discharge measurements may be used to provide estimates of peak concentration, duration or persistence, and dispersion, Because these data may be related to the velocity and dispersion of a potential ground-water pollutant, quantitative dye tracing is an especially useful tool to managers of water supplies located in karst terrane, where springs or wells are susceptible to the introduction of contaminants into the ground-water system. The following discussion summarizes techniques for quantitative dye tracer tests and analysis of the results. Also included

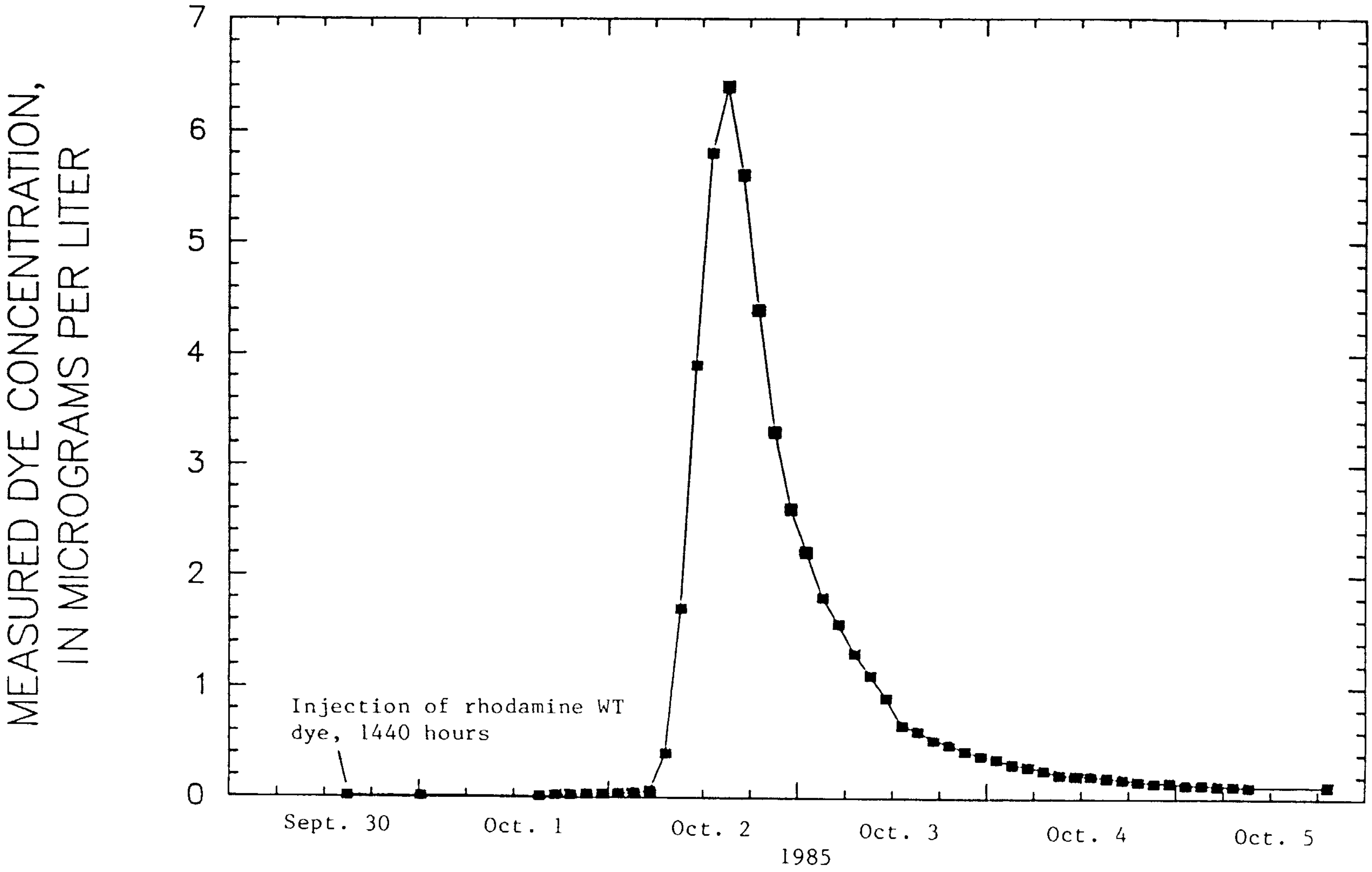


Figure 6.--Typical dye-recovery (time-concentration) curve. Dye was injected at sinking stream and sampled at City Spring, near Elizabethtown, Kentucky, a map distance of 11,500 feet from the injection site.

are references that describe, in detail, the procedures used. The discussion describes each phase of quantitative dye tracing, generally in operational. sequence.

3.3.2 Selecting Dye for Injection

The primary criteria for the selection of a fluorescent dye for quantitative tracing are its (1) water volubility, (2) detectability in low concentrations or whether it is strongly fluorescent, (3) separability from background fluorescence, (4) stability or conservancy in the karst environment, (5) non-toxicity in low concentrations, and (6) cost. Generally, detection limits are controlled by background conditions such as turbidity; the presence of substances that may fluoresce in the same range as the dye, such as algae; and the calibration of the fluorometer. Conservancy refers to the stability of the dye in the environment. No dye is 100 percent conservative because some dye is lost to sorption or chemical decay. Therefore, dye loss must be considered during quantitative analysis of the dye-recovery data.

Rhodamine WT is specifically made for water tracing and has been widely used for time of travel and dispersion tests in streams (Hubbard and others, 1982). Because of the relative similarity between ground-water flow in karst terrane and streamflow in most areas, and because it meets the above requirements, rhodamine WT is commonly selected for quantitative dye traces in karst terrane. Rhodamine WT was used by Mull, Smoot, and Liebermann (1988) for quantitative dye tracer studies in the Elizabethtown area, Kentucky, and is the dye used for all quantitative dye trace discussions in this manual.

3.3.3 Selecting Quantity of Dye for Injection

After identifying and selecting input and resurgence points on the basis of earlier qualitative traces, the quantity of dye to be injected for subsequent quantitative tests needs to be determined. The quantity of dye required for a quantitative trace depends on flow conditions, the distance of the trace, and the peak dye concentration expected at the dye-recovery site. Considerable experimentation may be required before the optimum quantity of dye can be selected, consistently. In general, the quantity of dye injected must be adequate to produce detectable dye concentrations at the monitored resurgence but ideally remain below the levels of visual detection. As stated earlier, dye studies conducted by the U.S. Geological Survey are usually designed so that the amount of fluorescent dye injected into a water course does not result in dye concentrations exceeding 0.01 mg/L at water user withdrawal points (Hubbard and others, 1982). This value may be exceeded if the dyed water in the water-supply spring or well can be diverted from use during passage of the dye cloud.

For initial quantitative traces, the quantity of dye per injection can generally be based on an equation for estimating the amount of a 20 percent solution of rhodamine WT needed for a slug injection (Kilpatrick and Cobb, 1985). The equation adapted to dye recovery from a spring or pumped well is as follows:

$$V_s = 3.79 \times 10^{-5} \frac{Q\ (L\ 1.5)}{v}\ C_p, \qquad \text{(eq. 2)}$$

where V_s = the volume of rhodamine WT, 20 percent solution, in milliliters;

Q = discharge, in ft^3/s;

L = the apparent length of the trace, (map distance) in feet;

v = the apparent ground-water flow velocity, in ft/s; and

C_p = the peak concentration at the sampling site, in micrograms per liter (µg/L).

For initial traces, the ground-water velocity can be estimated from the results of qualitative traces or from spring discharge measurements. To adjust for the meanderings of the subsurface flow passages, the apparent length of the trace (straight-line map distance) is multiplied by 1.5 (Sweeting, 1973 p. 231).

3.3.4 Dye-Handling and Recovery Procedures

Handling, transporting, and injecting dye for quantitative tracer tests requires even more care than that for qualitative tests, Considering that dye concentrations are commonly measured in parts per billion, or less, the slightest contamination can cause erroneous or misleading data. Rubber or disposable plastic gloves need to be worn during all handling of the tracer and extreme care used to avoid contaminating clothing or the area around injection or recovery points. Ideally, in both qualitative and quantitative traces, care needs to be taken to ensure that dye collection devices are not handled by the same person that previously handled the dye. Different people need to handle each, or if only one person is used, the collectors need to be placed before the dye is handled. The tracer needs to be stored and transported to the injection site in an opaque, non-breakable container. The quantity of dye to be injected needs to be measured with a graduated cylinder or equivalent and mixed with water in a metal pail for injection. A metal pail is used to lessen dye loss due to adhesion to plastic. The dye needs to be diluted about 10:1 before injection. The mixture needs to be carefully poured into water draining directly into a swallet or into the center of flow if water is ponded over the swallet.

Rhodamine WT normally comes from the manufacturer as a 20 percent solution in bulk containers. Over time, some dye may settle out of solution, Therefore, before the dye is withdrawn from the container, the contents need to be thoroughly mixed to ensure that the dye is appropriately mixed.

The collection of water samples over time and fluorometric or spectrofluorometric analysis of their dye content is necessary to adequately define the dye-recovery curve at a monitored spring or well. The samples can be collected by hand or by automatic samplers. Equipment required for sampling by hand will vary depending on conditions at the sampling site. Samples could be obtained from a bridge, a boat, or by wading.

Although hand sampling can suffice for quantitative tracing in certain situations, automatic samplers are more efficient because sampling may be required for a prescribed frequency over a period of several days or during inclement weather. In addition, the chance of missing part of the dye cloud is reduced because automatic samplers can sample for long periods prior to the arrival of the dye cloud. This may be necessary during initial quantitative dye tracing when ground-water velocities are not well defined. Also, simultaneous sampling from multiple sites is generally more efficient and may be less costly with automatic samplers because only one person is required to service several samplers. Because the passage of the dye cloud must be defined, the use of an automatic sampler may permit more precise detection of dye concentrations than might be achieved using the random hand sampling technique (Crawford, 1979, p. 43).

The use of automatic samplers is not without some disadvantages, however. A problem with both automatic and manual sampling is the potential for poor definition of the dye cloud if the selected sampling interval is too long. Accurate definition of the dye-cloud peak generally requires relatively frequent samples, but continuation of the same sampling frequency can lead to excessive sampling during the dye-cloud recession. In general, unnecessarily frequent sampling is preferred to inadequate definition of the dye-cloud peak due to long sampling intervals. Repeat traces may be needed to determine the most efficient sampling interval.

The samplers may be subject to vandalism and could malfunction, especially during severe winter weather. Covers made from boxes or barrels that are lockable and insulated can improve automatic sampler reliability under these conditions.

There are several types of automatic samplers commercially available, Also, Crawford (1979, p. 43) describes a “homemade” sampler consisting of a pump, pump activation clock, power source, and sample distribution and storage box. Automatic samplers are generally of two types: (1) bank-mounted samplers having a small diameter suction tube leading to the sampling point in the water, and (2) a floating, boat-like sampler (Kilpatrick, 1972) that is partially immersed in the flow. Commercially produced, bank-mounted samplers, also called sequential waste-water samplers, which collect samples in glass or plastic bottles, are available from several manufacturers. An ISCO sampler, model 2700 (table 2), was used during the dye tracing in the Elizabethtown, Kentucky area (Mull, Smoot, and Liebermann, 1988). Although superseded, this model can collect and hold as many as 24 samples with a sampling interval adjustable from 1 to 999 minutes and is powered by either self-contained batteries or an external power source.

Regardless of the method of sampling, glass sample bottles are preferable to plastic bottles because the dye may have a slight affinity for the plastic, resulting in dye loss, One ounce (approximately 32 milliliters) polyseal-cap glass bottles are commonly used for hand sampling. The dye content of each sample is then measured with a properly calibrated fluorometer or spectrofluorometer.

3.3.5 Fluorometer Use and Calibration

A filter fluorometer is an instrument that measures the intensity of light at a selected wavelength from a water sample containing a fluorescent substance. The intensity of fluorescence is proportional to the amount of fluorescent substance present. Fluorescence can also be measured with fluorescence spectrometers or spectrofluorometers (Udenfriend, 1962 p. 62-86 and Duley, 1986). These instruments are especially useful if several different dyes are being simultaneously used for tracing to the same point or if there is a high background level of dye from an earlier trace. In this manual, however, reference will only be made to the use of a fluorometer. Although a spectrofluorometer offers many capabilities not available with a fluorometer, the capital cost is about three times greater. A portable instrument, such as the Turner Designs Model 10 (table 2) filter fluorometer, provides direct reading of dye content as determined by prior calibration. This instrument reaches operational temperature in about 15 minutes, can be powered with either 115 volt a.c. or 12 volt d.c. current, does not adversely increase the temperature of the test sample, and can be equipped for continuous flow-through monitoring and recording.

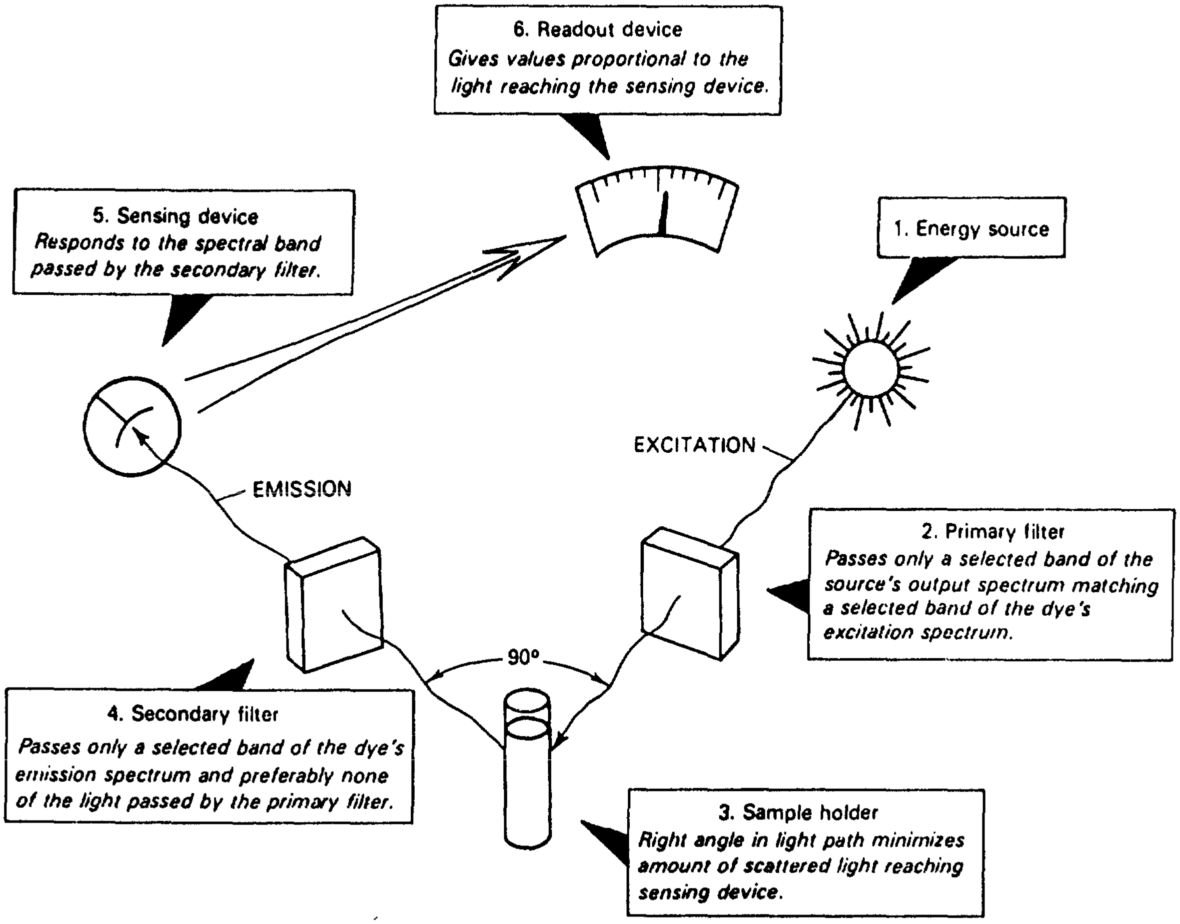
A filter fluorometer consists of six basic components as shown in figure 7 (Wilson and others, 1986). The light source and filters are selected for maximum sensitivity to the particular fluorescent tracer being used according to the manufacturers' specifications. Detailed information about the operation and calibration of fluorometers, is given by Wilson and others (1986). The calibration procedure is reiterated here because dye-recovery data acceptable for quantitative analysis is dependent on the use of a correctly calibrated fluorometer.

The preparation of calibration standards is basically the process of step by step reduction of the stock dye solution until concentrations that are expected during dye recovery are reached. This reduction is generally known as a serial dilution and is explained in detail by Kilpatrick and Cobb (1985). Precise measurements of the initial volume of dye and added diluent in each step of the procedure are necessary in order to prepare a set of standards for an accurate calibration of the fluorometer. The serial dilution procedure is based on the equation:

$$C_n = C_i \frac{W_d}{V_w + V_d} = C_i S_g \frac{V_d}{V_w + V_d} , \qquad \text{(eq. 3)}$$

where C_n = the new dye concentration, in micrograms per liter (ug/L);
C_i = the initial dye concentration, in micrograms per liter;
V_w = the volume of the added diluent, in milliliters (mL);
V_d = the volume of the dye solution added, in milliliters;
W_d = the weight of the initial solution, in grams (g); and
S_g = the specific gravity of the initial dye solution, 1.19 grams per cubic centimeter (g/cm^3) for rhodamine WT, 20-percent solution,

For rhodamine WT, 20-percent solution, (200 g/L) 3 serial dilutions are required to obtain concentrations on the order of 100 µg/L (table 3). In each step, the preceding C_n becomes the new initial concentration, C_i. This third dilution (100 µg/L) needs to be retained in quantity as a “working solution” and is used for further dilution if standards below 100 µg/L are needed. The use of the working solution eliminates the necessity to perform complete serial dilutions each time the fluorometer is calibrated so long as the same dye lot is being used. The same working solution needs to be used throughout an investigation as long as all dye used is from the same dye lot. The working solution needs to be sealed and stored out of light when not in use.



(from Wilson, Cobb, and Kilpatrick, figure 4, p. 10)

Figure 7.--Basic structure of most filter fluorometers.

Table 3.--Three-step serial dilution for preparation of standards for fluorometer calibration.

	Initial concentration (micrograms per liter)	Specific Gravity (grams per cubic centimeter)	Volume of dye (milliliter)	Volume of diluent (milliliter)	New concentration (micrograms per liter)
First dilution	200,000,000	1.190	20	2,068	2,280,000
Second dilution	2,280,000	1.002	20	3,000	15,100
Third dilution	15,100	1.000	20	3,000	100

Although an infinite number of combinations of water and dye can be used to prepare standards, table 3 shows the combinations for three dilutions to produce the working solution of 100 μg/L, a commonly used calibration standard. Distilled water is used for calibrating the fluorometer to zero background. Fluorometer calibration should be checked with temperature equilibrated solutions before the final measurements for all dye samples.

3.3.6 Calculating Mass of Injected and Recovered Dye

Analysis of dye-recovery data is based on a mass balance relation between the injected and recovered dye (Hubbard and others, 1982). Therefore, a critical element of this analysis is the determination of the mass of dye injected. It is calculated by the following equation:

$$\text{mass} - \text{volume} \times \text{density} \times \text{purity}. \qquad \text{(eq. 4)}$$

Thus, for a 10 mL injection of rhodamine WT, 20 percent solution, the mass is computed by multiplying the volume (10 mL) by the density (1.19 g/cm^3) and by the strength or purity (20 percent). In this case the mass injected is 2.38 grams.

Calculation of the mass of dye recovered is based on the dye-recovery (time-concentration) curve and on the discharge of the monitored resurgence. The time-concentration curve is a plot of time versus the dye content of water samples collected during the passage of the dye cloud. The curve is typically bell-shaped but skewed to the right, such that it is steeper on the rising limb than on the falling or recession limb of the curve as shown in figure 6. For the conditions of a variable flow rate the mass of dye recovered is:

$$M = \int_0^\infty QCdt , \qquad \text{(eq. 5)}$$

where

M = mass of dye recovered,
Q = discharge, and
C = dye concentration at time t.

If the flow rate is steady, the mass of the recovered dye is:

$$M = Q \int_0^\infty C dt . \qquad \text{(eq. 6)}$$

Equations 5 and 6 are given for conceptual purposes only, computational formulas are given in sections 4.2.1, and an example of the computation of the mass of recovered dye is given in section 4,2.6. Discharge is determined by current-meter measurements. If discharge varies, such as during a storm event, several discharge measurements are necessary to accurately characterize flow conditions and calculate dye recovery.

3.3.7 Sampling Procedures

Adequate definition of the time-concentration curve is dependent on an appropriate sampling interval that is based on an assessment of the flow conditions and hydrology of the test site. The sampling interval chosen during initial traces to a particular resurgence is frequently adjusted for better definition of the time-concentration curve during repeat traces, For example, the sampling interval varied from 20 to 60 minutes during traces in the Elizabethtown area (Mull, Smoot, and Liebermann, 1988), The adequacy of the sampling interval to define the dye-recovery curve can be determined by measuring the fluorescence with a properly calibrated fluorometer and plotting the results in the field,

The degree to which the dye is laterally and vertically mixed in the flow at the sampling site affects the sampling strategy. Sampling at a single point from a laterally unmixed concentration distribution cannot be used to properly calculate the mass of recovered dye for the sampling interval.

An acceptable mixing length may be defined as the distance needed for nearly complete lateral mixing of the dye tracer in the test stream. In the application of dye-tracer techniques to surface-water investigations, the mixing length can be estimated using techniques described by Kilpatrick and Cobb (1985) and the distance to sampling sites can be selected accordingly. In ground-water applications of quantitative dye-tracer techniques, however, this calculation has little application. In a single conduit system, the mixing length is typically the distance between the dye injection point, such as a sinkhole, and the point of dye recovery from a ground-water resurgence, such as a spring. This distance is fixed unless dye is sampled downstream of the resurgence point. In a converging flow system, the mixing length would not begin until the last convergence of flow took place. In this case, an adequate mixing length could, theoretically, extend beyond the resurgence spring or well.

Incomplete lateral mixing is usually the result of a short mixing length, Incomplete mixing can also occur when undyed ground water enters the flow system between the injection point and the sampling point. The addition of undyed water to the flow system upstream of the sampling point, may cause inaccurate estimates of recovered dye.

During quantitative dye tracing, a preliminary trace is usually needed to assess the degree of lateral mixing of dye at the recovery point. Dye is recovered from at least three points in the cross section at the resurgence and time-concentration curves are plotted for each sampling point in the section. Complete lateral mixing is reached when the areas under the time-concentration curves for each lateral position sampled are the same, regardless of curve shape or magnitude of the peaks. Kilpatrick and Cobb (1985 p, 3) considered that mixing was adequate for single point dye sampling when the mixing was about 95 percent complete at the resurgence or other sampling point. The relation of mixing length to curve areas is illustrated by figure 8.

In order for samples to represent the dye cloud with incomplete lateral mixing, the dye cloud needs to be sampled at several points laterally, such as at points a, b, and c as shown in figure 8. Selection of these sampling points is based on equal increments of flow as determined from a stream discharge measurement made with a current meter. For example, if three points in a section are to be sampled, the samples need to be collected at 1/6, 3/6, and 5/6 points of cumulative flow across the section (Kilpatrick and Cobb, 1985). However, in most karst ground-water situations, the recovery distance is hundreds to thousands of times greater than the diameter of the stream, or conduit width. Therefore, single point sampling should be adequate,

3.3.8 Sample Handling and Analysis

Specific procedures are required for the handling of water samples after collection because improper handling can affect the accuracy of the determination of dye content. All samples need to be transported and stored in light-proof containers to prevent reduction of fluorescence due *to* photochemical decay. Although some samples may be checked for fluorescence in the field, primarily as confirmation that the dye cloud was sampled, the samples need to be returned to the laboratory for fluorometric analysis of their dye content.

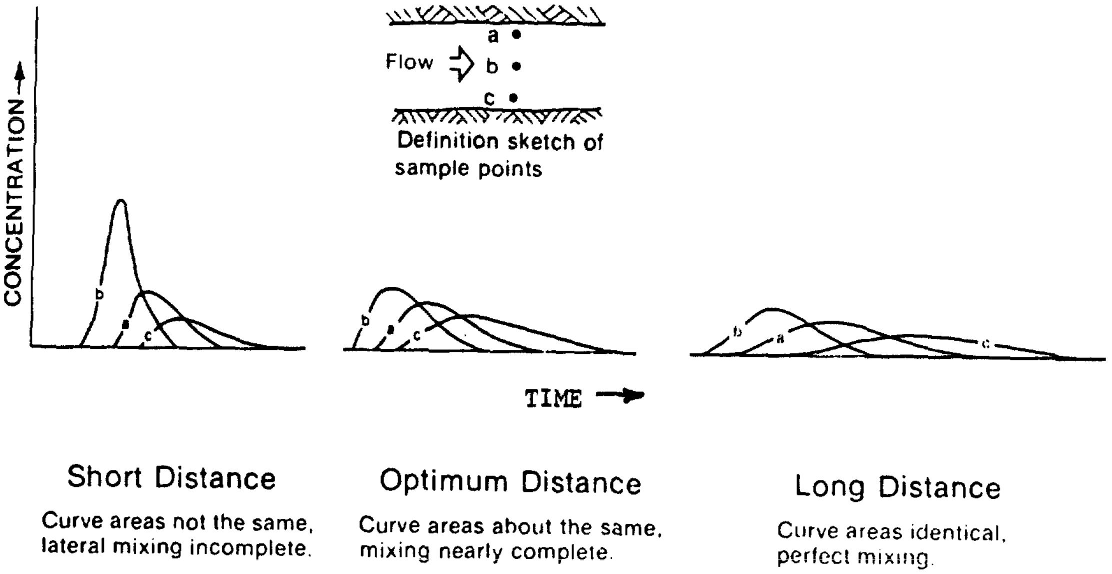
Also, if results of the dye trace may be used as evidence for litigation, it may be necessary to establish chain-of-custody control of the samples. This procedure ensures that the samples are secure at all times and a written log is maintained that identifies each person having access to the samples (Quinlan, 1986a).

The dye content of each water sample needs to be measured by determining its fluorescence in the laboratory using a properly calibrated fluorometer. Because fluorescence activity is significantly affected by temperature (fluorescence is inversely proportional to temperature), temperature effects must be accounted for in data analysis (Wilson and others, 1986). However, temperature effects can usually be ignored if the fluorometer used for measuring dye content does not increase the temperature of the sample during analysis and if the temperature of the sample and calibration standards are allowed to equilibrate, usually overnight, before analysis.

The results of the fluorometric analyses of the dye samples should be plotted as a dye-recovery (time-concentration) curve, which is discussed in section 4.2.1 of this manual.

3.3.9 Adjustment of Dye-Recovery Data

Because the dye is not completely conservative (that is, some of the dye is lost to decay and sorption during the trace), the measured dye



Short Distance

Curve areas not the same, lateral mixing incomplete.

Optimum Distance

Curve areas about the same, mixing nearly complete.

Long Distance

Curve areas identical, perfect mixing.

(from Kilpatrick and Cobb, 1985, figure 1, p. 3)

Figure 8.--Typical response curves observed laterally and at different distances downstream from a dye-injection point.

concentrations are adjusted to eliminate the effects of dye loss. This adjustment is required if the results of different traces are to be compared. In this procedure, the measured dye concentrations in each sample for a given dye trace are multiplied by the ratio of the dye mass injected to the mass of dye recovered.

Because the concentration of dye (tracer) recovered is affected by the quantity of dye injected, it may be desirable to “normalize” the dye-recovery data by dividing observed concentrations of each sample by the mass of the injected dye. The resulting concentrations are therefore adjusted to a particular unit of dye, for example, milligrams per liter per kilogram. This procedure compensates for variations in the mass of dye injected during different traces and simplifies analysis of the time-concentration data.

To adjust for dye loss and normalize to a unit mass of tracer, it is necessary to assume that none of the dye is trapped in the subsurface or flows to resurgences other than those sampled and included in the computation of the mass of dye recovered, This fact can usually be established with qualitative-tracer tests and confirmed with discharge measurements during the time of the quantitative test, The complexities of ground-water flow in karst terrane are such that some dye may escape detection by flowing *to* an unmonitored resurgence, especially during traces performed under high-flow conditions. In addition to incomplete mixing and nonconservative dye, the addition or subtraction of water to the flow stream might greatly affect the recovery and computed characteristics. The equations and methodology for these adjustments are shown in section 4.2.

3.4 Quality-Control Procedures

Extreme care must be used whenever handling dyes in order to avoid contamination of the dye detectors and sampling equipment. For this reason, detectors or “bugs” need to be fabricated and installed before the dye is handled and injected. This is also true for all sampling equipment including automatic samplers. Long-sleeved rubber or disposable plastic gloves need to be used during all dye handling operations, including recovery operations. This limits exposure to the dye and also reduces the possibility of cross-contamination between exposed detectors and samples through handling. The lock-top plastic bags used while returning the detectors to the laboratory should not be reused. The dye needs to be stored in a separate room from the detectors and sampling equipment and transported to the injection site in lock-top plastic boxes or in plastic jugs, in the case of liquid dye.

First-time users of a particular tracer should conduct laboratory tests *to* familiarize themselves with the characteristics of that tracer. In particular, learning to recognize weakly positive concentrations of dyes such as fluorescein requires practice, especially in locations where the background fluorescence may be increased by traces of fluorescein (or substances that may look like it) which are found in such products as antifreeze, dishwashing liquids, and toilet-bowl cleaners (Duley, 1983).

Repeat traces, both qualitative and quantitative, to the same point using the same dye should not be performed until after the occurrence of a major storm in order to allow any residual dye to be flushed from the system. This reduces the possibility that a later storm might flush slow-moving or residual dye-laden water from the first trace and cause an incorrect positive trace. Repeat traces during low-flow conditions must be delayed sufficiently to insure that residual dye has drained from the system. In the case of quantitative traces, this may be confirmed by near zero dye concentrations at a spring or well measured with a fluorometer prior to the start of each trace. In addition, fresh dye detectors may be kept in place for at least a week after the arrival of the initial dye cloud. This will help to define the level of background fluorescence and monitor the arrival of a second dye cloud from a single dye injection,

Quinlan (1987a) states that all dye-tracer tests be designed so that there is always a positive dye recovery somewhere. Dye traces without positive results generate questions such as, was enough dye used? Were the correct resurgences monitored? And were the resurgences monitored long enough? Also, subsequent traces in the same area with the same dye may be questionable until the specific point-to-point connections are defined.

During fluorometric analysis, careful handling of the cuvette (sample holder) is required to avoid an increase in sample temperature and the resulting incorrect determination of its dye content. The cuvettes need to be handled only by the open end and cleaned with distilled water or water from the next sample between each reading. All water and equipment used during fluorometric analysis needs to be temperature equilibrated.

In addition to the collection of water samples for fluorometric analysis during quantitative-tracer tests, passive detectors can also be used to confirm passage of the dye cloud. This check is useful in case the selected sampling interval misses the dye passage or in case the automatic sampler malfunctions. Passive detectors are used for a period of one to two weeks, after the passage of the dye cloud, in order to identify passage of a secondary dye cloud, or confirm that all dye has drained from the system.

The time that the detectors are installed is a convenient time to review changes in water use from resurgence points such as intermittent withdrawals by farmers for irrigation purposes. This is also a convenient time to explain to the landowner or water user the nature and purpose of the pending dye trace, which is especially important if the possibility exists that the dye may discolor the water. Ideally, this will simply be a review of earlier conversations when permission to monitor for the arrival of dye in privately owned springs or wells was obtained.

3.5 Summary Decision Charts

Decision charts are presented which summarize the material presented in the discussion of qualitative (fig. 9) and quantitative (fig. 10) dye tracing. These charts present key steps, in sequential order, for completion of qualitative and quantitative dye tracing in karst terrane.

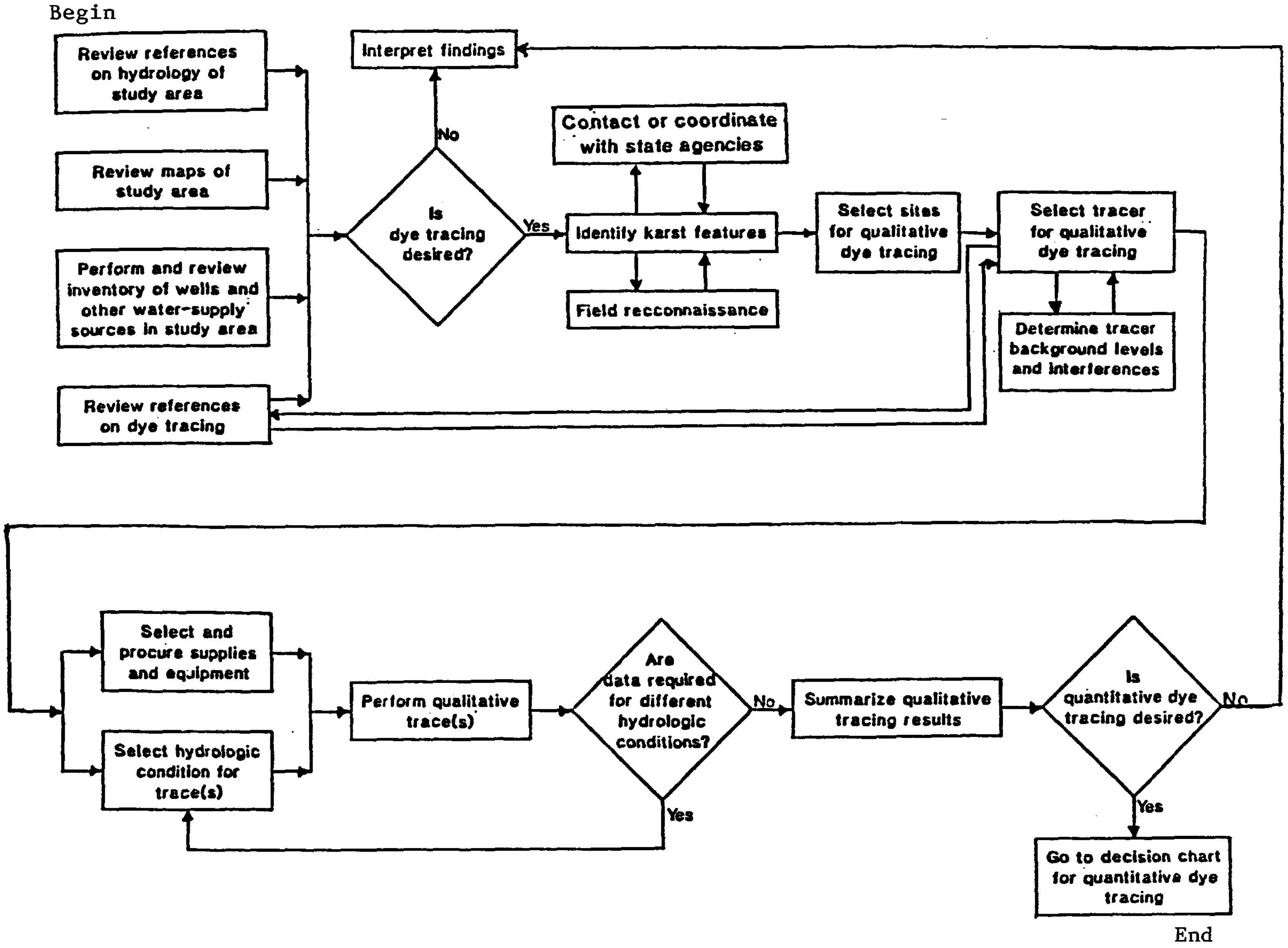


Figure 9.--Decision chart for qualitative dye tracing.

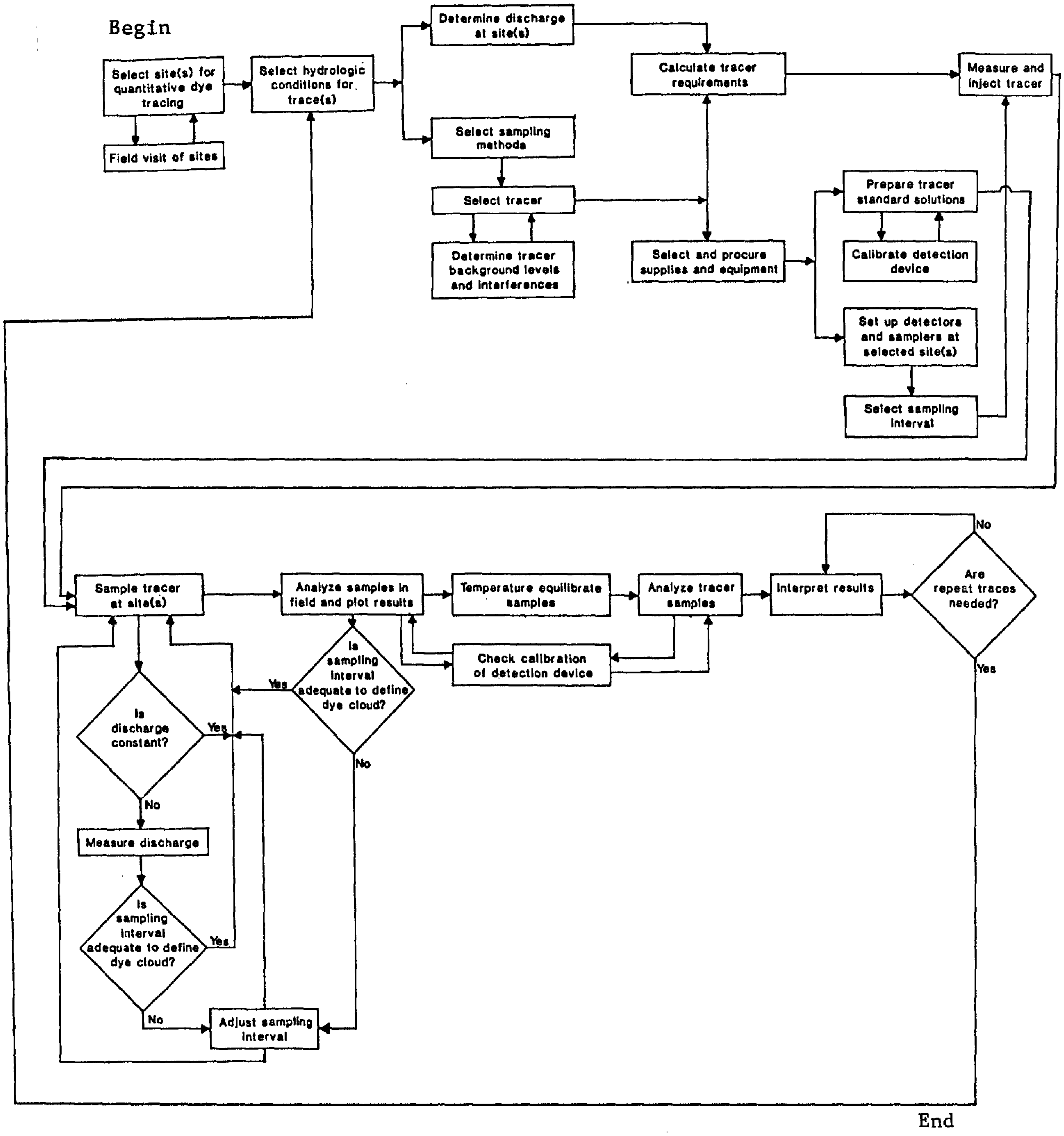


Figure 10---Decision chart for quantitative dye tracing.

4. ANALYSIS AND APPLICATION OF DYE-TRACE RESULTS

4.1 Introduction

Ground-water tracing has long been a valuable tool for investigating ground-water conditions in karst terrane. Atkinson and Smart (1981) classify the application of tracers into three use-categories: (1) determination of flow paths and residence times, (2) measurement of aquifer characteristics, and (3) mapping and characterization of karst conduit systems. Aley (1984) lists several applications of ground-water tracing that are especially useful in water pollution investigations. Specifically, tracing provides (1) direct proof of movement of water from one point to another, (2) results that are easily understood by the public, regulatory agencies, and the courts, (3) a qualitative indication of whether or not effective natural cleansing of water contaminants could occur along the flow path, and (4) an indication of underground travel rates, which tend to be underestimated by persons unfamiliar with ground-water flow conditions in karst terrane.

Analysis and application of the results of dye tracing is controlled, in part, by the design and implementation of the tracer tests and can generally be classed as qualitative or quantitative according to the nature of the trace and subsequent analysis. Perhaps the simplest and most frequent use of the data from dye tracing is to identify point-to-point connection between a discrete ground-water input point such as a sinkhole, and a downgradient discharge point such as a spring or well. Numerous investigators have used these results to define the ground-water basin or catchment area for a particular spring or group of springs (Aley, 1972; Atkinson and Smith, 1974; Quinlan and Ray, 1981; Quinlan and Rowe, 1977; Skelton and Miller, 1979; Smart, 1977; Crawford, 1981; Thrailkill and others, 1982). These data are useful for a variety of purposes but, from the standpoint of water-supply protection, are especially useful for the identification of potential sources of contaminants detected in springs or wells and are almost always a necessary first step to quantitative dye tracing.

Results of qualitative dye tracing can confirm the validity of water-level contours and thus the direction of ground-water movement. Qualitative dye tracing can also identify the nature of the system draining to a particular spring, that is, whether the flow system is convergent or distributary to the spring. If distributary, qualitative dye tracing is the most practical technique to identify the springs that drain the system. These techniques can also efficiently show changes in flow routes when drainage from a particular sinkhole or karst window is traced to different or additional springs during high-flow conditions.

With the aid of the filter fluorometer and conservative fluorescent dyes, the analysis of data from ground-water tracer tests can be quantitative in that mass-balance analysis of dye-recovery data is possible. These data, in combination with a carefully measured discharge, permits a hydraulic characterization of the underground conduit network and the definition and estimation of flow characteristics that is not generally available from other techniques. For example, repeated traces between the same input and recovery points showed the relation between traveltimes and discharge (Smart, 1981; Stanton and Smart, 1981; Mull and Smoot, 1986). Smart and others (1986) demonstrated the advantages gained from quantitative tracing over the qualitative methods for definition of a karst conduit system on the basis of mass balance of the fluorescent tracers.

In recent years, significant advances have been made in the application of quantitative dye tracing to the description of flow characteristics such as dispersion. The analysis of results of quantitative dye tracing was used by Mull, Smoot, and Liebermann (1988) to describe predictive relations between discharge, mean traveltime, apparent ground-water flow velocity, and solute transport characteristics in the Elizabethtown area, Kentucky. Because of the similarity between a water-soluble contaminant and the fluorescent dyes used for dye tracing, the results of these studies can be applied to predict probable impacts on a water supply arising from the spill of water-soluble contaminants. Contaminants that are not soluble in water do not migrate at the same rate as do soluble contaminants. Quantitative dye tracing is therefore, not applicable in determining flow rates of immiscible contaminants. Crawford (1986) presented the hypothesis that floating contaminants carried by cave streams accumulate upgradient from the point where cave passages become completely filled, Section 6 describes, in detail, the application of results of quantitative dye tracing to predicting flow and transport characteristics of potential contaminants in karst water supplies,

4.2 Definition of Quantitative Characteristics

The initial result of quantitative dye tracing is a set of measured dye concentrations, each sampled at a selected time and place. For dye tracing in streams, it is possible to sample at many locations within a cross section and at many stations along the flow path, measuring concentration as a function both of cross-sectional location, longitudinal distance, and elapsed time since injection. For karst ground-water flow, however, one is generally restricted to sampling at one or a few fixed locations, measuring concentration only as a function of time.

Quantitative characteristics are the numeric descriptors of a dye-response curve. They may be derived from quantitative dye trace data. Some characteristics, such as elapsed time to peak dye concentration, may be taken directly from the measured data, Others, such as mean traveltime and normalized dye concentration, are calculated from the measured data. Still others, notably the dispersion coefficient, may be estimated from the data only if simplifying assumptions are made.

This section describes the primary quantitative characteristics for dye-tracing analysis and how they are derived. A summary table of these characteristics is given in section 4.2.5. An example of the computation of quantitative characteristics for an actual dye trace is given in section 4.2.6. A computer program code that calculates quantitative characteristics is discussed in section 6, and is listed in Appendix A.

Application and interpretation of these quantitative characteristics is discussed in section 5 of this manual. It includes the development of relations among characteristics, and their use in the prediction of contaminant transport.

4.2.1 Dye-Recovery Curve

The development of quantitative information from dye traces is based primarily on the analysis of dye-recovery curves, which are plots of concentration versus elapsed time since injection. Such curves are also known as time-concentration, breakthrough, or dye-response curves. Plotted dye-recovery data typically gives a positively skewed, bell-shaped curve that is steeper on the rising limb than on the falling limb.

A dye-recovery curve yields several quantitative characteristics by simple inspection, The time of injection (t_0) is used as the beginning of the dye-recovery curve (fig. 11) and is taken as zero. The measured dye concentration at t_0 becomes the background concentration. Time to leading edge (t_L) is the elapsed time, or time of travel, before concentration increases above background. Time to trailing edge (t_T) is the time of travel until concentration decreases to the background level, and may be called the elapsed time for dye passage. Time to peak concentration (t_{peak}) is the time of travel from dye injection to the peak of the dye-recovery curve. Persistence is the length of time that any given concentration is exceeded. Other characteristics may be defined, such as time of travel from the leading edge until the concentration has decreased to 10 percent of the peak value (Hubbard and others, 1982).

The shape and magnitude of dye-recovery curves are influenced, primarily, by the amount of dye injected, the velocity-and magnitude of flow, the mixing characteristics within the flow system, the sampling interval, and whether the discharge is diluted by non-dyed waters. The data from a single dye trace generally reflect conditions for that particular test, and especially for that particular discharge. Repeated quantitative dye traces between the same injection and recovery points are needed to describe the dye-trace characteristics under different flow conditions.

The mass of dye recovered, is summed from the time-concentration data for a dye trace, by the following relation:

$$M_{out} = 0.1019 \sum_{i=1}^{n} Q_i (C_i' - C_0') \Delta t_i, \qquad \text{(eq. 7)}$$

where M_{out} = mass of dye recovered, in kilograms (kg);

0.1019 = a unit conversion factor;

n = number of sampling intervals, equal to the total number of samples minus one;

i = the i^{th} sampling interval;

Q_i = mean discharge during the i^{th} sampling interval, in cubic feet per second (ft^3/s);

C_i' = mean measured dye concentration during the i^{th} interval, equal to the mean of the two samples taken at the beginning and end of the interval, in mg/L;

C_0' = background dye concentration, measured at time of injection, in milligrams per liter (mg/L); and

Δt_i = duration of i^{th} sampling interval, in hours.

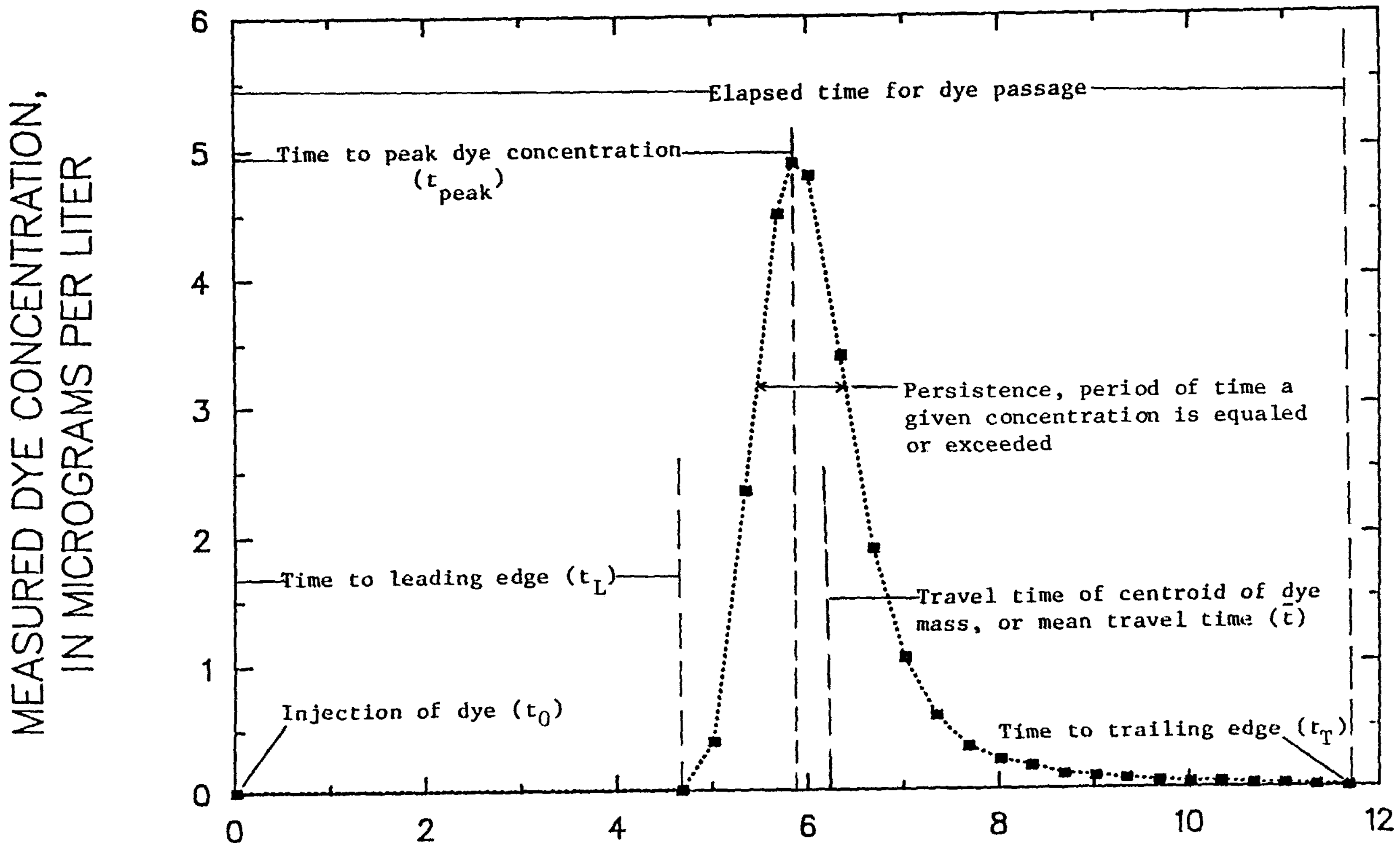


Figure 11.--Dye-recovery curve illustrating measures of elapsed time since injection.

If the unit of concentration used in equation 7 is µg/L, then the mass of dye recovered will be computed in grams. Note that the sampling interval is the period of time between two successive samples or observations, and that the summation was computed from the mean values within each sampling interval. In this manual, concentrations that pertain to a sampling interval are identified with the subscript "i"; concentrations that pertain to a given sample are not subscripted.

For verification, total dye recovery needs to be compared with the amount of dye injected. If the dye is known or suspected to move from the injection point along more than one conduit, it is necessary to sample each resurgence and sum the masses of dye recovered. If the difference between total dye recovery and the amount injected is appreciably more than what is expected to be lost to decay and sorption, the results need to be re-examined. Such results may occur if the conduit system has not been well-defined and all resurgences have not been sampled. Also, calculated dye recoveries may exceed the injection quantity if the dye is not well mixed in the cross-section, if water samples are not representative of the discharge cross section, or if discharge measurements are erroneous.

Measured dye-recovery concentration needs to be adjusted for background concentration and reasonable dye loss by:

$$C'' = (C' - C'_0)\,\frac{M_{in}}{M_{out}}, \qquad \text{(eq. 8)}$$

where C'' = adjusted concentration, in mg/L;
C = measured concentration, in mg/L; and
M_{in} = mass of dye injected, in kg.

4.2.2 Normalized Concentration and Load

Because the quantity, or mass, of injected dye may be different for different dye traces, dye concentrations for each trace are normalized to give the concentration that would have occurred if a standard mass of one kilogram of dye had been injected. Normalized dye concentrations are calculated as:

$$C = C''\,\frac{1}{M_{in}} = (C' - C'_0)\,\frac{1}{M_{out}}, \qquad \text{(eq. 9)}$$

where C - normalized dye concentration, in milligrams per liter per kilogram of dye injected, in (mg/L)/kg.

Normalized concentrations are useful for deriving relations among quantitative characteristics and discharge, and are used for the prediction of concentrations resulting from the injection of a known mass of contaminant.

A plot of normalized concentration gives a true picture of concentration versus time, for a particular hydrologic condition. Dye-recovery curves of normalized concentration for seven different dye traces between the same sites, but under different hydrologic conditions, are shown in figure 12. Because the concentrations have been scaled for a standard injection mass, one

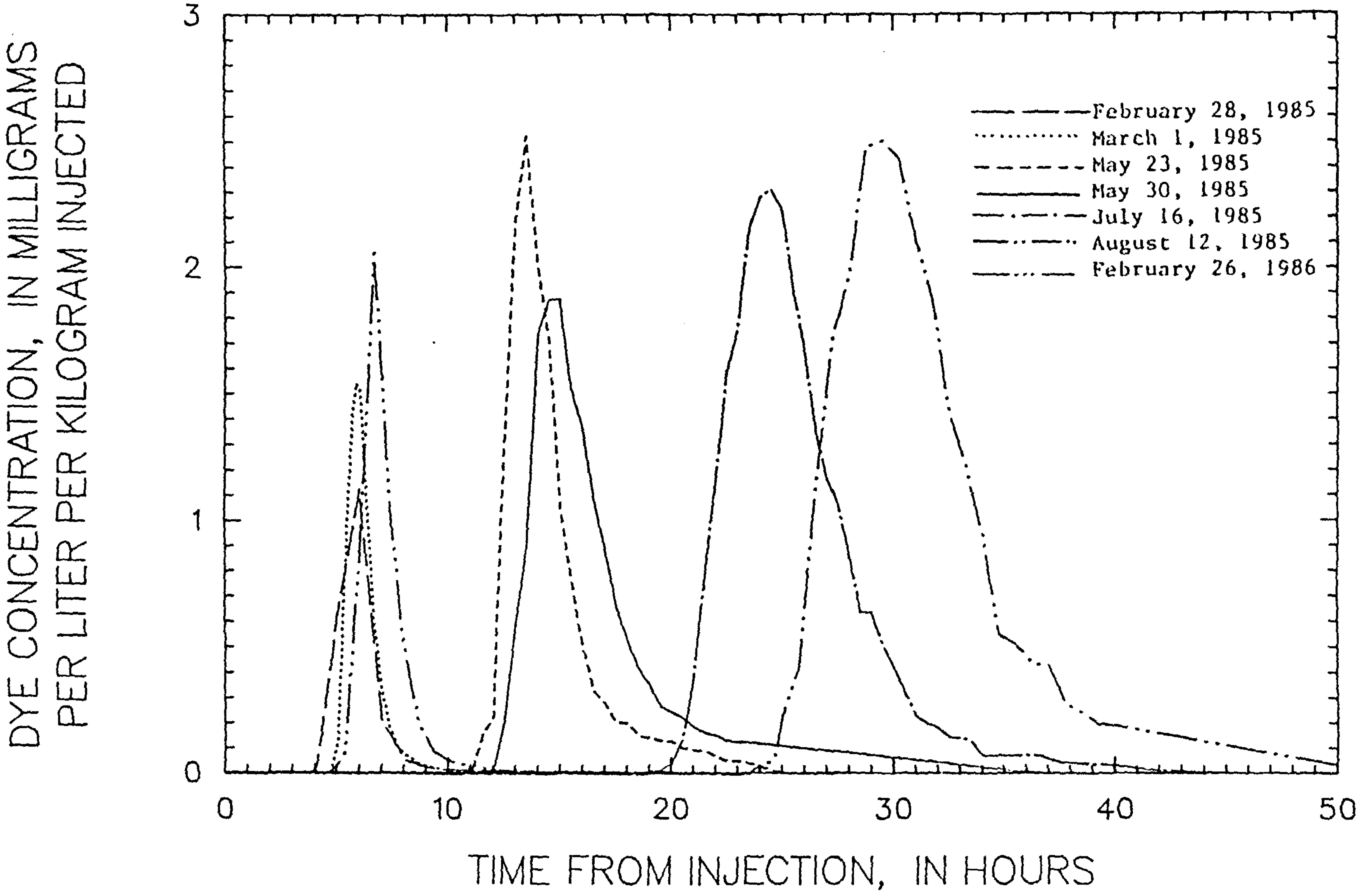


Figure 12.--Normalized dye-recovery curves for seven dye traces made for various discharges at Dyers Spring

might expect the seven curves to have equal areas under their curves. This is not the case because there is increased dilution with increased discharge; the faster traveltimes and higher discharges, hence, greater dilutions are measured by the response tunes to the left in figure 12. The effects of discharge variation between traces may be removed, however, by converting normalized dye concentrations to normalized dye loads.

The normalized dye load, or mass flux, is the amount of dye per kilogram injected passing the sampling point at a given time. Load is dye concentration times discharge, and normalized load is normalized concentration times discharge, calculated as:

$$L = 28.32\ C\ Q, \qquad \text{(eq. 10)}$$

where L = normalized dye load, in milligrams per second per kilogram of dye injected, in (mg/s)/kg; and
28.32 = a unit conversion factor; and
C = normalized dye concentration in (mg/L)/kg,
Q = discharge, in ft^3/s.

Areas under different normalized dye-load curves are equal and by definition sum to 1 kg per kilogram injected over the duration of each test. Normalized load curves from different dye traces may be plotted on the same graph, to illustrate the passage of the dye cloud under different hydrologic conditions, The normalized dye load for seven dye traces made between the same sites is shown in figure 13. Curves toward the left of the graph were obtained under high-flow conditions, and show that the dye cloud traveled more rapidly and with less spreading than the curves toward the right, which represent low-flow conditions.

4.2.3 Time-of-Travel Characteristics

Time of travel is the time required for movement of the dye cloud between the injection site and the sampling site. The dye cloud spreads as it moves, however, so the leading edge of the dye cloud can pass the sampling point long before the trailing edge, with the time to peak dye concentration somewhere in between. The time to peak concentration gives an indication of the time of travel, but because of the typical asymmetry of the dye-recovery curve, it is not representative of the time of travel for the bulk of the dye cloud. For quantitative analysis, the time of travel is best represented by the centroid, or mass-weighted mean, of the dye-recovery curve. The time of travel of the centroid of the dye mass, or simply the mean traveltime, is computed as:

$$\bar{t} = \frac{\sum_{i=1}^{n} t_i\ C_i\ \Delta t_i\ Q_i}{\sum_{i=1}^{n} C_i\ \Delta t_i\ Q_i}\ , \qquad \text{(eq. 11)}$$

where $\bar{t}$ = mean traveltime, in hours; and
t_i = elapsed time since injection during the ith sampling interval, in hours; and
C_i = normalized dye concentration during the ith sampling interval, in (mg/L)/kg.

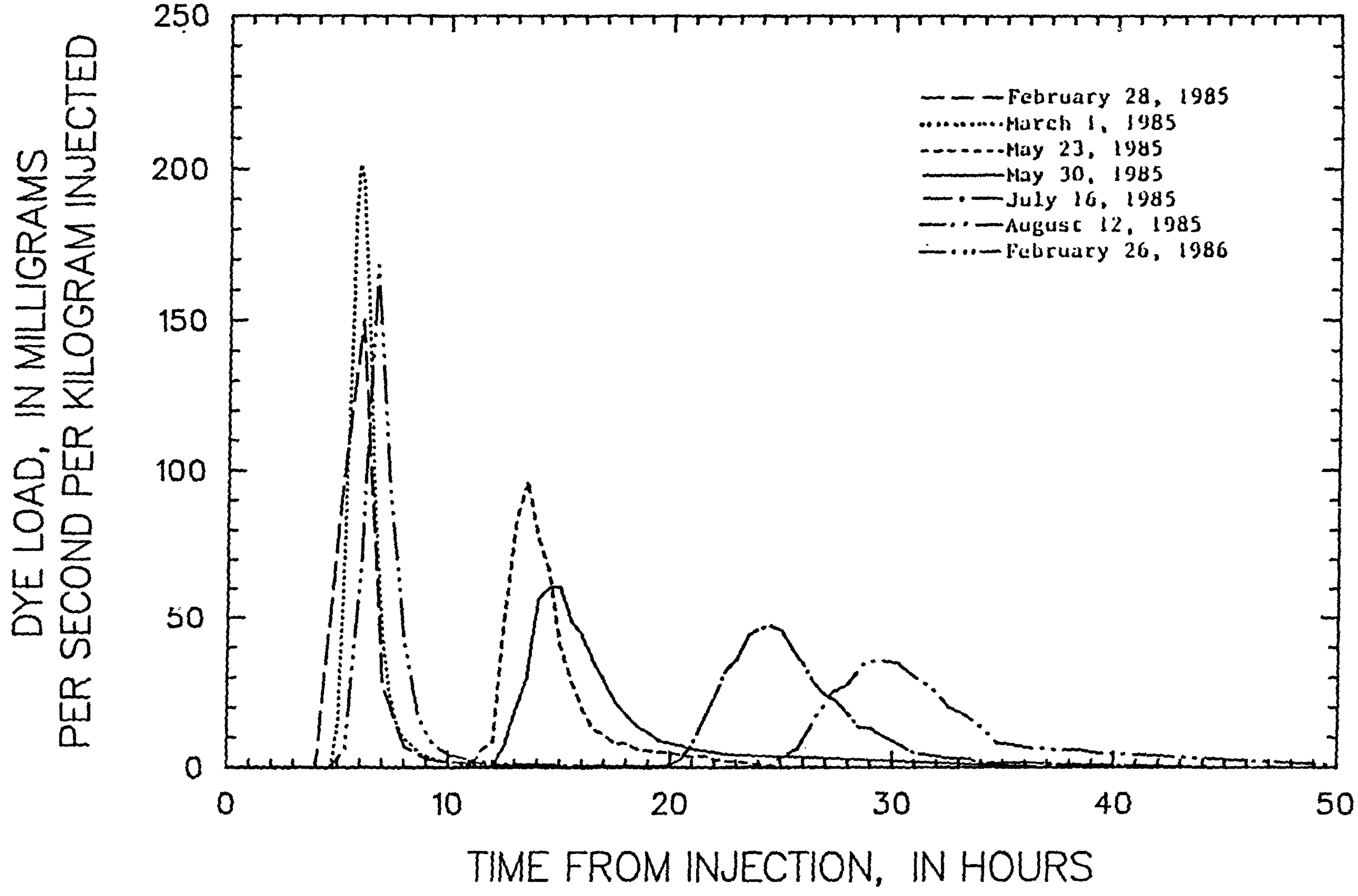


Figure 13.--Normalized dye-load curves for seven dye traces made for various discharges at Dyers Spring.

Computation of the apparent mean velocity of ground-water flow follows directly from the mean traveltime:

$$\bar{u} = \frac{d}{3600\ \bar{t}}, \qquad \text{(eq. 12)}$$

where $\bar{u}$ = mean-flow velocity, in feet per second (ft/s);
d = map distance of the trace, in feet;
3600 = a unit conversion factor, and
$\bar{t}$ = mean traveltime, in hours.

Because the exact flow path and distance between the dye input and recovery points is not known, d and $\bar{u}$ are are apparent values, computed as if the dye followed a straight line between the points. Thus, the actual flow velocity is probably somewhat greater than the apparent velocity because of the longer, meandering nature of the actual flow path in most karst aquifers. The term $\bar{u}$ does give, however, a general idea of ground-water velocity that may be compared between dye traces for different flow conditions. It may also be used in estimating the dispersion coefficient discussed in section 4.2.4.

The standard deviation of the time of travel of the dye mass is a temporal measure of the amount of dispersion of the dye mass that occurred during the dye trace. In other words, it indicates how much the dye cloud has spread out in time, between the injection and the sampling site. It is related to the time of travel and the rate of dispersion, and is computed by the equation:

$$\sigma_t = \left[\frac{\sum_{i=1}^{n} (t_i - \bar{t})^2\ C_i\, \Delta t_i\ Q_i}{\sum_{i=1}^{n} C_i\, \Delta t_i\ Q_i} \right]^{0.5}, \qquad \text{(eq. 13)}$$

where σ_t = standard deviation of the traveltime of the dye mass, in hours.

The standard deviation of traveltime is used in creating the dimensionless dye-recovery curve, in calculating the dispersion coefficient, and in developing relations among the quantitative characteristics and discharge. Because it is a measure of the total amount of dispersion that has taken place, σ_t generally increases when the time of travel is long or when the rate of dispersion is great.

The skewness coefficient is a measure of the lateral asymmetry of the time-concentration curve. This non-dimensional statistic is computed as:

$$\gamma = \frac{\sum_{i=1}^{n} (t_i - \bar{t})^3\ C_i\, \Delta t_i\ Q_i}{n\ \sigma_t^3 \sum_{i=1}^{n} C_i\, \Delta t_i\ Q_i}, \qquad \text{(eq. 14)}$$

where γ = = skewness coefficient.

A symmetrical curve would have a skewness coefficient of zero. The dye curves shown in figures 12 and 13 are positively skewed. Positive skewness indicates that the time-concentration curve is weighted to the right, and that concentration recedes more slowly than it rises.

As presented, the skewness coefficient is not applied directly for predictive purposes for ground-water protection. Rather, it is used to compare dye-recovery curves, to interpret the way in which the dye cloud disperses, and to synthesize standardized dye-recovery curves, as discussed in section 5.2.

4.2.4 Dispersion Characteristics

The longitudinal dispersion coefficient is a measure of the rate at which the concentrated dye mass spreads out along the flow path, and is defined as the temporal rate of change of the variance of the dye-trace cloud (Fischer, 1968). Longitudinal means lengthwise, or along the flow path; dispersion means spread; and a dispersion coefficient is a rate of spread. In this manual, dispersion is considered only in one dimension, and longitudinal dispersion is referred to simply as dispersion. A consideration of dispersion is appropriate because it is the general term to describe the spreading of the dye mass that results both in increasing persistence and decreasing concentration as time passes. In surface-water studies, determination of the dispersion coefficient is one of the primary goals of tracer tests. Although the dispersion coefficient is not used directly for predictive purposes in ground-water studies, it is useful for making comparisons among dye traces of the relative rate of spreading and, more importantly, as a conceptual tool for understanding observed dye-trace results, as seen in section 5.2.

Two methods of estimating the dispersion coefficient are presented. Both are based on equations presented by Fischer (1968), with the assumptions of constant velocity and uniform flow characteristics between the injection and sampling points for the entire duration of the dye trace. This first and more general equation is based on the definition of dispersion coefficient from a slug injection of dye:

$$D_1 = \frac{3600}{2} \bar{u}^2 \frac{\sigma_t^2}{\bar{t}} , \qquad \text{(eq. 15)}$$

where D_1 = first dispersion coefficient, in (ft^2/s).

The second equation is based on the further assumption that the dye-response curve is normally distributed, with zero skew along the flow path. When sampled at the peak of the dye-recovery curve,

$$C_{peak} = \frac{588.5}{A\sqrt{4 \pi D_2 t_{peak}}} , \qquad \text{(eq. 16)}$$

where C_{peak} = peak of the normalized concentration curve, in mg/L/kg;

588.5 = a unit conversion factor;

π = 3.1416;

A = the effective cross-sectional area of the flow medium, in square feet (ft^2), estimated as discharge divided by mean flow velocity; and

D_2 = second dispersion coefficient, in ft^2/s.

On the basis of equation 16, the second estimate of the dispersion coefficient may be computed as:

$$D_2 = \frac{346{,}400}{4 \pi t_{peak} (C_{peak} A)^2}, \qquad \text{(eq. 17)}$$

where 346,400 = a unit conversion factor.

The value of the dispersion coefficient is affected by the flow velocity and the characteristics of the flow medium. In a water body, the observed amount of dispersion is affected by turbulent forces as well as by simple, hydrodynamic dispersion, and the computed dispersion coefficient reflects the combination of both processes. In the case of simple dispersion alone, the dye spreads outward by molecular diffusion, and concentration within the dye cloud is normally distributed in space. Even so, the dye-recovery or time-concentration curve for the case of simple dispersion is expected to have a slightly positive skew. This slight skew results from the transformation of a dye cloud that is normally distributed longitudinally at any given time into a set of dye samples from a fixed location at different times. In other words, by the time the trailing point of the dye cloud passes the sampling point, it has had more time to disperse, thus lagging and extending the tail of the observed curve. This is, however, a relatively small effect. In practice, the skewness of the observed dye-response curves is typically much greater than that expected from this axis transformation. Most of the skewness, or lengthened recession of the dye-recovery curve is not accounted for by simple dispersion alone, but results mainly from unequal flow lengths and velocities along and across the flowpath, or in other words, turbulence.

If the dye-recovery curve were normally distributed and perfectly sampled, values of D_1 and D_2 computed from the curve would be equal. In practice, however, several factors typically lead to different values of D_1 and D_2 computed from the same curve. The assumption of zero skewness, used in computing D_2, usually does not hold. The quantities u and A are not simple constants, but rather apparent average values. The computed dispersion coefficient is a composite term for the combined action of simple dispersion and turbulent action. Turbulence not only introduces skewness, but also increases the computed value of standard deviation of traveltime, thus increasing the value of D_1. If the sampling interval is not adequate to precisely measure the peak concentration and the time it occurred, the value of D_2 will be affected. An inadequate sampling interval also affects the computed values of the other quantitative characteristics from which the dispersion coefficients are estimated. Based on this discussion, it is difficult to determine which of the two values is more correct. Both are relative values, and the reader is cautioned not to attach undue numeric accuracy to the computed values of D_1 and D_2. When comparing dye-recovery curves, however, the use of either coefficient gives a relative idea of the rate of spread of the dye cloud along the flowpath. At present, consideration of the dispersion coefficient is appropriate mainly as a conceptual tool for understanding relations among the quantitative characteristics under different hydrologic conditions.

4.2.5 Summary of Quantitative Terms

Table 4 gives a summary of the main terms used in the development of quantitative characteristics. Measured data are plotted to make a time-concentration or dye-recovery curve of a particular dye trace. The area under the time-load curve is summed to give the total mass of dye recovered and percent recovery is computed. Concentrations are adjusted by subtracting the background concentration and dividing by the percent recovery, Concentrations are normalized to a standard injection by dividing by the mass injected. Loads may be normalized by multiplying normalized concentration by discharge.

Statistical descriptors of the dye-recovery data are based on mass-weighted moments of the data. Mean traveltime is the best estimate of the time of travel. Standard deviation of traveltime is a measure of the amount of dispersion that occurred during the trace. The skewness coefficient measures the asymmetry of the curve, and is indicative of the time delay for passage of the trailing edge of the dye cloud.

Dispersion simply means the gradual outward spread of the dye from an initial slug to an expanding dye cloud. It is caused by simple molecular diffusion, known as hydrodynamic dispersion, and the turbulence of the water body . The dispersion coefficient is an estimate of the rate at which the dye cloud expands. Its application to ground-water flow in karst terranes is presently limited to conceptual use in interpretation of repeated dye traces under differing hydrologic conditions.

4.2.6 Example of Computation of Quantitative Characteristics

A dye trace performed on May 30, 1985 at Dyers Spring near Elizabethtown, Kentucky (Mull, Smoot, and Liebermann, 1988) produced the time-concentration data shown on the left side of table 5. Including the end points, 26 observations of dye concentration were made. Map distance from injection to sampling point was 3,000 ft. Discharge of 1.14 ft^3/s was measured by current meter at the spring, and was constant throughout the dye-trace period. A quantity of 15 mL of 20 percent rhodamine WT was injected. From equation 4, the mass of dye injected was:

$$\text{Mass - volume x density x purity}$$
$$M_{in} = (15\ cm^3)\ (1.19\ g/cm^3)\ (0.20) - 3.57\ g.$$

Background concentration (C was 0.01 μg/L, time of injection (t was 1015 hours. The measured time-concentration data are displayed in figure 14a.

The data were processed using the computer program DYE, described in section 6.1. Output from the program is shown on the right side of table 5.

Table 4--Summary of terms used in definition of quantitative characteristics

Characteristic	Method of Computation	Definition or primary use
Dye-recovery curve	Measured	Measured concentration as a function of time. Basis for all further computations.
Time to leading edge	Measured Figure 11	Comparison of curves, synthesis of standardized curves.
Mass of dye recovery	Equation 7	Computation of percent recovery, correction for dye leas.
Adjusted dye concentration	Equation 8	Correction for back-ground and dye loss.
Normalized dye concentration	Equation 9	Correction for unit mass of injection. Analysis and prediction.
Normalized dye load	Equation 10	Compensation for discharge dilution, for comparison of rapeat traces.
Time of travel	---	Time required for passage of the dye cloud. Also called traveltime.
Mean traveltime	Equation 11	Best estimate of time of travel. Analysis and prediction.
Mean flow velocity	Equation 12	Computation of dispersion coefficients. Analysis and prediction.
Standard deviation of traveltime	Equation 13	Amount of spread of the dye cloud. Analysis and prediction.
Skewness coefficient	Equation 14	Asymmetry of the dye-recovery curve. Synthesis of standardized curves.
Dispersion	---	General term for the gradual spreading of the dye cloud, Strictly speaking, longitudinal dispersion.
Dispersion coefficient	Equations 15, 17	Rata of dispersion. Conceptual analysis.

Table 5.--Measured and computed data for dye trace at Dyers Spring, May 30, 1985

[(mg/L)/kg, milligrams per liter per kilogram injected; (mg/s)/kg, milligrams per second per kilogram injected]

Measured data			Computed data[1]				
Time of day	Measured concentration, in micrograms per liter	Discharge, in cubic feet per second	Observation, in hours	Elapsed time, in hours	Concentration minus background, in micrograms per liter	Normalized concentration [(mg/L)/kg]	Normalized load [mg/s)/kg]
10 15	0.010	1.140	1	0.0	0,000	0.000	0.000
21 45	.010	1.140	z	11.5	.000	.000	.000
22 15	.060	1.140	3	12	.050	.022	.723
22 45	.500	1.140	4	12.5	.490	.220	7.086
23 15	1.320	1.140	5	13	1.310	.587	18.945
23 45	2.050	1.140	8	13.5	2.040	.914	29.502
15	3.900	1.140	7	14	3.890	1.743	56.257
45	4.200	1.140	8	14.5	4.190	1.877	60.596
1 15	4.200	1.140	9	15	4.190	1.877	60.596
1 45	3.400	1.140	10	15.5	3.390	1.519	49.026
2 15	3.050	1.140	11	16	3.040	1.362	43.964
2 45	2.450	1.140	12	18.5	2.440	1.093	35.287
3 15	2.000	1.140	13	17	1.990	.892	28.779
3 45	1.500	1.140	14	17.5	1.490	.668	21,548
4 15	1.200	1.140	15	18	1.190	.533	17.210
4 45	.950	1.140	16	18.5	.940	.421	13,594
5 15	.600	1.140	17	19	.790	.354	11.425
5 45	.600	1.140	18	19.5	.590	.264	6.533
6 15	.550	1.140	19	20	.540	.242	7.809
6 45	.500	1.140	20	20.5	.490	.220	7.066
7 15	.420	1.140	21	21	.410	.184	5.929
7 45	.370	1.140	22	21.5	.360	.161	5.206
8 15	.350	1.140	23	22	.340	.152	4.917
8 45	.300	1.140	24	22.5	.290	.130	4.194
13 45	.200	1.140	25	27.5	.190	.085	2.748
22 45	.010	1.140	26	36.5	.000	.000	.000

[1] The following summary statistics were computed from the data:

Mass of dye recovered, 2.232 grams;
Mean discharge, 1.140 (ft^3/s);
Mean traveltime, 17.146 hours;
Elapsed time to pack concentration, 14.500 hours;
Standard deviation of traveltime, 4.370 hours;
Peak normalized concentration, 1.877 (mg/L)/kg;
Peak normalized load, 60.596 (mg/s)/kg;
Apparent mean velocity, 0.049 ft/s;
First dispersion coefficient (Dl), 4.737 ft^2/s;
Second dispersion coefficient (D2), 0.981 ft^2/s;
Skewness coefficient, 1.998.

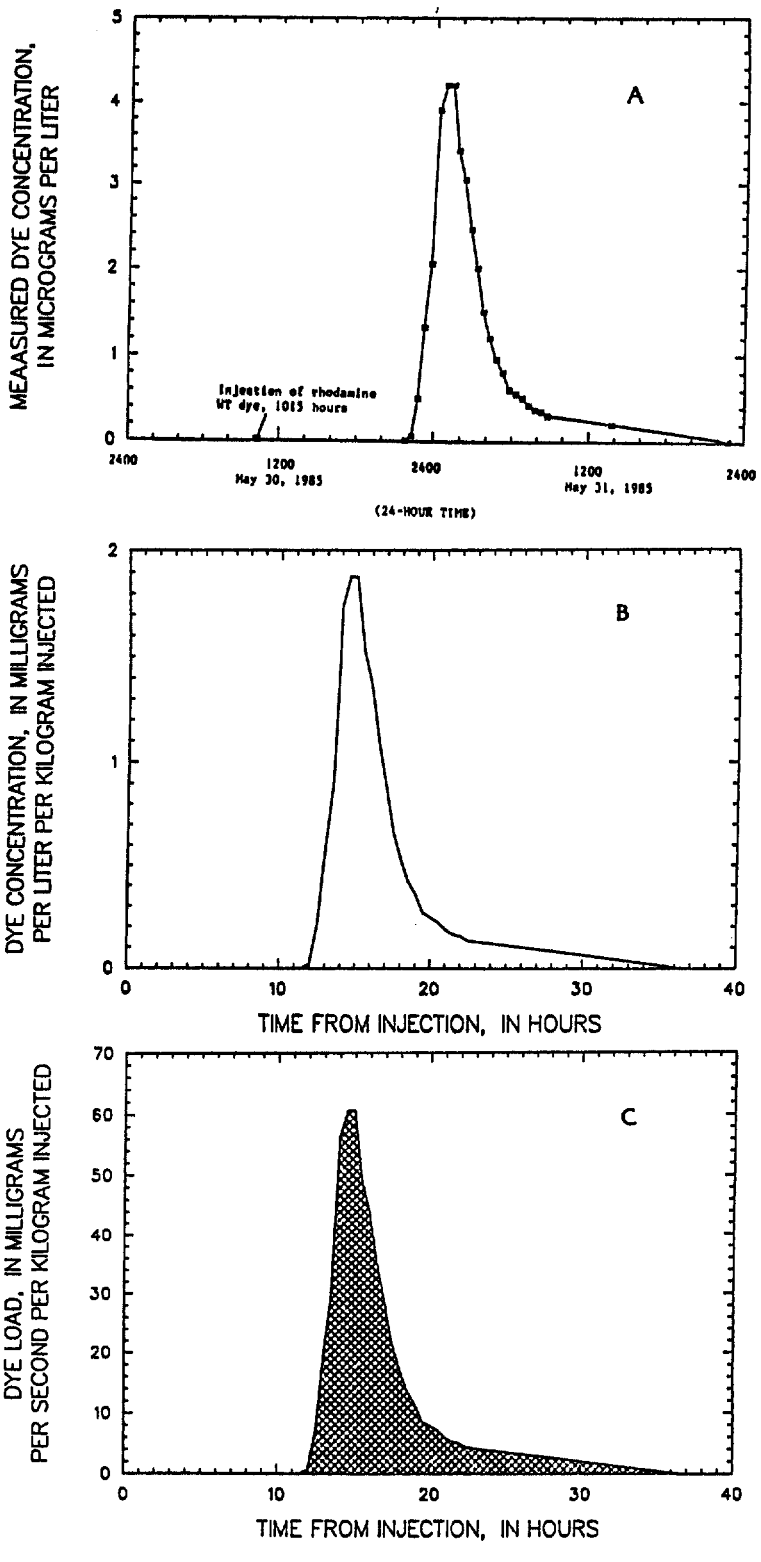


Figure 14.--Development of selected quantitative characteristics for dye trace at Dyers Spring, May 30, 1985: A. Measured data prior to any computations; B. Normalized dye concentration versus elapsed time from injection; C. Normalized dye load versus elapsed time from injection. The shaded region under the curve in 14C has an area of exactly one.

Summary statistics computed from the data are shown at the bottom of table 5. A summary of the method used in computing the quantitative characteristics follows.

For computational purposes, 25 sampling intervals were obtained by averaging values between the 26 consecutive observations, or samples. For example, for the fifth sampling interval--the period of time between the fifth and sixth observations--concentration was the mean of 1.32 and 2.05, less the background, giving 1.67 µg/L or 1.67 x 10^{-3} mg/L. For a duration of 0.5 hours and a mean discharge of 1.14 ft^3/s, the mass of dye recovered during the internal, from equation 7, was 9.73 x 10^{-5} kg, or 0.0973 g. The same general procedure was used for all subsequent calculations involving sampling intervals.

The total mass of dye recovered during the trace, from equation 7, was 2.23 x 10^{-3} kg, or 2.23 g. Percent recovery, based on 3.57 g injected, was 62.5 percent.

Normalized dye concentration and load were computed for each observation, using equations 9 and 10. Note that a quantity expressed in units of µg/L/g has the same magnitude as in units of mg/L/kg. Thus, for convenience, in equation 9 µg and g may be used for the computation, with the result given in mg/L/kg. For example; for the sixth observation in table 5,

$$C = (2.05 - 0.01)\ 1/2.23 = 0{,}914 \text{ mg/L/kg}$$
$$\text{and } L = 28.32\ (0.914)\ (1.14) = 29.5 \text{ mg/s/kg}$$

Graphs of normalized concentration and load versus time are shown in figures 14b and 14c, respectively.

Mean traveltime, standard deviation of traveltime, and skewness are calculated from equations 11, 13, and 14 respectively. These equations are based on the statistical definitions of mean, standard deviation, and skewness coefficient. In equation 11, the time term t_i is used to give the first moment about the origin or, in other words, the mean. In equations 13 and 14, the time term $(t_i - t)^n$ refers to the n^{th} central moment of the data. The term $C_i \Delta t_i Q_i$ is used to weight the time term by the corresponding mass of dye for the interval

As shown in table 5, the mean traveltime for the example was 17.15 hours. Note that the mean traveltime occurred later than the normalized peak concentration, which reached 1.88 mg/L/kg at 14.5 hours. A skewness coefficient of 2.0 reflects the asymmetry of the curves in figure 14, which shows the lagging effect of the passage of the trailing edge of the dye cloud. Based on the apparent flow length of 3,000 ft, the mean-flow velocity was computed from equation 12 as 0.049 ft/s, or 176 ft/hr.

Computation of the two estimates of the dispersion coefficient follows from equations 15, 16, and 17, using quantities that have already been determined.

In this example,

$$D_1 = \frac{3600}{2}\,(0.049)^2\,\frac{4.37^2}{17.15} = 4.74\ \mathrm{ft}^2/\mathrm{s},$$

$$A = 1.14/0.049 = 23.5\ \mathrm{ft}^2, \text{ and}$$

$$D_2 = 346{,}400/(4\pi(14.5)\quad[(1.88\quad 0.98\quad \mathrm{ft}^2/\mathrm{s}.$$

The different values for D_1 and D_2, assuming that sampling was adequate, is primarily due to the skewness, or asymmetry, of the curve introduced by turbulent action of the water body. The value of D_2 is primarily dependent on the peak of the dye trace; D_1 on the standard deviation, which is influenced by the asymmetry of the curve, D_2 may be thought of as being more representative of the molecular diffusion and D_1 of the turbulent forces. It should be remembered that these are not precise estimates and that neither value is necessarily more correct, but that these values may be compared to values obtained from other dye traces.

5. APPLICATION OF QUANTITATIVE DYE-TRACE RESULTS FOR PREDICTING CONTAMINANT TRANSPORT

5.1 Introduction

Because the movement of dye used for tracer studies is similar to most conservative soluble contaminants, dye-trace results can be used to predict the transport characteristics of such contaminants. For example, normalized dye consentrations from a dye trace, in (mg/L)/kg, can be multiplied by a given mass of contaminant to estimate the time-concentration response at the sampling site that would result from a contaminant spill at the injection site under the same hydrologic conditions.

The use of results from repeated dye traces extends the range of hydrologic conditions for which the time-contaminant response may be estimated. Furthermore, results from repeated dye traces may be compared and analyzed to derive relations among the quantitative characteristics and the hydrologic conditions as shown by Mull, Smoot, and Liebermann (1988), and Smart (1981). If such relations can be established, then the interpretation of the results, the understanding of the karst ground-water flow system, and the ability to predict contaminant response are all strengthened.

5.2 Relations among Quantitative Characteristics

In most cases, discharge is the variable that characterizes the hydrologic conditions associated with a dye trace. By use of data from repeated dye traces, each quantitative characteristic can be plotted as a function of discharge. Least-squares regression or another reliable method of fitting curves to data may be used to establish a relation between each characteristic and discharge. If a statistically significant relation can be established for a given characteristic (such as mean traveltime), then its value can be predicted for a given discharge. As with any empirically derived relation, predictions should be used with caution, and may not be valid if discharges are outside the range of the original data.

As an example, relations were developed for quantitative characteristics from seven dye traces at Dyers Spring (Mull, Smoot, Liebermann, 1988). A summary of the characteristics is given in table 6. In the table, the second estimate of the dispersion coefficient (D_2) is shown. By use of standard least-squares regression techniques, best-fit models were developed, that used several transformations of discharge as the independent variable. The best transformation for a given characteristic was chosen, based on the greatest value of R^2, where R is the correlation coefficient of the regression. If several transformations resulted in close fits, the simplest or most readily understood was chosen. For example, the inverse transformation was chosen for mean traveltime, because traveltime is inversely proportional to velocity. Figure 15 shows examples of the relations of the quantitative characteristics to discharge developed from seven dye traces to Dyers Spring. When appropriate, it may also be useful to derive relations among various quantitative characteristics such as peak dye load as a function of mean traveltime.

Once established, the relations may be used for prediction and to gain an understanding of the movement and spread of solutes in the karst ground-water system. Interpretations of the quantitative characteristics should be based on the established relations and on an understanding of solute transport, both in general and in a specific karst ground-water system. The quantitative characteristics computed for a given dye trace result from complex interactions within the flow system, mainly between the length of time that the dye is in the system and the rate and pattern with which the dye disperses. Although the best empirical fit among variables may differ for different locations, it is likely that certain general relations will hold for most karst ground-water flow systems. For a specific flow path, if discharge increases from one dye trace to another, then:

(1) Apparent flow velocity will increase and the mean traveltime will decrease;
(2) The dispersion coefficient will increase, because of increased turbulence and mixing brought about from the increased velocity;
(3) Standard deviation of traveltime will probably decrease, because even though the dye cloud disperses more rapidly, it has less time to disperse;
(4) Peak normalized load may increase, because the time of passage is shorter and the response curve is steeper and narrower; and
(5) Peak normalized concentration may decrease, because the dye is diluted by the increased discharge.

To illustrate interpretation of a specific set of dye-trace results, the relations derived from the dye traces at Dyers Spring, as shown in figure 15, may be interpreted as follows. Discharge is the controlling factor of the quantitative characteristics for the seven dye traces. The relations between discharge, mean traveltime, and the dispersion coefficient may be used to explain other dye-response characteristics. As discharge increases, velocity increases (fig. 15a) and time of travel decreases (fig. 15b). Thus the dye cloud has less time to disperse, which tends to decrease the standard deviation. In the same circumstance, however, the dispersion coefficient increases (fig. 15c); thus the dye cloud disperses more rapidly, which tends to increase the standard deviation. The net result of these contrary tendencies is that as discharge increases, standard deviation decreases

Table 6.--Quantitative characteristics of seven dye traces at Dyers Spring

[(mg/L)/kg, milligrams per liter per kilogram injected;
(mg/s)/kg, milligrams per second per kilogram injected]

Date of dye trace	Mass of dye injected, in grams	**Discharge, in cubic** feat per second	Mean travel-time of **dye mass, in hours**	Apparent mean velocity, in feet per second	Normalized peak dye concentration [(mg/L)/kg]	Normalized peak dye load [(mg/s)/kg]	Standard deviation of traveltime of dye mass, in hours	Dispersion coefficient, in square feet per second
2-28-85	2.38	4.72	6.05	0.138	1.12	150	1.48	3.07
3-1-85	2.38	4.59	6.19	.135	1.55	201	.82	1.61
5-23-85	3.57	1.35	14.6	.057	2.53	96.5	2.17	.52
5-30-85	3.57	1.14	17.1	.049	1.88	60.6	4.37	.98
7-16-85	2.36	.72	25.4	.033	2.23	45.5	3.69	.46
6-12-85	2.38	.53	31.4	.027	2.48	35.1	4.68	.37
2-26-66	7.14	2.88	7.18	.116	2.06	168	1.46	1.46

(fig. 15d). This indicates that traveltime exerts a greater influence on the relative amount of dispersion than does the dispersion coefficient. The same interaction of traveltime and dispersion coefficient also affects the peak value of the normalized dye load, or peak load. As discharge increases, the peak load increases (fig. 15e); because the traveltime is shorter, the rate of mass transport is greater. When considered as mass per unit volume, or concentration, this increased load is diluted by the increased volume of water, resulting in an overall decrease in peak concentration (fig. 15f). At this location, the amount of downstream dispersion is dependent mainly on the length of time since injection, which in turn is dependent on the travel distance and discharge.

Interpretations such as these allow one to conceptualize the transport of dye or other soluble materials within the karst system. This understanding may then be applied to predict the behavior of solutes in the karst system under different flow conditions.

5.3 Development and Use of Dimensionless Dye-Recovery Curve

Knowledge of quantitative response characteristics is useful in predicting the peak concentration or mean traveltime of the dye cloud for a given injection, but it is knowledge of the dye-recovery (time-concentration) curve itself that allows prediction of variables such as the time to leading edge of persistence--variables of importance to water-supply managers. This section describes one procedure for developing a generalized curve that can be used for predictive purposes.

Simulations of dye-recovery curves that are based on simple dispersion theory yield dye-cloud concentrations that are normally distributed along the

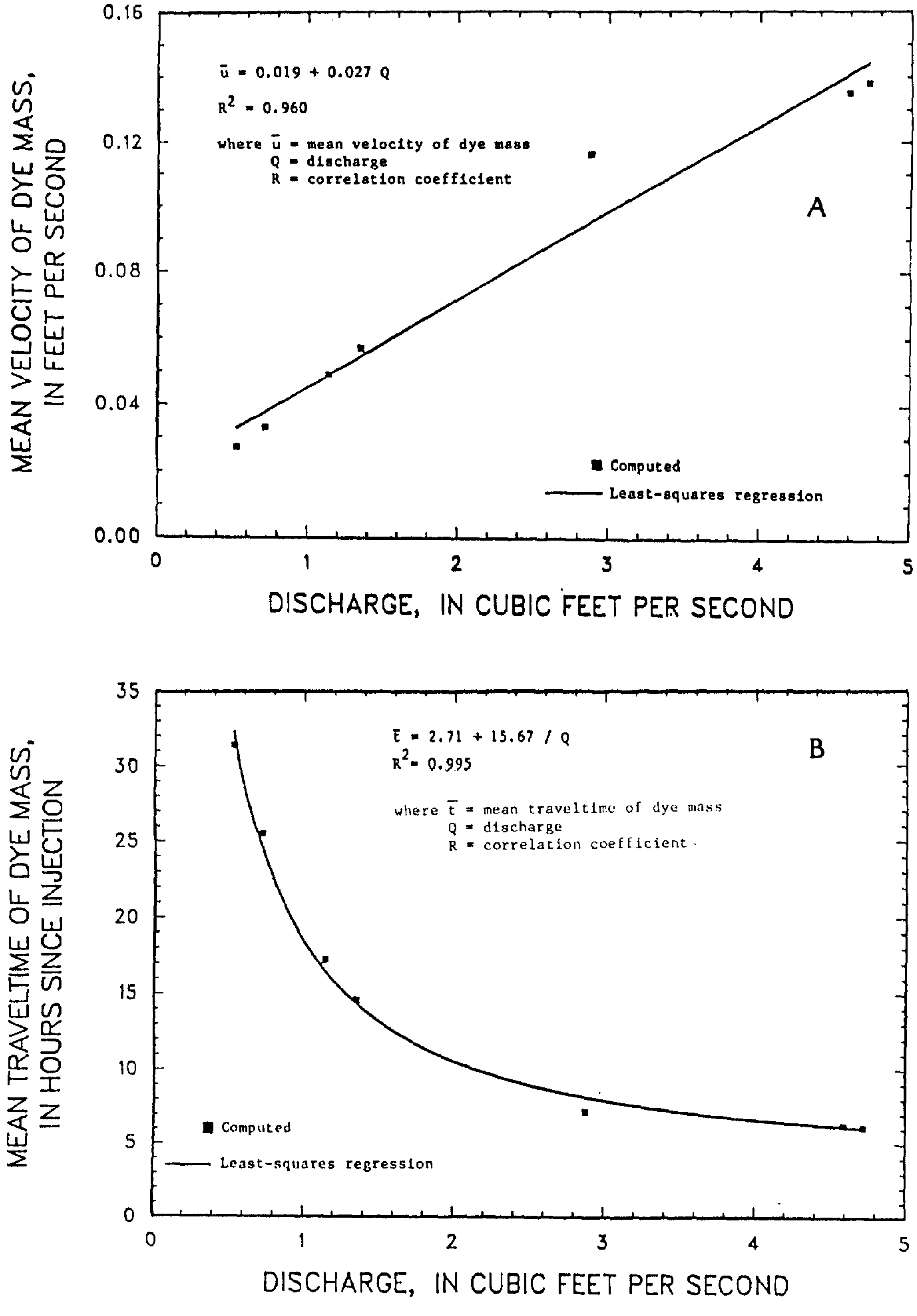


Figure 15.--Relation of selected quantitative characteristics to discharge based on seven dye traces to Dyers Spring: A. Apparent mean velocity; B. Mean traveltime;

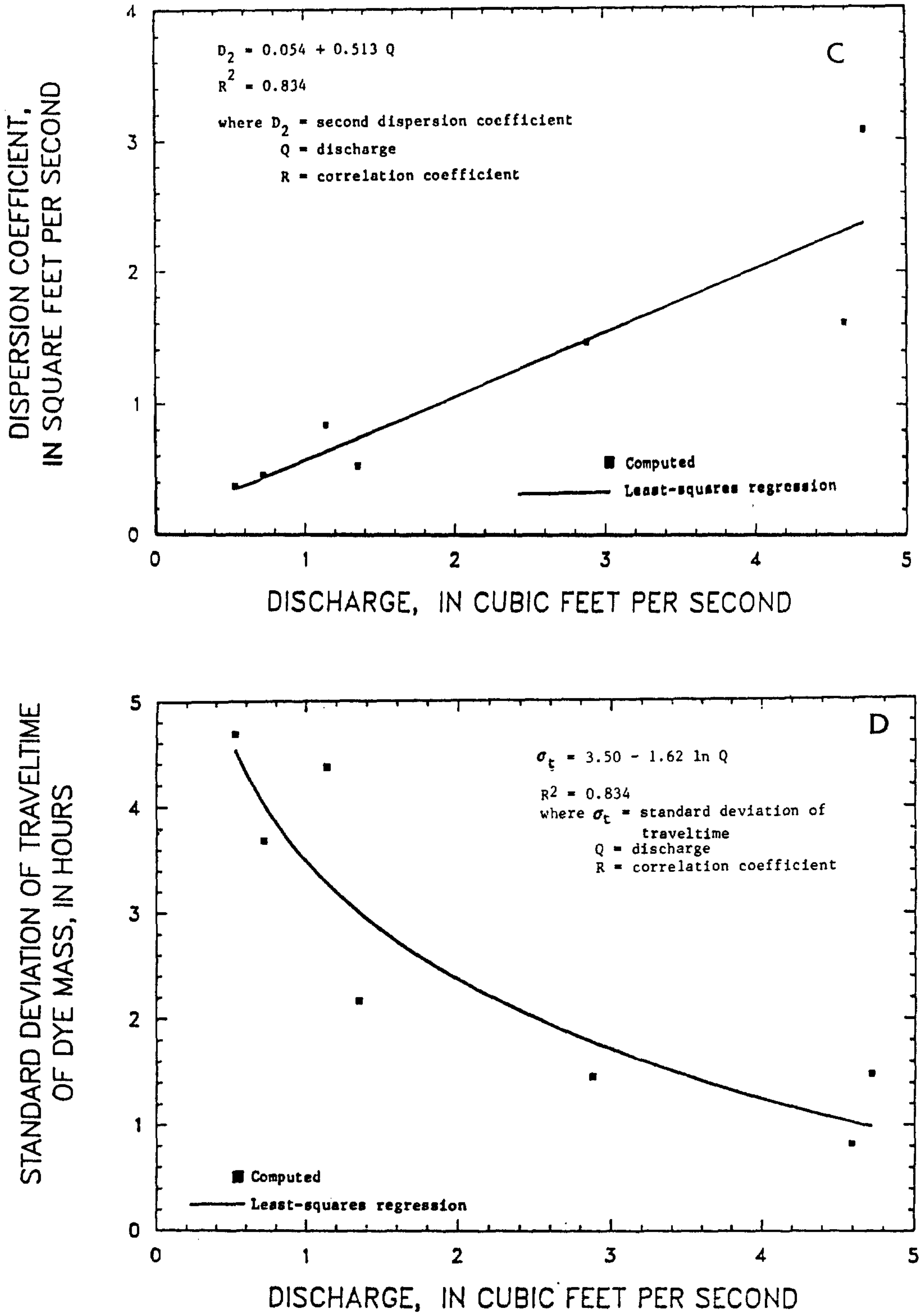


Figure 15 (continued.--Relation of selected quantitative characteristics to discharge based on seven dye traces to Dyers Spring: C. Dispersion coefficient; D. Standard deviation of traveltime;

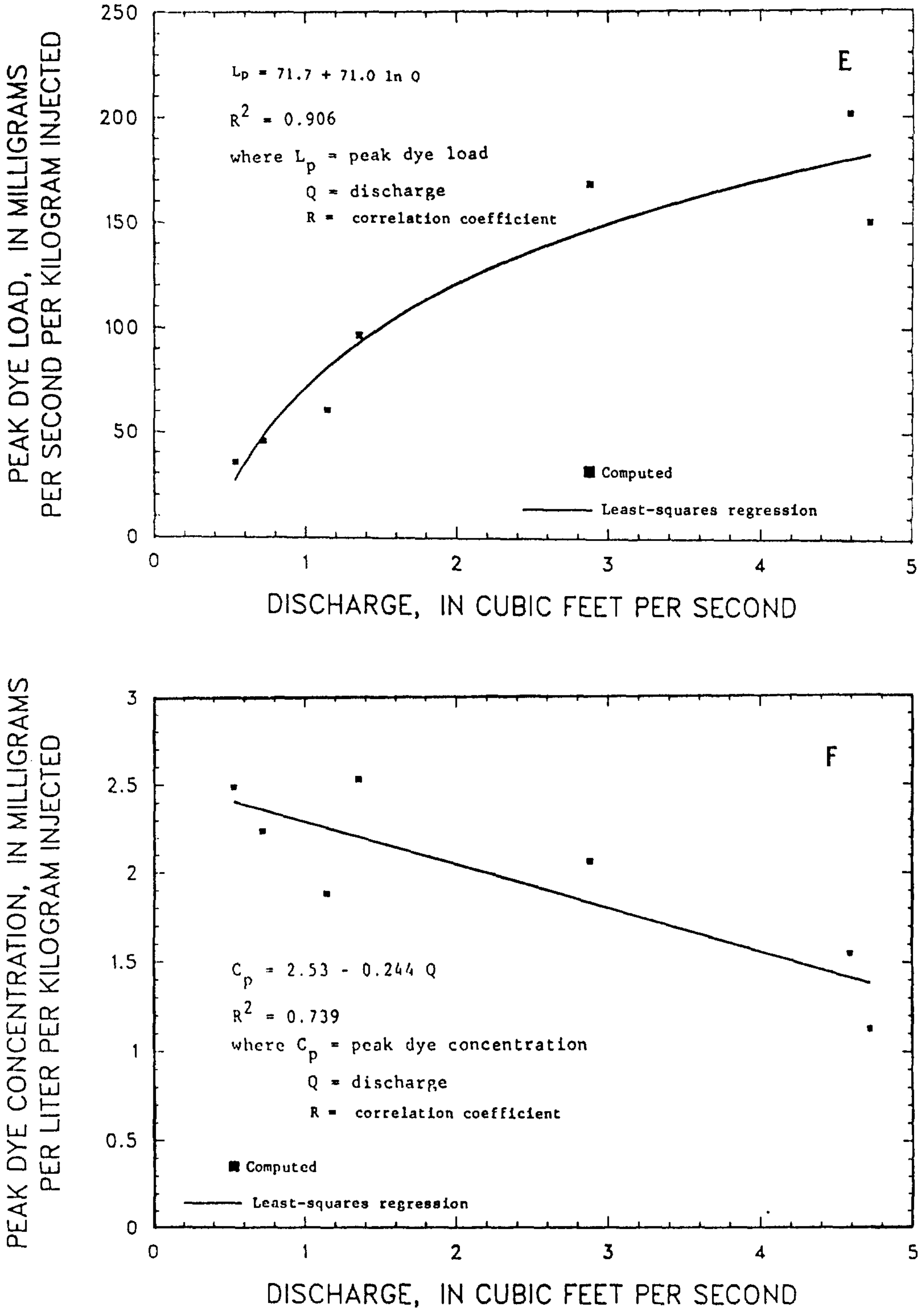


Figure 15 (continued).--Relation of selected quantitative characteristics to discharge based on seven dye traces to Dyers Spring: E. Normalized peak load; F. Normalized peak concentration.

flow path. Transformation of a dye cloud that is normally-distributed in space at a given time into a set of dye samples from a fixed location will introduce a slight positive skewness but will not adequately reproduce the skewed shape of observed time-concentration curves. The skewed shape results mainly from unequal flow lengths and velocities along and across the flow path. If in general, the shapes of a set of observed curves are similar, a standardized recovery curve can be developed to simulate time-concentration curves for the site under study.

In the absence of an adequate theoretical model or frequency distribution that generates curves of the proper shape, a graphical solution can be applied. Individual dye-response curves for which discharge is constant should be resealed so that the peak value of each curve equals one, the mean traveltime is zero, and the standard deviation of traveltime is one. A sample of computer program code that will accomplish this is the program SCALE, discussed in section 6.2. The resulting standardized curves all should be plotted on the same axis. If the shapes and the skewness coefficients are similar, then the curves can be overlaid and redrawn into a single, representative dimensionless curve. This standardized, dimensionless recovery curve can be used to derive response curves of dye or contaminant concentrations or loads under constant discharge conditions.

An example of the development of a dimensionless recovery curve is shown in figure 16, using data from five of the dye traces at Dyers Spring. Figure 16a shows normalized dye concentration as a function of time for the five traces. For each trace, concentration and time were standardized using the computer program SCALE (section 6.2), based on :

$$C_s = C/C_{peak} \qquad \text{(eq. 18)}$$

where C_s = standardized concentration

$$\text{and } t_s = (t - \bar{t})/\sigma_t \qquad \text{(eq. 19)}$$

where t_s = standardized time.

C_s represents the fraction of the peak concentration; t_s represents the number of standard deviations away from the mean travel time.

The standardized values were plotted on the same graph (fig. 16b). By definition, for each trace the peak value is one, mean traveltime is zero, and standard deviation of traveltime is one. Skewness coefficients for the five traces ranged from 1.4 to 2.0. On the basis of the skewness coefficients and visual inspection of figure 16b, the five curves were judged to be similar. Although there are more rigorous methods for deciding whether the curves could be from the same population (similar), their use and description are beyond the scope of this manual.

A composite curve was sketched that represented the typical shape of the five standardized dye-trace curves. Coordinates of C_s and t_s were taken from the curve. Figure 16c shows this representative curve and selected coordinates. This is the dimensionless recovery curve.

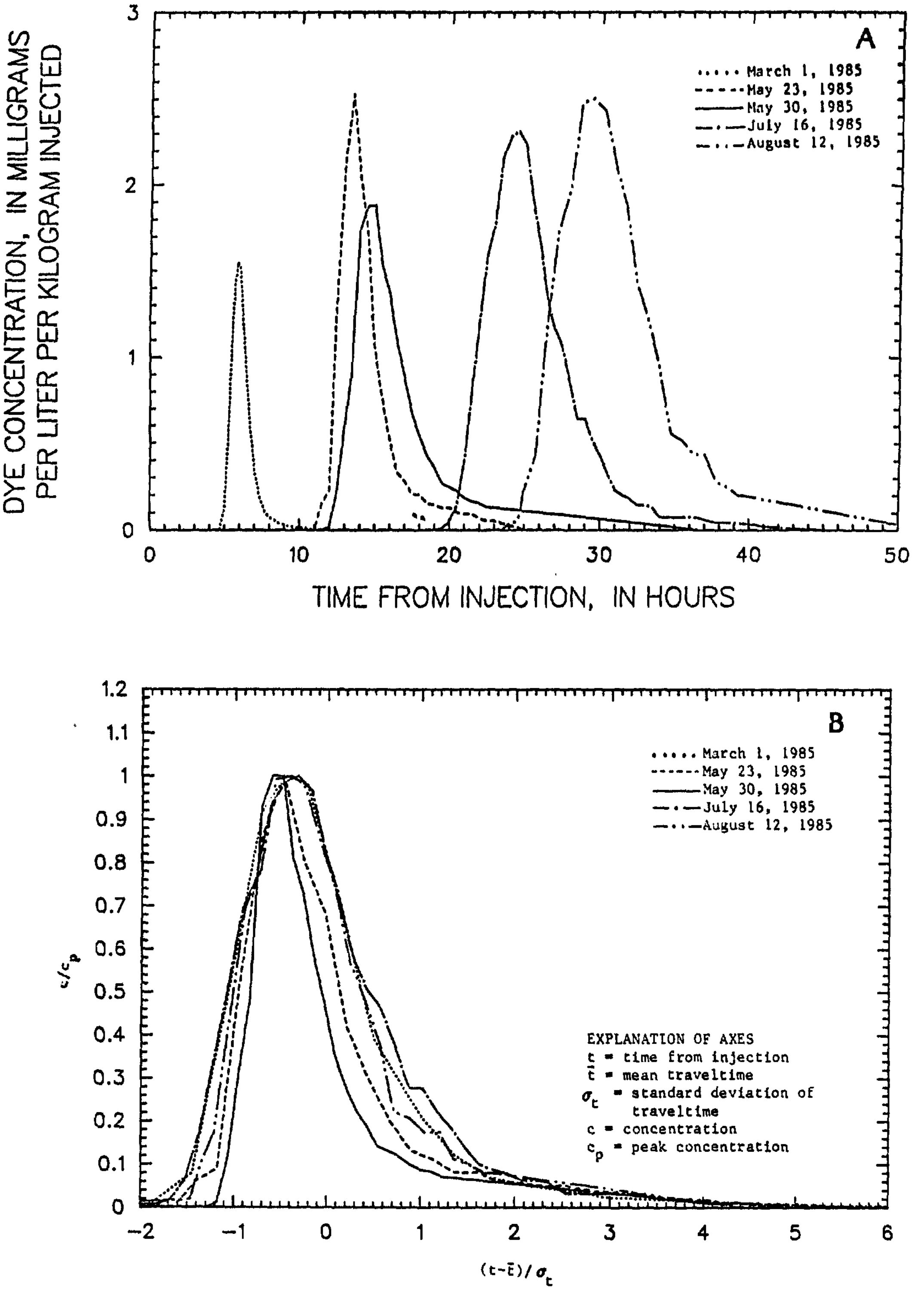


Figure 16.--Development of a standardized, dimensionless recovery curve for Dyers Spring: A. Curves of normalized dye concentrations from five dye traces; B. Standardized curves from the same dye traces;

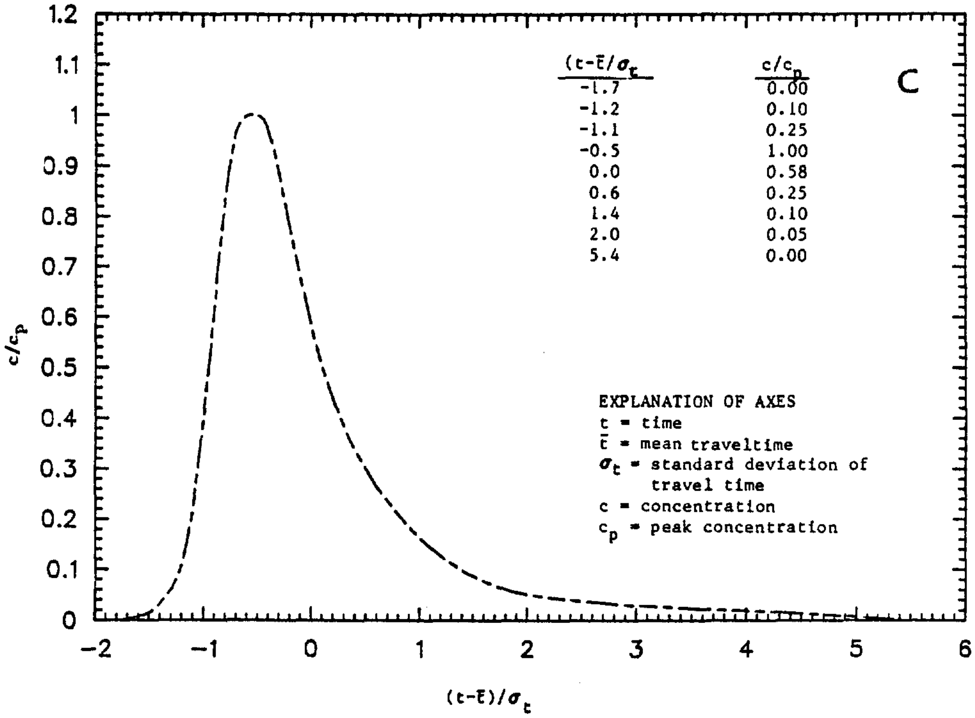


Figure 16 (continued).--Development of a standardized, dimensionless recovery curve for Dyers Spring: C. The resulting standardized, dimensionless recovery curve, composite from the five standardized curves.

All curves in figures 16 b - c have a mean of zero, a standard deviation of 1, and a peak value of 1.

At this point an iterative procedure was used to adjust the curve. The coordinates were adjusted slightly until the representative curve met the design criteria: mean - 0,0, standard deviation = 1.0, and skewness coefficient - 2.0. Design criteria can be evaluated by processing the coordinates using the program SIMULATE (section 6.3) to generate simulated dye-trace data, then processing those data through the program DYE (section 6.1) to compute the summary statistics. For example, suppose that in the program SIMULATE, one specified that $\bar{t}$ should equal 10 and σ_t should equal 1. However, summary statistics from program DYE might indicate that $\bar{t}$ = 10.4, σ_t - 1.2, and γ = 2.8. One might adjust the coordinates of the curve to give it a shorter and thinner recession tail. The process continues until one is satisfied that the design criteria are met. The dimensionless recovery curve shown in figure 16c has been adjusted for this example such that $\bar{t}$ = 10.01, σ_t = 0.996, and γ - 2.03.Because this is an iterative, graphical solution, some degree of perseverance, skill and intuition may be required. Numerical methods of compositing curves into a single representative curve with desired characteristic are currently being investigated by the authors.

Once the curve has been developed, three characteristics are needed to convert the dimensionless recovery curve into real values: mean traveltime, standard deviation of traveltime, and peak concentration or load. If these three values are known or can be estimated from previously derived relations, then a simulated curve may be obtained from the dimensionless recovery curve. An ideal situation would exist if relations were derived such that these three values could be estimated based only on the discharge at the sampling point. A sample of computer programming code that will accomplish this is the program SIMULATE, discussed in section 6.3. The curve of concentration as a function of time, or C as a function of t, is simulated from the dimensionless recovery curve, by use of the three scaling factors C_p, $\bar{t}$, and σ_t:

$$C = C_s C_p \, , \qquad \text{(eq. 20)}$$

$$\text{and} \quad t = \bar{t} + \sigma_t t_s \, . \qquad \text{(eq. 21)}$$

Likewise, loads can be simulated by substituting L and Lp for C and Cp, respectively. A comparison of the actual dye trace for Dyers Spring on May 30, 1985 with the simulated curve is shown in figure 17, The scaling factors were estimated as functions of discharge, by using the regression relations shown in figures 15b, d, and f, respectively; $\bar{t} = 16.46$, $\sigma_t = 3.29$, Cp = 2.25. Residual errors of the regression, notably peak concentration in this case, are reflected in the simulated curves when compared with actual data.

Another graphical approach for synthesizing a response curve, described by Kilpatrick and Taylor (1986) for surface-water applications, is to approximate the shape of the dye-response curves by scalene triangles. The three corners of the triangle are taken from the curve as the following time-concentration coordinates: time to leading edge, background concentration; time to peak, peak concentration; and time until a recession concentration equal to 10 percent of the peak is reached, background concentration. Four characteristics (three time values and peak concentration) are required in this approach. As with the dimensionless recovery curve, if these characteristics are known or can be estimated, a simulated response triangle may be derived.

5.4 Prediction of Contaminant Transport

Given the vulnerability of karst aquifers to contamination, it is important that the manager of a water system supplied by a karst aquifer have the capability to predict flow characteristics of the aquifer. This capability is needed to develop preventive measures and to be prepared to take emergency actions in case of the introduction of contaminants into the aquifer. Once quantitative relations are known for a given ground-water flow path between an injection and resurgence point, the time variation of concentration, as well as quantitative characteristics for a given injection may be predicted. If a dimensionless recovery curve has been developed, the time-concentration curve itself may be simulated. A general procedure that allows such prediction follows. Items 1 through 4 have been discussed earlier, and the reader is referred to the appropriate section of the manual. Steps 5 through 7 are presented here with an example.

(1) Establish connection between injection and resurgence point by qualitative dye tracing (section 3.2);

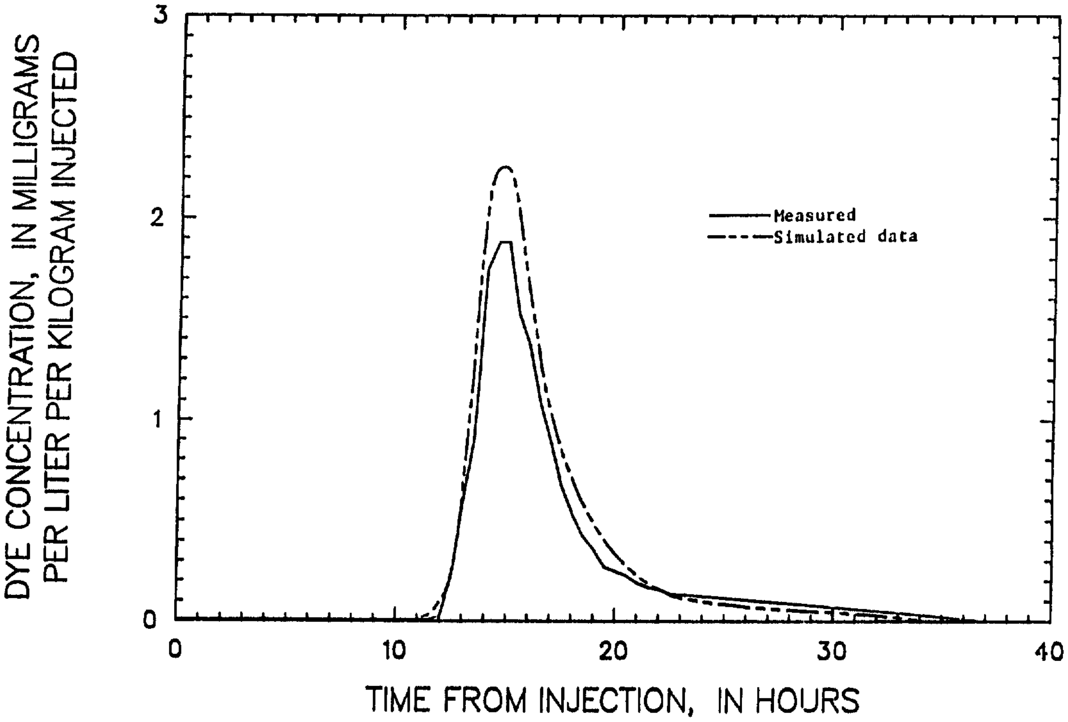


Figure 17.--Comparison of normalized dye-recovery to simulated curve for Dyers Spring, May 30, 1985. The parameters of the simulated curve were estimated solely as a function of discharge.

(2) Perform quantitative dye traces under several discharge conditions (section 3.3);

(3) Determine relations such that peak concentration, mean traveltime, and standard deviation of traveltime can be predicted, ideally, as simple functions of discharge (section 5.2);

(4) If the general shapes of the dye-recovery curves are similar, composite the curves into a single dimensionless recovery curve (section 5.3);

(5) Assume a discharge and a mass of contaminant to be spilled or injected;

(6) Compute peak concentration, mean traveltime, and standard deviation of traveltime from the derived relations;

(7) Scale the dimensionless recovery curve using these variables, to predict the time-concentration curve of the contaminant at the sampling point; and

(8) For the case of a series of injections, time-concentration curves can be predicted for each injection and then superposed to derive the resultant time-concentration curve.

For the purpose of illustration, suppose we wish to consider the effect of a chemical spill at the karst window, which was used as the injection site for the Dyers Spring dye traces. Qualitative dye traces had previously confirmed that the karst window drains to Dyers Spring, a water-supply source for the city of Elizabethtown, Kentucky. Before the hypothetical spill, steps 1 through 4 had already been completed. Step 5: Assume that 50 gallons of 5-percent copper sulfate solution are spilled into the karst window and that we are interested in predicting the concentration of dissolved copper at the sping. That quantity of copper sulfate solution, a common agricultural chemical, contains 1.13 kg of copper. Assume that the discharge at Dyers Spring is 0.9 ft^3/s and stable.

Step 6: From the empirical relations shown in figures 15b, 15d, and 15f, the following values are estimated:

mean traveltime,
$\bar{t} = 2.71 + 15.67 / (0.9) = 20.1$ hours;

standard deviation of traveltime,
$\sigma_t = 3.50 - 1.62 \ln (0.9) = 3.67$ hours; and

normalized peak concentration,
$C_p = 2.53 - 0.244 (0.9) = 2.31$ (mg/L)/kg.

Because 1.13 kg of the copper sulfate was spilled, the peak concentration would be (2.31 mg/L/kg)(1.13 kg) or 2.61 mg/L of dissolved copper.

Step 7: Use these values to scale the dimensionless response curve with the program SIMULATE (section 6.3). The time-concentration response at Dyers Spring can be predicted and plotted (fig. 18). The time-concentration values may also be processed through the program DYE (section 6,1) to give summary statistics. The following information is gained:

The leading edge of the solute mass would be expected at Dyers Spring about 14 hours after the spill occurred;

Concentration at the spring would be expected to peak at 18 hours, decrease to 2 percent of the peak by 34 hours, and be virtually undetectable about 40 hours after the spill occurred; and

The drinking-water standard of 1 mg/L for copper (U.S. Environmental Protection Agency, 1986) would be exceeded for about 5 hours at the spring, beginning about 16 hours after the spill event.

Step 8: Steps 5 through 7 can be repeated for different combinations of contaminant mass and discharge to provide an ‘in-advance” estimate of the timing and magnitude of contaminant spills. For the case of multiple or continuous injections, a valid approach is to consider the sequence as a series of discrete events. Estimate the response curve for each event and plot them on graph paper. For any given time, the resultant concentration is the sum of the curves at that time. An example of this procedure is not presented here.

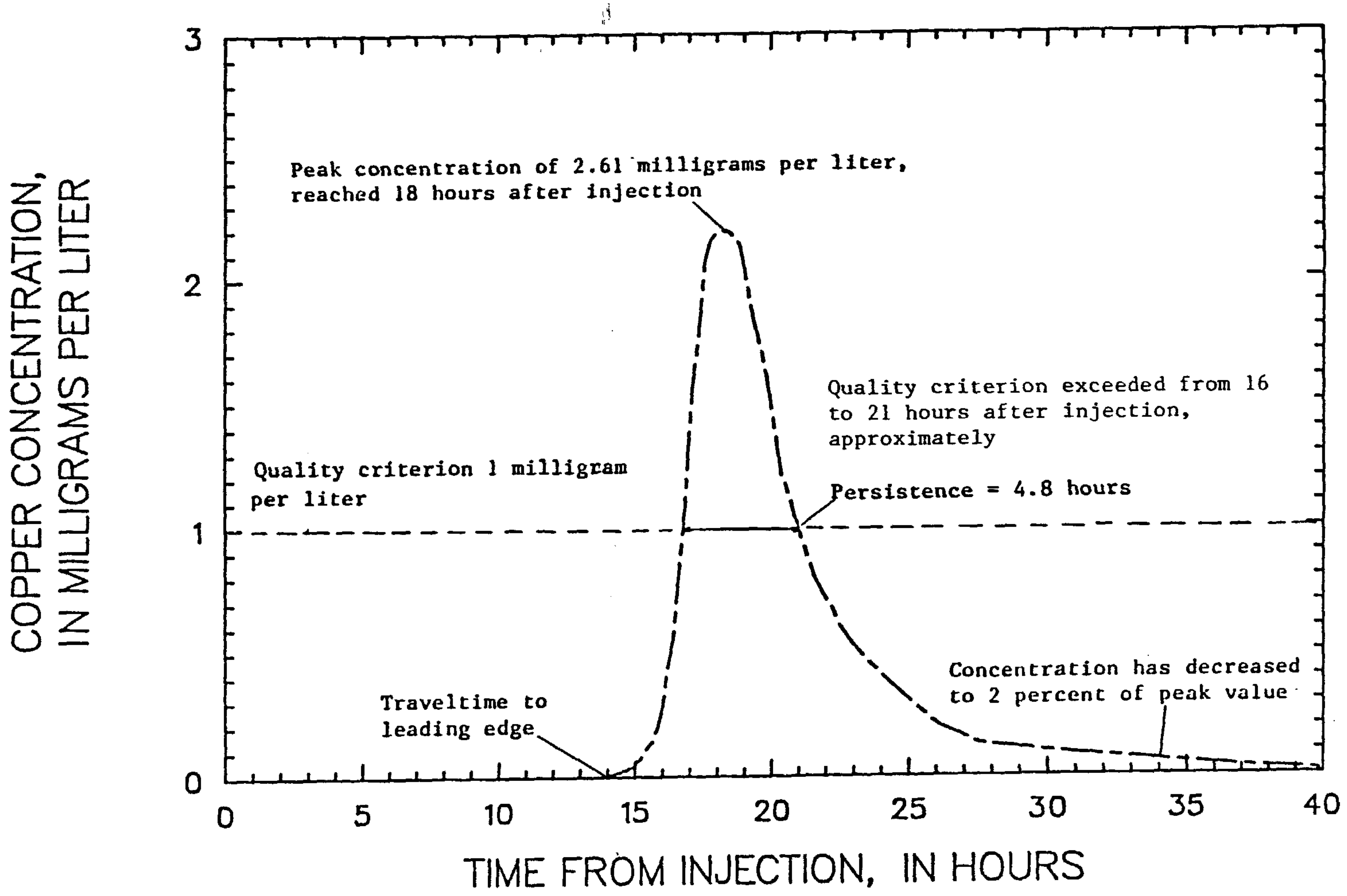


Figure 18.--Simulation of dye-recovery (time-concentration) curve resulting from a hypothetical contaminant spill near Dyers Spring.

With this information, the manager of the public water supply can take appropriate steps to protect the safety of the community’s drinking water, such as using an alternative water source, increasing the volume of treated water in storage, providing treatment to lower the concentration of copper in the water supply to acceptable levels, or diverting the unsafe water until the concentration of the contaminant reaches acceptable levels.

The procedures demonstrated in this section are intended to serve as a framework to help interpret dye tracing results, and make predictions or estimates based on those interpretations. If a dimensionless recovery curve is not developed, much useful information may still be obtained from the results of quantitative dye tracing by developing relations among the quantitative characteristics and discharge. Predictions of traveltime and peak concentration may still be made. Characteristics other than those related in figure 15 (section 5.2) may also be examined. For example, elapsed time to peak concentration and elapsed time to the leading edge of the dye mass also might be estimated as a function of discharge. If discharge measurements are not feasible, another variable, such as stage or depth to water, might be used as the indicator of hydrologic conditions.

6. USE OF COMPUTER PROGRAMS

This section describes three computer programs that are used to execute the calculations described in sections 4 and 5. The three programs are written in BASIC programming language and are designed to execute on commonly available microcomputers. The programs were written with several goals in mind: perform calculations in equations 7 through 21; use a common format for input and output of data; allow flexibility in scaling, simulating, and evaluating sets of data; and interactive execution with a minimum of user effort.

6.1 Program DYE

The program inputs “raw” clock time and concentration, computes mass of dye recovered, computes normalized dye concentration and load, and computes summary quantitative characteristics. Equations 7-17 are used. The source code for the program and examples of input and output are listed in appendix A. The user is required to enter the name of the input data file, the name of an output file, and the map distance of the trace (d), in feet.

The format of the input data file is as follows: a period in column 1, clock hour in columns 3-5, clock minutes in columns 7-8, measured concentration in columns 10-16, and measured discharge in columns 18-24. Each sample occupies one line. The first line should show the time of injection and the background concentration at the time of injection. The period in column 1 is required to maintain proper spacing of the output.

The output file contains the same data as the input file, with these additional columns: the number of the sample; elapsed time from injection, in decimal hours; measured concentration minus background; normalized concentration; and normalized load. Column headers are added to the beginning of the file. The summary statistics are added at the end of the file.

When executing the program the user has the option of scaling normalized concentration and load in the output file. For actual dye-trace data, this option should be ignored (that is, enter zero). However, program DYE can use the output file from program SIMULATE as input. When this is the case, the user can use this option to ensure that the normalized values are of the proper magnitude, as shown below.

This is one example of executing the program DYE. User entries appear in lower case and to the right of the colons. The file SAMPLE.DYI contains measured dye-trace data and is shown in Appendix A.2. The output file SAMPLE.DYO is shown in Appendix A.3.

```
basic
load “dye”
run
ENTER NAME OF INPUT FILE       : sample.dyi
ENTER NAME OF OUTPUT FILE      : sample.dyo
SCALE THE OUTPUT ? 0=NO 1=YES          :0
ENTER DISTANCE TRAVELED IN FEET        :3000
FINISHED. . .
```

This is an example using simulated dye-trace data. The input file, called SAMPLE.SIO was generated using the program SIMULATE and is shown in Appendix C.3. The peak normalized concentration is arbitrarily set at 2.5 (mg/L)/kg. All other normalized concentration & load values are scaled accordingly.

```
basic
load “dye”
run
ENTER NAME OF INPUT FILE        :sample.sio
ENTER NAME OF OUTPUT FILE       :sample.out
SCALE THE OUTPUT ? 0=NO 1=YES          :1
ENTER PEAK NORM. CONCENTRATION         : 2.5
ENTER DISTANCE TRAVELED, IN FEET       : 3000
FINISHED. .,
```

Output from the program DYE may be used several ways. The data may be plotted, as in figure 14. The output for several dye traces may be combined, as in table 6 and figure 12. The relations shown in figure 15 were derived from the values output by this program.

6.2 Program SCALE

The program inputs data that was created by the program DYE and scales it so that the output data have these characteristics: mean traveltime = 0, standard deviation of traveltime = 1, and peak concentration = 1. The source code for the program and examples of input and output are listed in Appendix B. The user is required to enter the name of the input data file, the name of an output file, and three scaling factors: peak concentration, mean traveltime, and standard deviation of traveltime. These three factors may be obtained from the summary statistics given by the program DYE.

Time and normalized concentration are taken from columns 30-35 and 45-51, respectively, of the input file. Equations 18 and 19 are used. The output file of the program DYE may be used as input to the program SCALE, but first the headers and summary statistics must be removed from the file. Any appropriate editor may be used for this purpose. The output file from program SCALE contains two items: standardized time and standardized concentration.

This is one example of executing the program SCALE. The input file called SAMPLE.SCI is shown in Appendix B.2. The output file called SAMPLE.SCO is shown in Appendix B.3. The three scaling factors were taken from Appendix A.3.

```
basic
load “scale”
run
ENTER NAME OF INPUT FILE      : sample.sci
ENTER NAME OF OUTPUT FILE     : sample.sco
PEAK NORMALIZED CONCENTRATION        : 1.877
MEAN TRAVELTIME                      : 17.146
STD. DEVIATION OF TRAVELTIME         : 4.37
FINISHED. . .
```

Output from the program SCALE is primarily useful for development of a representative dimensionless recovery curve, as shown in figure 16b. The output may immediately be resealed, if desired, by using it as input for the program SIMULATE.

6.3 Program SIMULATE

The program inputs a data file containing coordinates for a standardized curve and simulates a dye trace based on the desired characteristics. The source code for the program and examples of input and output are listed in Appendix C. The user is required to enter the name of the output file, dishcharge, and the factors: peak concentration, mean traveltime, and standard deviation of traveltime.

Standardized time and concentration are input by the program from columns 2-10 and 12-20, respectively, of the input file. Equations 20 and 21 are used. The input file is assumed to have the file name “SIMULATE.DAT”. Typically, this file would contain the coordinates for the representative, dimensionless recovery curve. If desired, output from the program SCALE can also be used without modification.

The output file contains clock time, concentration, and discharge, and also contains the “sample” number and decimal time. It may be used as input to the program DYE without modification.

This is an example of executing the program SIMULATE. The file called SAMPLE.SIO is shown in Appendix C.3. The scaling factors used here were obtained from the regression relations shown in figure 15, using a discharge of 1.14 ft^3/s

```
basic
load “simulate”
ENTER NAME OF OUTPUT FILE        : sample.sio
PEAK  CONCENTRATION              : 2.25
MEAN  TRAVELTIME                 : 16.46
STD. DEVIATION OF TRAVELTIME      : 3.287
DISCHARGE (for output only)      : 1.14
FINISHED. . .
```

Output from the program SIMULATE can be plotted and evaluated, as shown in figures 17 and 18. Summary statistics for the output may immediately be calculated by using it as input for the program DYE. This is the best way to evaluate the dimensionless recovery curve as it is being adjusted to meet the design criteria.

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APPENDIX A -- Computer program DYE

A.1 -- Programming code

```
5 REM PROGRAM ‘DYE.BAS’
10 REM PC- BASIC PROGRAM TO COMPUTE DYE-TRACE CHARACTERISTICS
15 REM INPUTS CLOCK TIME, CONC., & Q
20 REM OUTPUTS NORMALIZED CONC. & LOAD, PLUS STATISTICS
25 REM
30 DEFINT I-K,M-N
35 DIM T(500), C(500), CN(500), Q(500)
40 DIM S$(500)
45 PI-4!*ATN(1!)
50 I=0
55 DAYS=0!
60 CMAX=0!
65 LMAX=0!
70 REM
75 REM EXAMPLE OF INPUT FORMAT --- DATA MUST CONFORM
80 REM FIRST LINE IS REGARDED AS THE TIME OF INJECTION & BACKGROUND CONC.
85 REM COLUMN 1 MUST CONTAIN A PERIOD TO ENSURE PROPER SPACING
90 REM . HHH MM CCCCCCC QQQQQQQ
95 REM .   10 15   .01       2.56
100 REM
105 INPUT “ENTER NAME OF INPUT FILE : “,X$
110 OPEN "I",#2,X$
115 INPUT “ENTER NAME OF OUTPUT FILE : “,Y$
120 OPEN "0",#3,Y$
125 ISC=1
130 INPUT “SCALE THE OUTPUT? 0= NO   1= YES : “,ISC
135 IF ISC=1 THEN INPUT “ ENTER PEAK NORM. CONCENTRATION : “,SCPEAK
140 INPUT “ENTER DISTANCE TRAVELED, IN FEET : “,X
145 REM
150 REM READ INPUT FILE, ADJUST FOR BACKGROUND
155 REM CONTINUE
160 IF EOF(2) THEN GOTO 250
165 INPUT#2 ,STIN$
170 TH=VAL(MID$(STIN$,3,3))
175 TM=VAL(MID$(STIN$,7,2))
180 CC=VAL(MID$(STIN$,10,7))
185 QQ=VAL(MID$(STIN$,18,7))
190 REM TH-HOURS, TM-MINUTES, CC-CONCENTRATION, QQ-DISCHARGE
195 IF TM<0 OR QQ<.01 GOTO 155
200 I=I+1
205 IF I=1 THEN BACK=CC : BEG=TH+(TM/60) ELSE IF THLAG>TH THEN DAYS=DAYS+l
210 REM ADD 24 HOURS IF CLOCK RESETS AT MIDNIGHT
215 T(I)=TH+(TM/60)-BEG+(DAYS*24)
220 C(I)=CC-BACK
225 Q(I)=QQ
230 S$(I)==MID$(STIN$,1,24)
235 IF C(I)>CMAX THEN CMAX=C(I) : TPEAK=T(I)
240 THLAG=TH
245 GOTO 155
```

```
250 REM CONTINUE
255 REM COMPUTE DYE RECOVERY FOR EACH INTERVAL
260 TOTAL-0
265 K=I-1
270 FOR J=1 TO K
275 DT=T(J+1)-T(J)
280  CCC=(C(J+1)+C(J))/2
285  QQQ=(Q(J+1)+Q(J))/2
290  TOTAL=TOTAL+CCC*QQQ*DT
295 NEXT J
300 REM TOTAL = GRAMS RECOVERED
305  TOTAL=TOTAL*28.316*3600*.000001
310 REM
315 REM COMPUTE SCALING FACTOR
320 IF ISC=l THEN SCAL-SCPEAK/(CMAX/TOTAL) ELSE SCAL=l!
325 PRINT#3, “   TIME    CONC     Q    OBS   TIME C-BACK NORM C NORM L“
330 PRINT#3, “   hh mm   ug/L   ft3/s       hours   ug/L   mg/L/kg mg/s/kg”
335 PRINT#3, “ “
340 CPEAK=0!
345 PEAKL=0!
350 REM
355 REM COMPUTE NORMALIZED CONCENTRATION AND LOAD FOR EACH SAMPLE
360 REM CN(J) IS NORMALIZED TO MG/L/KG INJECTED
365 REM CADJ = C(J) * INJECTED/RECOVERY
370 REM CADJ IS NOT USED OR COMPUTED IN THIS PROGRAM
375 REM CN(J) = CADJ/INJECTED = C(J)/RECOVERED
380 REM
385 FOR J=1 TO I
390 CN(J)=C(J)/TOTAL *SCAL
395 IF CN(J)>CPEAK THEN CPEAK=CN(J)
400  CLOAD=CN(J)*Q(J)*28.316
405 IF CLOAD>PEAKL THEN PEAKL=CLOAD
410 PRINT#3, S$(J) TAB(25);
415 PRINT#3, USING” ###";J;
420 PRINT#3, USING” ###.##";T(J);
425 PRINT#3, USING” ###.###";C(J);CN(J);CLOAD
430 NEXT J
435 REM
440 TTOT=0                  : REM SUM OF TIME
445 QTOT=0                  : REM SUM OF DISCHARGE
450 CTOT=0                  : REM SUM OF WEIGHTS
455 TCTOT=0                 : REM SUM FOR FIRST MOMENT OF TIME
460 TTCTOT=0                : REM SUM FOR SECOND MOMENT OF TIME
465 TTTCTOT=0               : REM SUM FOR THIRD MOMENT OF TIME
470 REM SUMMATIONS USING MEAN VALUES FOR EACH INTERVAL
475 FOR J=1 TO K
480 DT=T(J+1)-T(J)
485  CCC=(C(J+1)+C(J))/2
490  TIME=(T(J+1)+T(J))/2
```

```
495 QQQ=(Q(J+1)+Q(J))/2
500 WEIGHT=CCC*QQQ*DT
505 TTOT=TTOT+ DT
510 QTOT=QTOT+ DT*QQQ
515 CTOT=CTOT+ WEIGHT
520 TCTOT=TCTOT+ TIME*WEIGHT
525 TTCTOT=TTCTOT+ TIME*TIME*WEIGHT
530 TTTCTOT=TTTCTOT+ TIME*TIME*TIME*WEIGHT
535 REM PRINT J,DT,CCC,TIME,QQQ,CTOT,TCTOT,TTCTOT,TTTCTOT
540 NEXT J
545 REM
550 REM COMPUTE STATISTICS
555 QBAR=QTOT/TTOT
560 TBAR=TCTOT/CTOT
565 SECBAR=TBAR*3600
570 TVAR=(TTCTOT/CTOT)-TBAR*TBAR
575 SECVAR=TVAR*3600*3600
580 TDEV=TVAR^,5
585 TSKEW=(TTTCTOT/CTOT)-3*TBAR*(TTCTOT/CTOT)+2*TBAR*TBAR*TBAR
590 TSKEWC=TSKEW/(TDEV*TDEV*TDEV)
595 TCV=TDEV/TBAR
600 U=X/SECBAR
605 D1-.5*U*U*SECVAR/SECBAR
610 AA=Q(I)/U
615 D2-346400!/(4*PI*TPEAK*((CPEAK/SCAL)*AA)^2)
620 PRINT#3, " " :   PRINT#3, " "
625 PRINT#3, "DISTANCE (feet)          ";
630 PRINT#3, USING"#########.##";X
635 PRINT#3, "TOTAL RECOVERED (grams)     ";
640 PRINT#3, USING"####.###";TOTAL
645 IF ISC <>1 THEN GOTO 660
650 PRINT#3, "SCALING FOR NORMALIZED VALUES   ";
655 PRINT#3, USING"####.###";SCAL
660 PRINT#3, "MEAN DISCHARGE (ft³/s)     ";
665 PRINT#3, USING"####.###";QBAR
670 PRINT#3, "TIME TO CENTROID OF MASS (hours)   ";
675 PRINT#3, USING"####.###";TBAR
680 PRINT#3, "TIME TO PEAK (hours)      ";
685 PRINT#3, USING"####.###";TPEAK
690 PRINT#3, "STD. DEVIATION OF TIME (hours)   ";
695 PRINT#3, USING"####.###";TDEV
700 PRINT#3, "PEAK NORM. CONC. (mg/L/kg)    ";
705 PRINT#3, USING"####.###";CPEAK
710 PRINT#3, "PEAK NORM. LOAD (mg/s/kg)    ";
715 PRINT#3, USING"####.###";PEAKL
720 PRINT#3, "VELOCITY (ft/s)         ";
725 PRINT#3, USING"####.###";U
730 PRINT#3, "DISPERSION COEFF. (D1) (ft²/s)   ";
735 PRINT#3, USING"####.###";Dl
```

```
740 PRINT#3, "DISPERSION COEFF.  (D2) (ft²/s) ";
745 PRINT#3, USING"####.###";D2
750 PRINT#3, "SKEWNESS  COEFFICIENT       ";
755 PRINT#3, USING"####.###";TSKEWC
760 PRINT#3, "COEFF. OF VARIATION        ";
765 PRINT#3, USING"####.###";TCV
770 CLOSE #2
775 CLOSE #3
780 PRINT "FINISHED....."
```

```
. 10 15 0.010   1.140                                    This file
. 21 45 0.010   1.140                                    is called
. 22 15 0.060   1.140                                    SAMPLE.DYI
. 22 45 0.500   1.140
. 23 15 1.320   1.140
. 23 45 2.050   1.140
.     15 3.900   1.140
.     45 4.200   1.140
.  1 15 4.200   1.140
.  1 45 3.400   1.140
.  2 15 3.050   1.140
.  2 45 2.450   1.140
.  3 15 2.000   1.140
.  3 45 1.500   1.140
.  4 15 1.200   1.140
.  4 45 0.950   1.140
.  5 15 0.800   1.140
.  5 45 0.600   1.140
.  6 15 0.550   1.140
.  6 45 0.500   1.140
.  7 15 0.420   1.140
.  7 45 0.370   1.140
.  8 15 0.350   1.140
.  8 45 0.300   1.140
. 13 45 0.200   1.140
. 22 45 0.010   1.140
```

APPENDIX A -- Computer program DYE

A.3 -- Sample of output

```
   TIME    CONC      Q     OBS   TIME   C - BACK  NORM C  NORM L       This file
   hh mm   µg/L   ft³/s          hours   µg/L    mg/L/kg  mg/s/kg      is called
                                                                       SAMPLE.DYO
.  10 15  0.010   1.140    1   0.00    0.000    0.000    0.000
.  21 45  0.010   1.140    2  11.50    0.000    0.000    0.000
.  22 15  0.060   1.140    3  12.00    0.050    0.022    0.723
.  22 45  0.500   1.140    4  12.50    0.490    0.220    7.086
.  23 15  1.320   1.140    5  13.00    1.310    0.587   18.945
.  23 45  2.050   1.140    6  13.50    2.040    0.914   29.502
.     15  3.900   1.140    7  14.00    3.890    1.743   56.257
.     45  4.200   1.140    8  14.50    4.190    1.877   60.596
.   1 15  4.200   1.140    9  15.00    4.190    1.877   60.596
.   1 45  3.400   1.140   10  15.50    3.390    1.519   49.026
.   2 15  3.050   1.140   11  16.00    3.040    1.362   43.964
.   2 45  2.450   1.140   12  16.50    2.440    1.093   35.287
.   3 15  2.000   1.140   13  17.00    1.990    0.892   28.779
.   3 45  1.500   1.140   14  17.50    1.490    0.668   21.548
.   4 15  1.200   1.140   15  18.00    1.190    0.533   17.210
.   4 45  0.950   1.140   16  18.50    0.940    0.421   13.594
.   5 15  0.800   1.140   17  19.00    0.790    0.354   11.425
.   5 45  0.600   1.140   18  19.50    0.590    0.264    8.533
.   6 15  0.550   1.140   19  20.00    0.540    0.242    7.809
.   6 45  0.500   1.140   20  20.50    0.490    0.220    7.086
.   7 15  0.420   1.140   21  21.00    0.410    0.184    5.929
.   7 45  0.370   1.140   22  21.50    0.360    0.161    5.206
.   8 15  0.350   1.140   23  22.00    0.340    0.152    4.917
.   8 45  0.300   1.140   24  22.50    0.290    0.130    4.194
.  13 45  0.200   1.140   25  27.50    0.190    0.085    2.748
.  22 45  0.010   1.140   26  36.50    0.000    0.000    0.000


DISTANCE (feet)                         3000.00
TOTAL RECOVERED (grams)                    2.232
MEAN DISCHARGE (ft³/s)                     1.140
TIME TO CENTROID OF MASS (hours)          17.146
TIME TO PEAK (hours)                      14.500
STD. DEVIATION OF TIME (hours)             4.370
PEAK NORM. CONC. (mg/L/kg)                 1.877
PEAK NORM. LOAD   (mg/s/kg)               60.596
VELOCITY (ft/s)                            0.049
DISPERSION COEFF.   (D1) (ft²/s)           4.737
DISPERSION COEFF.   (D2) (ft²/s)           0.981
SKEWNESS COEFFICIENT                       1.998
COEFF. OF VARIATION                        0.255
```

APPENDIX B -- Computer program SCALE

B.1 -- Programming code

```
5 REM PROGRAM ‘SCALE.BAS’
10 REM PC- BASIC PROGRAM TO SCALE DATA SO THAT OUTPUT WILL
15 REM    HAVE PEAK=1, MEAN=0, AND STD=1
20 REM READS TIME & NORMALIZED CONC. FROM DYE PROGRAM’S OUTPUT FILE,
25 REM    BUT REMEMBER TO STRIP AWAY COLUMN HEADINGS, ETC. FIRST
30 REM OUTPUT FROM THIS PROGRAM IS IN THE SAME FORMAT AS THE INPUT TO
35 REM    THE ‘SIMULATE’ PROGRAM
40 DEFINT I-N
45 INPUT "ENTER NAME OF INPUT FILE :  ",X$
50 INPUT "ENTER NAME OF OUTPUT FILE :  ",Y$
55 OPEN "I",#2,X$
60 OPEN "O",#3,Y$
65 INPUT "PEAK NORMALIZED CONCENTRATION :  ",CP
70 INPUT "MEAN TRAVELTIME        :  ",TBAR
75 INPUT "STD. DEVIATION OF TRAVELTIME : ",STD
80 REM CONTINUE
85 IF EOF(2) GOTO 125
90 INPUT #2, S$
95 CIN= VAL(MID$(S$,45,7))
100 TIN= VAL(MID$(S$,30,6))
105 C= CIN/CP
110 T= (TIN-TBAR)/STD
115 PRINT #3, USING "###.#####"; T; C
120 GOTO 80
125 REM CONTINUE
130 CLOSE #2
135 CLOSE #3
140 PRINT "FINISHED . . . . ."
```

APPENDIX B -- Computer program SCALE
B.2 -- Sample of input

```
. 10 15  0.010   1.140    1  0.00   0.000   0.000    0.000
. 21 45  0.010   1.140    2 11.50   0.000   0.000    0.000
. 22 15  0.060   1.140    3 12.00   0.050   0.022    0.723
. 22 45  0.500   1.140    4 12.50   0.490   0.220    7.086
. 23 15  1.320   1.140    5 13.00   1.310   0.587   18.945
. 23 45  2.050   1.140    6 13.50   2.040   0.914   29.502
.    15  3.900   1.140    7 14.00   3.890   1.743   56.257
.    45  4.200   1.140    8 14.50   4.190   1.877   60.596
.  1 15  4.200   1.140    9 15.00   4.190   1.877   60.596
.  1 45  3.400   1.140   10 15.50   3.390   1.519   49.026
.  2 15  3.050   1.140   11 16.00   3.040   1.362   43.964
.  2 45  2.450   1.140   12 16.50   2.440   1.093   35.287
.  3 15  2.000   1.140   13 17.00   1.990   0.892   28.779
.  3 45  1.500   1 140   14 17.50   1.490   0.668   21.548
.  4 15  1.200   1.140   15 18.00   1.190   0.533   17.210
.  4 45  0.950   1.140   16 18.50   0.940   0.421   13.594
.  5 15  0.800   1.140   17 19.00   0.790   0.354   11.425
.  5 45  0.600   1.140   18 19.50   0.590   0.264    8.533
.  6 15  0.550   1.140   19 20.00   0.540   0.242    7.809
.  6 45  0.500   1.140   20 20.50   0.490   0.220    7.086
.  7 15  0.420   1.140   21 21.00   0.410   0.184    5.929
.  7 45  0.370   1.140   22 21.50   0.360   0.161    5.206
.  8 15  0.350   1.140   23 22.00   0.340   0.152    4.917
.  8 45  0.300   1.140   24 22.50   0.290   0.130    4.194
. 13 45  0.200   1.140   25 27.50   0.190   0.085    2.748
. 22 45  0.010   1.140   26 36.50   0.000   0.000    0.000
```

This file
is called
SAMPLE.SCI

APPENDIX B -- Computer program SCALE
B.3 -- Sample of output

```
-3.92357   0.00000
-1.29199   0.00000
-1.17757   0.01172
-1.06316   0.11721
-0.94874   0.31273
-0.83432   0.48695
-0.71991   0.92861
-0.60549   1.00000
-0.49108   1.00000
-0.37666   0.80927
-0.26224   0.72563
-0.14783   0.58231
-0.03341   0.47523
 0.08101   0.35589
 0.19542   0.28396
 0.30984   0.22429
 0.42426   0.18860
 0.53867   0.14065
 0.65309   0.12893
 0.76751   0.11721
 0.88192   0.09803
 0.99634   0.08578
 1.11076   0.08098
 1.22517   0.06926
 2.36934   0.04529
 4.42883   0.00000
```

This file
is called
SAMPLE.SCO

APPENDIX C -- Computer program SIMULATE

C.1 -- Programming code

```
5 REM PROGRAM ‘SIMULATE.BAS’
10 REM PC- BASIC PROGRAM TO SIMULATE DYE-TRACE DATA FROM
15 REM    A STANDARDIZED CURVE
20 REM THE PROGRAM ASSUMES THAT THE INPUT DATA IS ON THE FILE ‘SIMULAT.DAT’
25 REM OUTPUT FROM THIS PROGRAM CAN BE USED AS INPUT TO THE ‘DYE’ PROGRAM
30 DEFINT I-N
35 INPUT "ENTER NAME OF OUTPUT FILE : ",Y$
40 OPEN "I", #2,"SIMULATE.DAT"
45 OPEN "O",#3,Y$
50 INPUT "PEAK CONCENTRATION : ",CP
55 INPUT "MEAN TRAVELTIME : ",TBAR
60 INPUT "STD. DEV. OF TRAVELTIME : ",STD
65 INPUT "DISCHARGE (for output only) : ",Q
70 PRINT #3, ".  0  0  0.000";
75 PRINT #3, USING "###.###";Q;
80 PRINT #3, "  1  0.00"
85 I=1
90 REM CONTINUE
95 IF EOF(2) THEN GOTO 170
100 INPUT#2, TIN,CIN
105 I=I+1
110 C= CIN*CP
115 T= TBAR +TIN*STD
120 IHR=INT(T)
125 FRAC=T-IHR
130 IMIN=FRAC*60 +.5
135 IF IMIN =>60 THEN IHR=IHR+1 : IMIN=IMIN-60
140 PRINT #3, ". ";
145 PRINT #3, USING "###"; IHR;IMIN;
150 PRINT #3, USING " ###.###"; C;Q;
155 PRINT #3, USING " ###"; I;
160 PRINT #3, USING " ###.##"; T
165 GOTO 90
170 REM CONTINUE
175 CLOSE #2
180 CLOSE #3
185 PRINT "FINISHED. . . . . "
```

APPENDIX C -- Computer program SIMULATE

C.2 -- Sample of input

This file
is called
SIMULATE.DAT

```
-1.73200   0.00000
-1.65482   0.00344
-1.59544   0.00663
-1.53723   0.01009
-1.47426   0.01650
-1.41342   0.02792
-1.34895   0.04447
-1.29280   0.05966
-1.23160   0.08767
-1.17368   0.12800
-1.11610   0.19577
-1.07168   0.26170
-1.00689   0.38133
-0.94844   0.49700
-0.89185   0.62070
-0.85594   0.71164
-0.81937   0.79504
-0.76230   0.89150
-0.71937   0.94598
-0.69300   0.96831
-0.66626   0.98136
-0.63871   0.99169
-0.60658   0.99601
-0.58038   0.99940
-0.54700   1.00000
-0.50805   0.99941
-0.47257   0.99555
-0.43956   0.98841
-0.41139   0.97665
-0.35554   0.93566
-0.30576   0.88924
-0.26539   0.84527
-0.22400   0.79693
-0.15661   0.73000
-0.07825   0.65412
-0.01571   0.59677
 0.03057   0.55198
 0.07120   0.51865
 0.13532   0.47602
 0.20188   0.43611
 0.26964   0.39702
 0.33400   0.36339
 0.39976   0.33500
 0.47735   0.30700
 0.57371   0.27050
 0.66184   0.24400
 0.76068   0.21690
 0.88085   0.18647
```

APPENDIX C -- Computer program SIMULATE--Continued

C.2 -- Sample of input

```
 1.03891   0.15325
 1.23134   0.11917
 1.44169   0.09025
 1.62979   0.07199
 1.84284   0.05533
 2.03238   0.04716
 2.44606   0.03650
 2.92505   0.02800
 3.55459   0.02100
 4.16994   0.01600
 4.73544   0.00900
 5.37800   0.00000
```

C.3 -- Sample of output

This file
is called
SAMPLE.SI0

```
.  0  0  0.000  1.140   1   0.00
. 10 46  0.000  1.140   2  10.76
. 11  1  0.008  1.140   3  11.02
. 11 13  0.015  1.140   4  11.21
. 11 25  0.023  1.140   5  11.40
. 11 37  0.037  1.140   6  11.61
. 11 49  0.063  1.140   7  11.81
. 12  2  0.100  1.140   8  12.02
. 12 13  0.134  1.140   9  12.21
. 12 25  0.197  1.140  10  12.41
. 12 36  0.288  1.140  11  12.60
. 12 48  0.440  1.140  12  12.79
. 12 57  0.589  1.140  13  12.93
. 13  9  0.858  1.140  14  13.15
. 13 21  1.118  1.140  15  13.34
. 13 32  1.397  1.140  16  13.52
. 13 39  1.601  1.140  17  13.64
. 13 46  1.789  1.140  18  13.76
. 13 58  2.006  1.140  19  13.95
. 14  6  2.128  1.140  20  14.09
. 14 11  2.179  1.140  21  14.18
. 14 16  2.208  1.140  22  14.27
. 14 22  2.231  1.140  23  14.36
. 14 28  2.241  1.140  24  14.46
. 14 33  2.249  1.140  25  14.55
. 14 40  2.250  1.140  26  14.66
. 14 48  2.249  1.140  27  14.79
. 14 55  2.240  1.140  28  14.90
. 15  1  2.224  1.140  29  15.01
. 15  7  2.197  1.140  30  15.10
. 15 18  2.105  1.140  31  15.29
. 15 28  2.001  1.140  32  15.45
. 15 36  1.902  1.140  33  15.58
. 15 44  1.793  1.140  34  15.72
. 15 57  1.643  1.140  35  15.94
. 16 12  1.472  1.140  36  16.20
. 16 25  1.343  1.140  37  16.40
. 16 34  1.242  1.140  38  16.56
. 16 42  1.167  1.140  39  16.69
. 16 55  1.071  1.140  40  16.90
. 17  8  0.981  1.140  41  17.12
. 17 21  0.893  1.140  42  17.34
. 17 34  0.818  1.140  43  17.55
. 17 47  0.754  1.140  44  17.77
. 18  2  0.691  1.140  45  18.03
. 18 21  0.609  1.140  46  18.34
. 18 38  0.549  1.140  47  18.63
. 18 58  0.488  1.140  48  18.96
```

C.3 -- Sample of output

```
. 19 22   0.420   1.140  49 19.35
. 19 53   0.345   1.140  50 19.87
. 20 31   0.268   1.140  51 20.50
. 21 12   0.203   1.140  52 21.19
. 21 49   0.162   1.140  53 21.81
. 22 31   0.124   1.140  54 22.51
. 23  9   0.106   1.140  55 23.14
. 24 30   0.082   1.140  56 24.50
. 26  5   0.063   1.140  57 26.07
. 28  9   0.047   1.140  58 28.14
. 30 10   0.036   1.140  59 30.16
. 32  2   0.020   1.140  60 32.02
. 34  9   0.000   1.140  61 34.13
```

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