CHAPTER 8

Tracer techniques

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8.1 INTRODUCTION

Investigation of the origin, movement and destination of groundwater is a fundamental goal of hydrogeology where groundwater trajectories and catchments are not immediately apparent. Tracing is a powerful tool for such investigations, particularly in karst areas. In hydrogeology, a tracer is any type of substance in the water or property of the water that can be used to obtain information on the groundwater flow and transport of matter.

Initially, convenient, but inappropriate tracers such as chaff and sawdust were used, until the invention of uranine in 1871 provided the first powerful, safe, water-soluble tracer dye. The first quantitative tracer test was carried out in 1877, when uranine, salt and shale oil were injected into the sink of the Danube River in the karst of the Swabian Alb, Germany, and reappeared two days later at the Aach spring, over 12 km away (Knop 1878). Although most tracer tests involve deliberate addition of tracers, sometimes traces occur accidentally. For example, a fire at a chemical warehouse in Basel, Switzerland, in 1986, released 2.6 tons of rhodamine pigments into the River Rhine. The tracer was detected 14 days later over 700 km downstream (Schmitz 1989, Suijlen et al. 1994). In 1909, an early radioactive trace was made using 38 kg of uranium oxide ore to link the River Reka in the Slovenian karst with the Timavo springs at the Adriatic coast (Vortmann & Timeus 1910). Increasing concern over the environment and health has virtually eliminated radioactive tracing today.

Today, several professional and scientific organisations work on water tracing, such as the Association of Tracer Hydrology (ATH) and the International Committee on Tracers (ICT) of the International Association of Hydrological Sciences (IAHS). Several IAHS publications (Gaspar 1987a,b, Peters et al. 1993, Leibundgut et al. 1995, Dassargues 2000) deal with water tracing. Also the IAH has published several edited volumes on karst including tracing (LaMoreaux et al. 1989, 1993, Paloc & Back 1992). Käss (1998, 2004) provides excellent texts on tracing in hydrogeology, including karst (Hötzl 1998).

Natural or environmental tracers are those that occur without intervention by the investigator, including natural substances (e.g. ionic composition, stable isotopes of water), anthropogenic contaminants (e.g. chlorinated organic solvents, road salt, nuclear bomb tritium) and physical properties (e.g. temperature). Artificial tracers are those injected or induced by the investigator, for example fluorescent dyes, soluble salts or even flood impulses. Natural hydrochemical and isotopic tracers are discussed in chapters 6 and 7 respectively, while this chapter focuses on artificial tracing.

A basic tracer test consists of placing a tracer into a stream and then monitoring for the tracer downstream. In karst, tracers are often injected into sinking streams, and then springs are monitored to identify underground connections, define spring catchments, localise groundwater divides and define the geometry, morphology and hydraulics of the conduit. More sophisticated tracer analysis allows derivation of hydrogeological data for the parameterisation and calibration of groundwater flow and transport models. Tracer tests are also used to simulate the transport, fate and attenuation of different types of contaminants both in the unsaturated and saturated zone.

A multi-tracer test is where several distinctive tracers are injected at different sites during the same experiment, allowing characterisation of several underground connections under particular conditions. In a comparative tracer test, several different substances are simultaneously injected at the same site, allowing comparison of the fate and transport of different tracers in order to gain knowledge either about the tracers or the geochemical system. Serial tracer tests are used to study changes in aquifer links over time. The use of intermediate points in the karst system as sampling or injection sites, such as dripping points in caves, underground streams or observation wells, makes it possible to better characterise water movement and contaminant transport in different parts of the system.

A tracer test requires preliminary investigations to determine possible groundwater linkages, including a search for published and unpublished information and field research. Legal restrictions and requirements and socio-economic aspects need to be considered as well. Ethically, a tracer test should have the lowest environmental and aesthetic impact.

8.2 TYPES OF ARTIFICIAL TRACERS

8.2.1 Overview

There are many types of tracers reviewed by Käss (1998). This chapter focuses on the most important tracers, summarised in Tab. 8.1. Water tracers for the movement of groundwater are ideally conservative in that they should be stable in the environment and not interact with the aquifer. The "ideal conservative tracer" is a substance that is unreactive, is absent from but readily soluble in water, easy to detect quantitatively, non-toxic, invisible, inexpensive, and easy to handle (Käss 1998). Fluorescent dyes are the most practical and widely used tracers because many are reasonably conservative, safe, inexpensive and highly detectable. Oxygen-18 and Deuterium might be considered ideal tracers, as they are part of the water molecule. However, these isotopes are expensive to obtain and analyse and so are rarely used as artificial tracers. Reactive tracers can be used to simulate the transport of contaminants and are acted on by processes such as adsorption, oxidation or filtration.

Two types of artificial water tracers are used: water-soluble substances and particles. Fluorescent dyes and salts are the most widely used water-soluble tracers. Radioactive tracers have extremely low background concentrations and detection limits, but have high analytical cost, demanding safety requirements and stringent legal restrictions (Behrens 1998); they are thus not considered here. Neutron activated stable isotopes are less constrained, but require irradiation for analysis. Particulate tracers simulate the transport of pathogens.

8.2.2 Fluorescent dyes

Many natural and synthetic organic substances that contain aromatic functional groups (carbon ring structures) are fluorescent; they absorb light at certain wavelengths (absorption,

Table 8.1. Properties of the most important groundwater tracers. The detection limits for fluorescent dyes represent an order of magnitude and are valid for clean waters and a modern spectral fluorimeter. The limits for salts strongly depend on the analytical method. The toxicological evaluation is based on Behrens et al. (2001).

	No.	Tracer	Detection limit (μg/L)	Natural background	Toxicology	Analytical interference with	Other specific problems
Fluorescent dyes	1	Uranine	10^{-3}	Absent	Safe	2, 6	Strong sorption at low pH
	2	Eosin	10^{-2}	Absent	Safe	1, 4	Very sensitive to light
	3	Sulforhodamine B	10^{-2}	Absent	Ecotox. unsafe	4, 5	
	4	Amidorhodamine G	10^{-2}	Absent	Safe	2, 3, 5	
	5	Rhodamine WT	10^{-2}	Absent	Genotoxic	3, 4	
	6	Pyranine	10^{-2}	Absent	Safe	1, 2	Not reliable (degradation)
	7	Naphthionate	10^{-1}	Absent	Safe	8, DOC	
	8	Tinopal	10^{-1}	Absent	Safe	7, DOC	Strong sorption
Salts	9	Sodium	*Dependent*	High	Safe	–	
	10	Potassium	*on method:*	Moderate	Safe	–	
	11	Lithium	*0.1 μg/L*	Very low	Safe with restr.	–	
	12	Strontium	*to 1 mg/L*	Moderate	Safe with restr.	–	Strong sorption
	13	Chloride		High	Safe with restr.	–	
	14	Bromide		Low	Safe with restr.	–	
	15	Iodide		Very low	(Not evaluated)	–	Chemically unstable
Particles	16	Dyed spores	*Detection*	Absent	Safe	Natural particles	Not quantitative
	17	Microspheres	*of single*	Absent	Safe	Natural particles	Time-consuming analysis
	18	Specific bacteria	*particles*	Absent	(Not evaluated)	(Other bacteria)	Time-consuming analysis
	19	Bacteriophages		Absent	(Not evaluated)	–	Time-consuming analysis

excitation or extinction) and re-emit light at higher wavelengths (fluorescence or emission). Some fluorescent dyes are excellent groundwater tracers and come close to the definition of an ideal tracer; they are commonly absent in natural waters, have a low detection limit, are highly water-soluble, non-toxic, relatively inexpensive and easy to handle. Most fluorescent dyes can be detected instrumentally at concentrations up to 1000 times less than the threshold for visual detection, allowing quantitative tracing at subvisible levels. Some fluorescent dyes breakdown in sunlight, or through microbial decay. While constraining test and sample duration, this also limits their environmental persistence.

The same dye manufactured by different companies or sold in different countries may have different names. In the following, only the most widely used names and synonyms, and (if available) the Chemical Abstracts Service Registry Numbers (CAS RN) are given. Dyes are also commonly referred to by their D&C and Colour Index numbers. Internet sites such as chemfinder.com may be consulted for further information and material safety data sheets.

Uranine (sodium fluorescein, CAS RN 518-47-8) is an inexpensive, safe dye with exceptionally low detection limits: $\sim$0.005 μg/L or even 0.001 μg/L under ideal conditions. The limit of quantitation is an order of magnitude higher. Uranine is visibly green above $\sim$10 μg/L, and red above $\sim$1 g/L. It is highly soluble (600 g/L at 20°C) and not harmful to humans and the environment. The uranine molecule forms a cation at pH $<$ 2, a neutral molecule at pH $<$ 5, an univalent anion at pH $<$ 7, and a bivalent anion at pH $>$ 7. The latter has the strongest fluorescence. The two anionic forms are conservative, while the neutral molecule and the cation are prone to sorption. Uranine is less suited to acid waters than to more basic karst. Uranine does not adsorb to clay minerals commonly present in karst aquifers.

Sunlight and strong oxidants, like chlorine bleach, destroy uranine, so it is not suitable for daytime use in surface waters or in chlorinated waters. Water samples should be stored cool and dark, and analysed as soon as possible in case of microbial degradation (Sayer 1991). Widespread use of uranine as a water tracer and industrial colorant for over 100 years (e.g. to label vehicle antifreeze) means that it is present in many groundwaters, especially those receiving road runoff or landfill leachate. Before carrying out a tracer test with uranine (or any other tracer), the background concentration should thus be measured.

Eosin (CAS RN 17372-87-1) is an orange coloured tracer dye. Like uranine it is highly soluble (about 300 g/L), not harmful, conservative but very sensitive to light. Its detection limit is significantly higher than for uranine, $\sim$0.05 μg/L; larger quantities are thus required. Overlapping uranine and eosin fluorescent spectra require special analytical attention (see section 8.3.5). Eosin is preferred in acid waters, when uranine cannot be used.

Rhodamines are a large group of chemically similar red fluorescent dyes, some of which are favourable tracers, while others are toxic and should not be used. The nomenclature is confusing, as there are often many synonyms for one dye. For example: Amidorhodamine G, Sulforhodamine G and Amidorhodamine BG are synonyms for the same dye. Rhodamine B (CAS RN 81-88-9), Rhodamine WT (CAS RN 37299-86-8), Rhodamine 6G (CAS RN 989-38-8) and Rhodamine 3G (CAS RN 3262-60-6) are not recommended for water tracing because of their toxicity and/or strong sorption properties (Käss 1998, Behrens et al. 2001).

Sulforhodamine B (CAS RN 3520-42-1) and Amidorhodamine G (CAS RN 5873-16-5) are less prone to adsorption. The former may be harmful to aquatic ecosystems at concentrations over 160 μg/L for an exposure period $>$48 h (Behrens et al. 2001). Rhodamine dyes absorb and emit light at higher wavelengths so can be readily distinguished from uranine and other tracers during analyses. They are also less sensitive to light and to pH than uranine.

Their detection limits are about 0.03 μg/L, and the limits of visibility are ~30 μg/L. Fluorescence of some rhodamine dyes depends quite strongly on temperature, so it is necessary either to bring samples or correct readings to a standard temperature (e.g. Smart & Laidlaw 1977).

Pyranine (CAS RN 6358-69-6) has similar fluorescence properties to uranine and is non-toxic (Benischke & Schmerlaib 1986, Behrens et al. 2001). Although the electrical charge and fluorescent properties of the pyranine molecule are highly pH-dependent, it never forms a cation and consequently shows low sorption properties. Pyranine can thus be used in acid waters, although care is necessary to ensure analysis at a standard pH. Although several successful tracer tests with pyranine are reported in the literature (Käss 1998, Reichert 1991), it cannot be considered a reliable tracer, as it often shows inexplicably low recovery (Bäumle et al. 2001, Goldscheider et al. 2001a, 2003).

Naphthionate (sodium-naphthionate, CAS RN 130-13-2) is a safe, non-adsorbent, ultraviolet-blue fluorescent dye that is invisible at concentrations <1 g/L. Naphthionate has a detection limit of ~0.1 μg/L, so that large injection masses are required. Although it has no interference with red and green dyes during analysis (Wernli 1986), it fluoresces at the same wavelengths as dissolved organic carbon (DOC), which limits the use of this tracer. Microbial decay of naphthionate has been observed (Goldscheider et al. 2001b), so samples should be stored cool and analysed shortly after sampling.

Tinopal CBS-X (CAS RN 27344-41-8) is another ultraviolet-blue dye frequently used as a tracer, but it is strongly adsorbed on clay so that recovery is often low with significant retardation. Tinopal is not recommended for acid groundwaters although in well-developed conduit systems, it can be used over long distances (Käss 1998).

8.2.3 Salts

A number of salts have also been used as tracers (Käss 1998). Salts dissolve in water into anions and cations, thereby increasing the specific electrical conductivity (EC). Most anions are conservative tracers because they show low sorption properties. In contrast, cations are prone to ion exchange (reactive tracers). The sorption strength of cations increases in the order of: $Li^+ < Na^+ < K^+ < Mg^{2+} < Ca^{2+} < Sr^{2+}$. Lithium salts are thus perferred as tracers.

Most salts have higher detection limit, background concentrations and variability in natural waters than fluorescent dyes. Higher injection masses are thus required, possibly resulting in concentrations that may be harmful near the injection point. Most salts do not cause visible colouring, are stable in light and resist microbial degradation. Salts show little analytical interference with fluorescent dyes and can be used in combined tracer tests.

Sodium chloride (NaCl) or common salt is very inexpensive, widely available, highly soluble and relatively safe. It dissolves into the sodium cation (Na^+) and the chloride anion (Cl^-), both of which can be analysed for as tracers. However, salt traces on relatively short distances are most conveniently monitored using electrical conductivity. As the analytical detection limits and natural background concentrations are relatively high, large, possibly harmful injection quantities are required.

Lithium is generally used as lithium chloride. It has low sorption properties and is the most mobile cation. The analytical detection limit is low (0.1 μg/L) and the natural background concentrations in karst groundwater are also low, often <1 μg/L (Käss 1998). Lithium salts are toxicologically "safe with restriction" (Behrens et al. 2001). Lithium has been

successfully used for tracer tests in karst and chalk aquifers (Behrens et al. 1992, Witthüser et al. 2003).

Potassium shows a slightly higher tendency to adsorption than sodium but occurs at lower background levels in natural groundwater. Lower injection amounts are thus required. The most commonly used potassium salt is KCl, which is highly soluble and toxicologically safe.

Strontium is safe, although a limit of 15 mg/L is recommended for drinking water (Behrens et al. 2001). Strontium chloride hexahydrate ($SrCl_2 \cdot 6H_2O$) is most often used for tracer tests. Traces of strontium are present in all type of groundwater, $\sim$40 µg/L in carbonates and >15 mg/L in gypsum (Käss 1998). Strontium adsorbs strongly and is most suitable for use in well-developed karst conduit systems, although it can also be used as an analogue for the transport of reactive heavy metals.

Bromide has little tendency to sorption and precipitation, and is chemically and microbiologically stable. The natural background concentrations in groundwater are 100 to 1000 times lower than Chloride, typically <0.1mg/L (Matthess 1994, Käss 1998). On the other hand, bromide analysis is relatively time-consuming and the detection limits are relatively high using ion sensitive electrodes ($\sim$50 µg/L) and ion chromatography ($\sim$15 µg/L). Bromide is toxicologically "safe with restrictions". In organic-rich waters or oxidising water purification systems it can be transformed into cancerous bromates and organo-bromides (Behrens et al. 2001).

Iodide occurs at even lower background concentrations in natural groundwater than bromide, often <10 µg/L (Matthess 1994). In contrast to chloride and bromide, it is chemically and microbiologically reactive. Iodide is thus not recommended for long transit times, and for tracer tests in groundwater with high dissolved organic carbon concentrations.

8.2.4 Particulate tracers

Natural particles in water comprise mineral and organic matter, and microorganisms (Atteia & Kozel 1997). Particles <1 µm are classified as colloids. Contaminants, such as heavy metals and radioisotopes are often transported adsorbed to particles and colloids. Viruses and small bacteria are <1 µm, large bacteria and most protozoans are >1 µm and are also commonly clustered in particle aggregations known as flocs. Particle tracers provide analogues for microbial pathogens, common contaminants of karst groundwater (Auckenthaler et al. 2002, Auckenthaler & Huggenberger 2003). Their limited analytical interference with other tracers makes them useful in multi-tracer tests.

Clubmoss spores of *Lycopodium clavatum* have an average diameter of 33 µm. They can be relatively easily identified under the microscope, particularly if they are marked using fluorescent staining. Spores are usually collected in plankton nets and then counted under a fluorescence microscope (Käss 1998). This sampling and analysis are not well controlled, precluding development of a quantitative breakthrough curve. Early spore tracing in the Austrian Alps suggested a radial-divergent drainage pattern (Zötl 1961) since shown to be incorrect, probably because of contamination arising from handling the spores (Bauer 1989, Herlicska et al. 1995).

Fluorescent microspheres are available with different diameters (0.05–90 µm), physical-chemical characteristics (e.g. density, electrical surface charge), and optical properties (excitation/emission wavelengths), allowing various multi-tracing options. Uncharged yellow-green (458/540 nm) polystyrene spheres with a diameter of 1 µm have replaced clubmoss spores for tracing. Microspheres <1 µm can be used to simulate colloid transport.

Microspheres can be quantitatively analysed from water samples, allowing definition of a breakthrough curve. Comparative tracer tests with microspheres and water-soluble tracers in karst, fissured and porous aquifers often show that uncharged and negatively charged microspheres travel faster, possibly as particles are less likely to diffuse into the aquifer matrix (Göppert et al. 2005). Neutral and negatively charged particles have lower recovery rates than conservative water-soluble tracers, while positively charged microspheres often disappear completely, presumably due to adsorption (Behrens et al. 1992, Bäumle et al. 2001, Kennedy et al. 2001).

Bacteriophages (phages) are viruses that attack a particular host bacterium. Phages range in size from 0.02 to 0.35 μm, making them ideal for simulation of the transport of viruses. Specific phage types that naturally occur in the marine environment can be used as artificial tracers in ground- and freshwater (Rossi et al. 1998, Rossi & Käss 1998). These phages are readily produced, do not interact with other microorganisms, are safe and stable and show favourable transport properties. Phages are analysed in water samples. It is possible to detect one single phage and to distinguish phage types. They are suitable for tracer tests in large karst aquifer systems, where very high dilution is anticipated (Harvey 1997), although the analytical sensitivity also demands careful handling.

Bacteria may be suitable particulate tracers, though analysis may be difficult. The bacteria type most often used in water tracing is *Serratia marcescens*, which can be used as a model substance to study the transport of pathogenic bacteria. However, *S. marcescens* is an opportunistic human pathogen (Kurz et al. 2003) and requires care. Bacteria can also be used with other non-toxic tracers (Harvey 1997, Hötzl et al. 1991).

8.3 PREPARATION AND OPERATION OF TRACER TESTS

8.3.1 Preliminary investigations and legal aspects

Tracer tests can provide excellent information on groundwater movement and contaminant transport, but they may take many months to execute, and can fail if poorly executed. Using too little tracer, sampling the wrong springs or mistiming sampling can lead to non-detection, an undesirable, ambiguous result. Likely groundwater pathway and flow velocity can often be derived from geological, hydrological, chemical and speleological information. An inventory of sinking streams, caves and springs, along with possible flow routes indicated by geology, geomorphology and hydrology is essential in selecting appropriate injection and sampling points, design of a sampling strategy and interpretation of results.

Legal regulations for groundwater tracing tests vary with country and jurisdiction. In some cases, official permission must be requested in advance from the water authorities. In other countries (e.g. Switzerland), it is sufficient to inform the authorities and provide the outcome for the national database (Schudel et al. 2003). Proof of environmental and human safety is often of paramount importance in obtaining permission for a tracer test. Behrens et al. (2001) provide a valuable resource base on tracer safety. Regardless of legal stipulations, concerned communities, individuals and authorities are best informed in advance of a tracer test.

8.3.2 Selection of the tracer type and injection quantity

In general, tracers should be "toxicologically safe" or "safe with restrictions" (Behrens et al. 2001), have low detection limits, and show little analytical interference. The tracers should

Table 8.2. Factors k and B for the tracer mass equation (Käss 1998).

Tracer	k	Framework conditions	B
Water soluble tracers: mass [kg]		Surface streams	0.1–0.9
Uranine	1	Karst aquifers (conduits)	
Eosin	5.5	Pure sand/gravel aquifers	
Sulforhodamine B	4	Highly fissured aquifers	
Amidorhodamine G	2	Impure sand/gravel aquifers	2–4
Pyranine	5.5	Injection into groundwater	
Naphthionate	15	through unsaturated zone	
Tinopal	3	Karst aquifers (matrix),	
NaCl	20000	Poorly fissured aquifers	
LiCl	1000	River bank filtration	
KCl	10000	Turbid sampling water or	
Particle tracers: number of particles		tracer background level > 0	
Microspheres	1E+12	Injection through thick or	5–10
Bacteriophages	1E+13	loamy unsaturated zone	
Bacteria (*Serratia marcescens*)	1E+13	High clay/silt contents	

ideally be absent from the groundwater or show low background concentrations. It may be possible to use tracers with relatively high but stable background, e.g. chloride during steady flow conditions. Photosensitive fluorescent dyes (e.g. eosin) are not recommended in surface waters. When visible colouration must be avoided, naphthionate, tinopal, salts, and particle tracers can be used.

The tracer used also depends on the objectives of the experiment. For tracer tests intended to characterise the movement of groundwater or the transport of stable and mobile contaminants, conservative tracers such as uranine or eosin should be selected. In karst conduits, several additional fluorescent dyes (e.g. naphthionate, eosin), some cations (e.g. lithium, sodium) and most anions (e.g. chloride, bromide) are reasonably conservative. Tracers are less likely to behave conservatively when used in porous media, organic-rich environments like soils, or in long duration tests. Non-conservative tracers may be used to establish underground linkages, or to simulate the transport of specific contaminants. For multi-tracer tests, the more detectable and conservative tracers (e.g. uranine) should be assigned to the longer expected trajectory, the highest dilution or the most important injection point.

The optimal tracer quantity will permit clear detection at the sampling point without excess expense, unacceptable colouration and environmental loading and additional work in the laboratory. If the hydraulic and transport parameters are known, it is possible to calculate injection mass based on the advection-dispersion equation resulting in a target concentration at the sampling point (e.g. Field 2003). More commonly, the required parameters are not known, and the tracer quantity must be estimated from an empirical relationship. For example, Käss (1998) suggests:

$$M = L \cdot k \cdot B$$

where M = required tracer quantity i.e. mass [kg] for soluble tracers and number of particles for particulate tracers; L = distance to the most important sampling site [km]; k = coefficient for the tracers; and B = factor for the hydrogeological conditions (Tab. 8.2).

The target tracer concentration is not a variable in this relatively liberal approximation, so that there is some risk of visible colouration. Worthington & Smart (2003) suggest a more

Figure 8.1. Left: Injection of 1 kg of uranine from a plastic container into a karst shaft in the Hochifen-Gottesacker area, Austro-German Alps. A helicopter delivered a tank with 800 L of flushing water (Goldscheider 2005). Right: Injection of 155 kg of naphthionate, dissolved in a tank of 2000 L, into an observation well in the confined karst aquifer of the mineral springs of Stuttgart, Germany (Goldscheider et al. 2003).

adaptable formula for karst tracing including system discharge and target concentration:

$$M = 1.9 \cdot 10^{-5}(LQC)^{0.95}$$

where L is distance [km], Q is discharge [L/s], and C is target peak concentration [μg/L].

8.3.3 Selection of the injection points and injection techniques

The tracer injection point depends on the objective of the tracer test. Clarification of the conduit network in karst requires injection directly into sinking or cave streams. Hydraulic characterisation demands a discrete spike injection. Large eddies or sediments should be avoided as they can modify the input signal by retaining tracer, and influence the breakthrough. If stream injection points do not exist, tracer can be flushed into solutionally enlarged fissures, dolines and karst shafts (Fig. 8.1). Flushing should start some time before the tracer injection to establish steady infiltration, and continued for some time in order to drive the tracer to the stream. Where the karst is mantled with sediment, there may be no adequate injection point. However, the cover can be excavated to bedrock and tracer flushed into an opening proven to accept injected water. The tracer can also be injected at the land surface or into a ditch and flushed (by a stream, or rainfall, e.g. Flury & Wai 2003) through the soil and unsaturated zone towards the groundwater. The low recovery rate of such tracer tests may require greater tracer injections (see B in Tab. 8.2). The diverse flow route, tracer retention in sediment and prolonged residence time means that such experiments do not allow evaluation of hydraulic characteristics.

Wells may also serve as injection points with tracer injected through a hose (Fig. 8.1). Karst wells may sometimes provide direct access to the conduit network. More commonly the tracer may take some time to travel through the rock matrix to reach a conduit. Successful injection and interpretation of such tests requires knowledge of the hydrology of the well, e.g. depth to water table, position of the well screen(s), hydrostratigraphy, and hydraulic response of the well (Flynn et al. 2005). Natural gradient tests require injection with minimal change in well volume, but induced gradients may be required to drive tracer into adjacent conduits.

Tracing of a contaminant source requires the tracer to be introduced with the contaminant. For example, tracer can be introduced into septic tanks, sewage shafts, leaking wastewater channels or dolines and caves filled with waste.

The greater the sensitivity of tracer analysis, the greater the efforts that are required to prevent autocontamination (Smart & Karunaratne 2001) in which the water samples become accidentally contaminated with the injected tracer. The preparation and injection of tracers is best undertaken in different places, by different staff and with different materials than those used for sampling and analyses. Handling is safest when tracers are dissolved or dispersed in water well beforehand, although the resulting mass may prove difficult to handle. Powdered dyes that do not dissolve readily in cold water may be progressively moistened and worked up as a paste to prevent insoluble lumps developing. Some tracers dissolve more readily in alcohol, warm water or alkaline media, or a small quantity of detergent may aid dispersion providing that this does not compromise their performance. Injection may require protective clothing and careful clean-up and disposal.

Tracer injections can either be done instantaneously or continuously. An instantaneous injection means introducing a known quantity of tracer into the water during a minimal interval. Typically the tracer is poured from a wide-mouthed container into the stream. Such injections should result in a tracer breakthrough curve with a clear maximum. Instantaneous injections are suitable to simulate the impact of accidental contaminations on the groundwater, and allow the breakthrough curve to be analysed for hydraulic properties of the flow route. Additional equipment and tracer are required for a continuous injection where a known tracer concentration is released at a known rate into the water for a sustained period. At the sampling sites, this will result in an increase of the tracer concentration to a plateau. Continuous injections can be used to simulate chronic contamination.

8.3.4 Selection of the sampling sites and sampling techniques

Groundwater sampling sites for tracer tests in karst aquifer systems comprise springs, cave streams and pumping or observation wells. Not all springs may be accessible or identified, so stream networks can be used to integrate outflows from many springs or selected reaches of stream channel, although samples may be poorly homogenised, and tracer concentrations reduced, or even undetectable. Known springs in the bed of rivers or lakes can be sampled by drawing water through a hose anchored at the opening and extending to dry land. Drips and seeps in caves or tunnels below an injection area can be used as unsaturated zone sampling sites (e.g. Veselic et al. 2001). However, samples from wells or cave seeps are unlikely to reflect the predominant flow route, thus limiting interpretation.

The sampling strategy depends on the objectives of the tracer test, the hydrogeological environment and the resources available (Fig. 8.2). Sampling sites (where tracer is anticipated) and control sites (where it is not, e.g. upstream of tracer injection) need to be

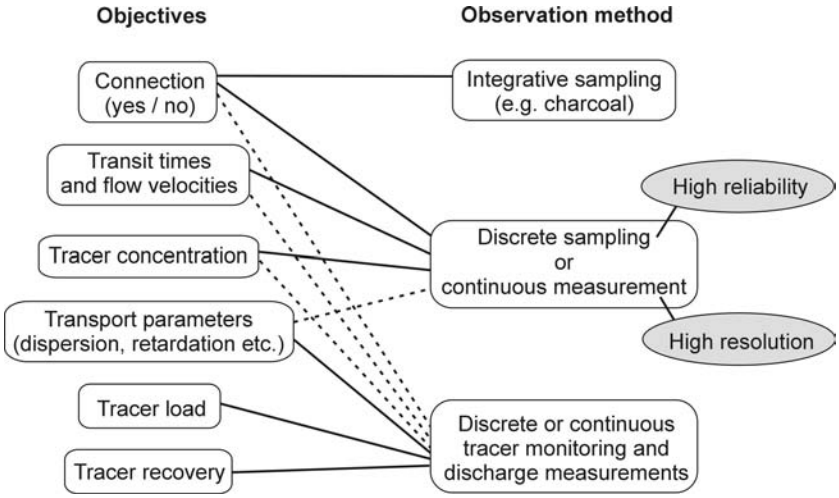

Figure 8.2. The selection of appropriate sampling methods depends on the objectives of the tracer test. Integrative sampling is sufficient to prove underground connections while the calculation of the recovery rate requires detailed discrete sampling or continuous measurement, and concurrent discharge measurements.

identified and their background fluorescence pattern established. Sampling sites are used prior to injection to established spatial background. Continued sampling at the control sites provides an indication of probable temporal variation in background during the tracer test. Simple underground pathways require relatively few sites to be sampled. More extensive multi-tracer tests require that all springs or spring groups in the region should be sampled. Proximity of springs does not necessarily indicate similarity of connection, so information from group sampling may be ambiguous. Flow paths in karst systems may be unexpectedly long, may go in unexpected directions, and may cross under topographic boundaries. Investigation of the hydraulics of a known link (e.g. travel time variations for different tracers or with discharge), requires less extensive sampling, although control is still desirable.

There are three fundamentally different sampling methods: discrete sampling, integrative sampling and continuous measurement (Fig. 8.2). Discrete (punctual or grab) sampling means collecting water samples at distinct times either manually, or using an automatic water sampler. The result allows construction of a time-concentration breakthrough curve with resolution depending on the sampling interval. In general, the shorter the travel time, the greater will be the rate of change in concentration and the necessary sampling frequency. Sampling intervals should therefore be short at the beginning, and then become progressively longer. Discrete samples can be stored in case of retrospective doubts or problems. Documented sample custody and handling history may be required for litigation. Automatic water samplers typically have 24 bottles set to be filled at preset intervals; for example, allowing daily servicing for hourly samples.

Online measurements are obtained from field fluorimeters, ion selective electrodes or conductivity cells inserted into streams and linked to data loggers. Typically, high frequency measurements (seconds) are averaged over longer time intervals (minutes), providing a real time record of tracer concentration, allowing adaptive sampling, better noise reduction and higher temporal resolution than is practical with discrete sampling. Such systems are less

prone to contamination, but samples are not retained. The data are seldom as accurate as can be obtained from laboratory analysis under controlled conditions, especially for tracers influenced by ambient conditions such as pH, temperature and background fluorescence. Online measurement is most useful for precise temporal resolution of tracer breakthrough at a limited number of sites where tracer is known to appear. Although on-line equipment is currently expensive, sampling logistics are simple once it is installed.

Integrative sampling means accumulation of tracer or water over a certain time. A common mode of integrative sampling uses granular activated charcoal or macroreticular resins to adsorb dyes (Close et al. 2002, Käss 1998). Permeable packets of a few grams can be deployed in streams over intervals of hours to days, to accumulate any fluorescent tracer that passes by. The detectors are then collected, rinsed in stream water and eluted (usually in an alkaline alcohol solution) to allow analysis. Adsorption and elution are sensitive to factors such as water chemistry, flow-through rate and timing, so that conditions must be carefully controlled. Even so, the data are generally ordinal rather than true concentrations, so detector results are often referred to as "qualitative" and are best used for establishing underground linkages or as backup and supplement to less robust and extensive quantitative sampling methods. Detectors are extremely cost-effective in providing time-integrated monitoring at a large number of sites, or where vandalism may be a problem. In clean waters or short exposure intervals, they may have a better detection threshold than water samples. Multiplexing where a number of sequential water samples are automatically pumped into single sample bottles is a discrete form of cumulative sampling that may be necessary where flows are small, e.g. cave seepages.

In many cases, the three sampling techniques can be combined (Fig. 8.3). Continuous measurement occurs at a few important sampling sites, where the instruments can be protected against vandalism, e.g. at water supply springs. Discrete sampling is necessary for tracers that cannot be measured in the field, e.g. particulate tracers. Integrative detectors are typically used to determine underground connections, as deployed as insurance in case of sampler failure, or for detailed resolution of a number of springs being monitored collectively, or at sites that are difficult to reach. They may not always require elution and analysis in such roles.

To avoid photodegradation of dyes (Käss 1998) sample locations should be close to springs. Brown-tinted glass bottles with Teflon cap liners are preferable, with cool and dark sample transport and storage. When this is done, fluorescent dye concentrations often remain stable for weeks, while rapid microbial degradation of naphthionate has been observed in uncooled samples from specific water types (Goldscheider et al. 2001b). Nguyet & Goldscheider (2006) used 13 mL plastic test tubes for sampling during a tracer test in a remote region in order to minimise the weight. Charcoal bag samples are stable when they are dried and stored in the dark. Water samples that are to be analysed for salts are less sensitive than dyes. Sampling for microbial tracers usually requires sterile sampling, cool and dark storage, and rapid analysis (e.g. Harvey 1997, Hötzl et al. 1991, Rossi & Käss 1998).

8.3.5 Laboratory analyses

Both grab sampling (water samples) and integrative samples (charcoal bags, resins) require laboratory analysis. Salts can be analysed using ion chromatography (IC), ion-specific electrodes, spectrophotometry, atomic absorption spectroscopy (AAS), atomic emission

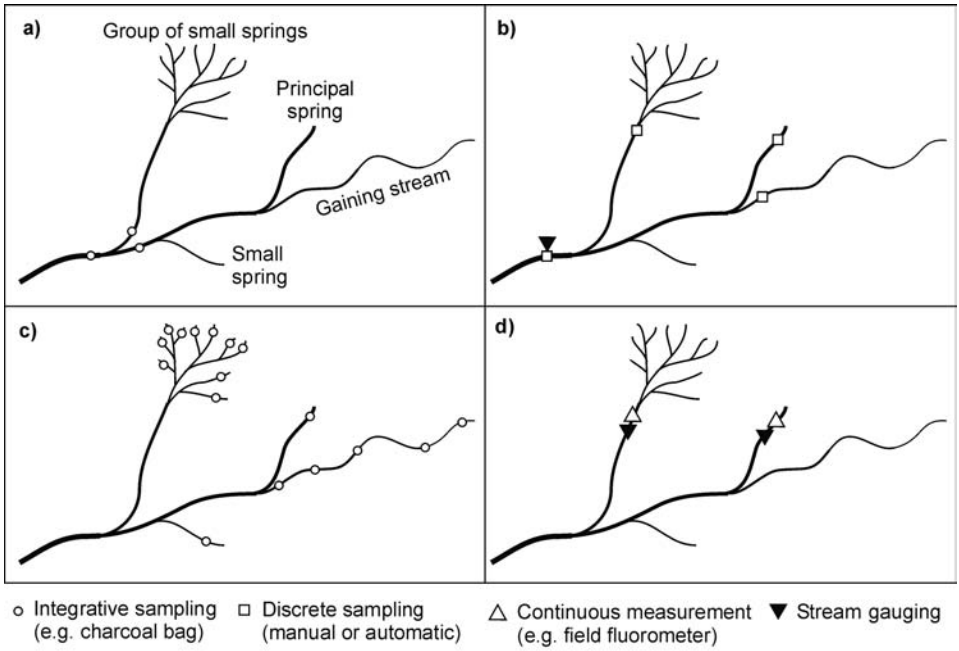

Figure 8.3. Schematic illustration of a set of karst springs with tracer sample schemes devised for different research questions. a) Reconnaissance investigations are used to demonstrate underground linkage with minimal cost. b) A precise travel time investigation requires breakthrough curves defined from discrete or continuous sampling. Overall tracer recovery requires simultaneous determination of discharge and breakthrough at a downstream location. c) Spring differentiation requires detailed spatial sampling most efficiently done using charcoal detectors. d) Conduit characterisation requires tracer breakthrough and discharge for each spring or spring group, and also allows local tracer recovery to be determined.

spectroscopy (AES) or inductively coupled plasma mass spectrometry (ICP-MS) (Dean 1995). Bacteria are usually analysed using cultivation techniques, direct count or other methods (Hurst et al. 2002, Madigan et al. 2000). The simplest analysis of fluorescent dyes is through filter fluorimetry where dye-specific colour filters control excitation and emission wavelengths. The fluorescence intensity includes background and contributions from similar dyes, so filter fluorimeters data require careful evaluation and correction.

Analysis for multiple fluorescent dyes or in the presence of significant natural organic background is best done using a scanning fluorescence spectrometer (Fig. 8.4). The excitation monochromator focuses a ray of monochromatic light onto a sample cuvette. When the water sample contains fluorescent dye, it will partly absorb the light and generate fluorescence light at longer wavelengths. The fluorescence light is detected perpendicular to the ray of excitation light with the wavelength determined by the emission monochromator. Synchronous scanning fluorimeters vary the excitation and emission wavelengths simultaneously with a constant wavelength difference to generate a fluorescence spectrum indicating fluorescence intensity with respect to excitation or emission wavelength (Behrens 1970).

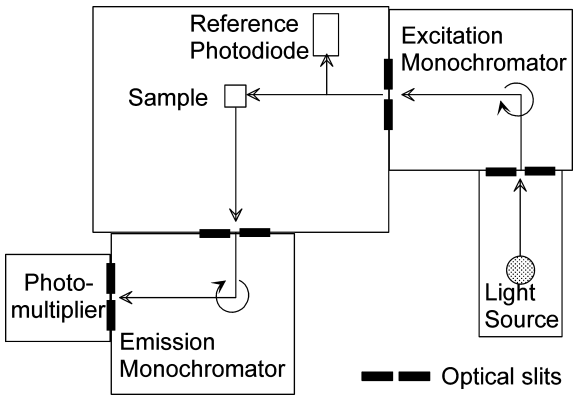

Figure 8.4. Schematic illustration of a spectral fluorimeter. The fluorescence (emission) light is adjusted to have higher wavelengths than the excitation (extinction, absorption) light. Slit settings are widened to adjust gain (sensitivity) and noise suppression, and narrowed to increase spectral resolution. The reference photodiode allows compensation for changes in intensity of the light source.

Table 8.3. Fluorescence characteristics of some tracer dyes (modified after Käss 1998).

Tracer	pH value	Absorption [nm]	Fluorescence [nm]	$\Delta\lambda$ [nm]	Fl. intenisty (uranine = 100)
Naphthionate	Neutral	320	430	110	8
Tinopal	Neutral	346	435	89	60
Pyranine	Acid	405	445	40	6
Pyranine	Basic	455	512	57	18
Uranine	Basic	491	512	21	100
Eosin	Acid	516	538	22	18
Amidorhodamine G	Neutral	530	551	21	14
Sulforhodamine B	Neutral	564	583	19	30

Different fluorescent dyes show distinctive spectra, i.e. absorption and fluorescence maxima, the wavelength difference between them ($\Delta\lambda$, Stokes' shift), and relative fluorescence efficiency (emission/absorption intensity) (Tab. 8.3). The presence of a dye in a sample is indicated by the appearance of the respective peak in the sample spectrum. The measured fluorescence intensity aggregates the contribution of all fluorescent compounds in a sample at the particular monochromator settings. Dyes can be distinguished in a water sample if their fluorescence spectra are clearly separated and known, e.g. naphthionate, uranine and Sulforhodamine B. However, overlapping spectra mean that peak height is not a direct indication of concentration, and very high concentrations of one tracer may mask low concentrations of another. In addition, background fluorescence (typically from natural organic matter or contaminants) is included in the spectrum. In these cases, the spectrum needs to be deconvolved, manually on a graph, or using specialised spectroscopy programs (Fig. 8.5). Such analyses require care and experience to avoid artefacts (Alexander 2005).

Fluorescence intensity is proportional to dye concentration up to tens of ppm allowing simple linear calibration of fluorimeters. More concentrated samples are less fluorescent

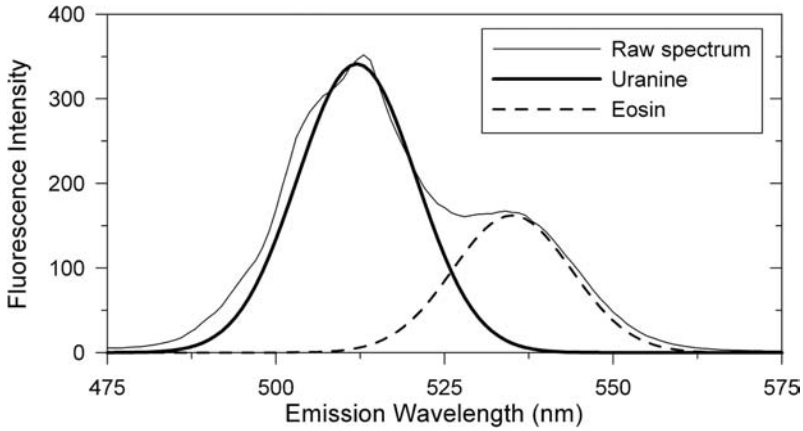

Figure 8.5. Synchronous scan spectrum ($\Delta\lambda = 20$ nm) for a visibly green mixture of uranine and eosin with negligible background fluorescence. The scan has been decomposed into peaks attributed to the two dyes by fitting normal curves centred at 512 and 535 nm using the program PeakFit (SSI). The height of the peaks indicates the concentrations of the two component dyes.

and require quantitative dilution. Samples containing dyes influenced by pH such as uranine and pyranine may require buffers.

Fluorescent dyes adsorbed on charcoal or resin have to be desorbed. For charcoal this can be done with alkaline solvent solution (elutant), e.g. a 1:1 mixture of 2-propanol and 40% NaOH solution for uranine (Käss 1998). A small quantity of the activated carbon (e.g. 5 g) and a small volume of the elutant (e.g. 20 mL) are agitated for several hours (e.g. 4 h), filtered and the tracer concentration is then measured in the strongly alkaline eluent. The fluorescent spectrum of the eluent depends on the composition of the stream water, the duration of exposure and the duration of elution (Smart & Simpson 2002). Unexposed activated charcoal may also exhibit slight fluorescence.

Water samples are analysed for bacteriophages using a small volume added to a culture of the corresponding host bacterium. Any phage present will kill the host bacterium creating a hole in the bacterial culture, thus giving an indication of concentration of phages in the water sample. Even a single phage can be detected with this method, but large concentrations need dilution to allow accurate counting (Rossi & Käss 1998).

Fluorescent particles are most conveniently analysed and differentiated using a flow cytometer (laser-based fluorescent particle detector, Niehren & Kinzelbach 1998, Kennedy et al. 2001). This expensive instrument has difficulty distinguishing microspheres from natural fluorescent particles. This may be overcome using a robust particle counter coupled with a fluorescent detector (Goldscheider et al. 2006). Counting of the fluorescent particles on filter paper under the fluorescence microscope is more time-consuming, but allows better sensitivity and differentiation (Göppert et al. 2005, Käss 1998).

8.3.6 Instruments for field measurement

Small portable filter fluorimeters and emission spectral fluorimeters are now available for grab sample analysis (e.g. Turner Designs Ocean Optics 2006). Fluorescent dyes can be measured continuously in the field with submersible (Fig. 8.6) or fibre-optic fluorimeters where the excitation and emission wavelengths are fixed using light-emitting diodes and

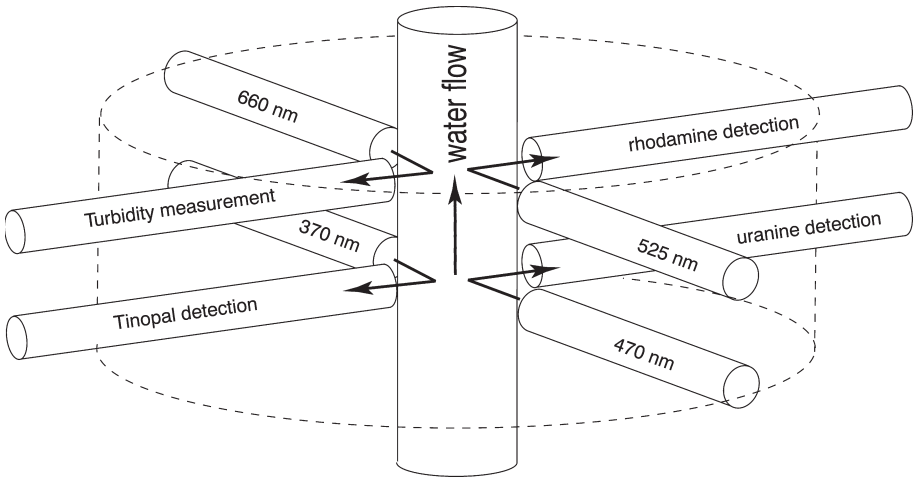

Figure 8.6. Through-flow fluorimeter with 4 channels for the measurement of 3 fluorescent dyes and turbidity. The 370 nm channel can also be used for the monitoring of organic carbon. The instrument also measures temperature; a conductivity probe can also be included (Schnegg 2002).

optical filters (Benischke & Leitner 1992, Smart et al. 1998, Schnegg 2002). The performance of field fluorimeters is comparable to laboratory instruments, although the natural variations of turbidity, organic carbon and pH in the water may require monitoring to allow correction of the apparent fluorescence to standard conditions. The optical separation of background and different fluorescent dyes with similar optical properties (e.g. pyranine, uranine and eosin) requires careful cross calibration and appropriate correction (Behrens 1988, Smart 2005).

Conductivity meters can be used to detect salt tracers if the injected quantity is sufficiently high and if there is little background variation during the sampling period. This is most likely for relatively rapid and short tracer tests, e.g. in dilution gauging of streams (Leibundgut 1998). Ion-specific electrodes attached to a pH meter allow monitoring of specific ions, e.g. for sodium, potassium, chloride, and bromide. However, all show limited sensitivity and are liable to interference from other compounds and may be too fragile for field deployment.

8.4 EVALUATION AND INTERPRETATION

8.4.1 Data requirements, data quality and error analysis

The applicability of tracer test data depends on sampling and analytical procedures. Integrative sampling (e.g. charcoal bags) will give ordinal data resolved to the exposure period. Laboratory analysis of water samples provides the best concentration data, but with time resolution determined by the sampling interval. Online measurement provides the best time resolution, although it may give less accurate analysis. Concurrent discharge data are required when the tracer recovery is to be calculated or flow dependence assessed.

Errors in water tracing can be classified as major, systematic or random, and all three can arise from injection, sampling, handling, analysis and data processing (Smart 2005). Major mistakes include sampling at the wrong site or after the tracer has passed, or direct contamination of the samples with tracer. Systematic errors result in coherent deviation in

the data from a true value that can significantly influence quantitative interpretation. For example, uncorrected high background levels can lead to overestimation of tracer concentration. Systematic error is generally tackled through a scheme of collection, processing and analysis of blanks and standards. Random error is the uncertainty remaining when major and systematic error has been removed. It can be reduced by replicating samples and analyses, and working with averages of multiple samples and measurements. Charcoal detector tracing is most vulnerable to major error, whereas more quantitative tracing is sensitive to all three types of error.

In practice, error in dye tracing is dominated by issues of background and contamination, loss of tracer (e.g. sorption) and aliasing (insufficiently frequent sampling). Rather than any formal analysis of error accepted practices currently address these issues. Background is dealt with below. Contamination can be considerably reduced using good handling protocol, proven through analysis of blanks. Tracer loss can be computed through analysis of recovery, if concurrent discharge data are available. However, batch tests may be needed to determine whether loss is from sorption, degradation or diversion of the tracer. Aliasing can be avoided by continuous analysis or by sampling frequently enough to define a serially coherent breakthrough curve. Knowledge about the uncertainty of measurements is particularly important if data are near the detection limit, particularly in the tail of a breakthrough curve where errors may significantly influence trace parameters.

8.4.2 Tracer background

Background can be defined as that part of measured tracer concentration not arising from the tracer injected. Background arises from extraneous tracer (contamination), other substances measured as tracer, or instrumental errors.

The primary source of contamination with the tracer is through mishandling. Fluorescent dyes like uranine and rhodamines are used as industrial colorants of automobile antifreeze, while blue fluorescent whitening agents are common in household detergents and ubiquitous in raw sewage (e.g. Boving et al. 2004). As a result they may be found in the environment. Fluorescence arising from organic contaminants or natural dissolved organic carbon (DOC) overlaps tracer spectra, especially in the blue end of the spectrum. This is a problem with filter fluorimeters that are unable to distinguish tracer from other material fluorescing in the same wave band. Tracer ions such as chloride, bromide, iodide, sodium, potassium and lithium, are present in almost all natural ground waters and can be substantially elevated in wastewater discharge, landfill leachate and winter road runoff. Environmental sources of background can act randomly or be influenced by runoff conditions, and so imitate a tracer breakthrough curve.

Instrument characteristics lead to analytical background. For example, fluorescence analyses generally have a background arising from stray light and thermal noise in the photodetector. Most instruments incorporate technical solutions to the problem of background, or offer the possibility of blanking out what the user considers to be meaningless background.

Environmental background is determined through pre-monitoring, i.e. collection of a series of samples prior to injection. It may be difficult to correct for background when the tracer is present, unless there is some means of separation of the two as is possible in spectrofluorimetric correction of organic background using curve fitting. The average of pre-monitoring concentrations is typically assumed to be sustained during tracer breakthrough, and is subtracted from the total observed concentration. If a suitable untraced

site analogous to the traced site is available, then co-monitoring (sampling during the tracer breakthrough) can indicate if background is likely to have changed. Analogue monitoring (observation of variables known to be correlated to background) may also allow approximate correction for background fluctuations, or at least demonstrate that changes are unlikely to have occurred. Correction of dynamic background in filter fluorimetry is possible by monitoring natural fluorescence in several channels and using the relationship between these signals and background to estimate background during tracer breakthrough (Smart 2005).

8.4.3 Tracer transport in groundwater

The quantitative interpretation of tracer tests is based on the principles of solute transport (e.g. Schulz 1998, Fetter 1999). The transport of conservative tracers is dominated by advection and dispersion. Additional geochemical processes govern reactive tracers, including reversible and irreversible adsorption, precipitation, oxidation, reduction, volatilisation, degradation and transformation. Non-aqueous phase and particulate tracers are affected by sedimentation, flotation and different types of filtration. Biological processes influence microbiological tracers, including reproduction, inactivation and die-off.

Advection describes the displacement of substances with the fluid (average linear velocity). In any aquifer variability of flow paths and flow velocities results in spatial and temporal spreading of the tracer cloud, referred to as mechanical dispersion. Tracer is also spread by molecular diffusion, which occurs in response to concentration gradients in the fluid, but is generally negligible compared to dispersion in discrete conduits. During turbulent flow in karst conduits mechanical dispersion is most important in the flow direction, giving the longitudinal advection-dispersion equation (Bear 1979):

$$\frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x}$$

where C = concentration, t = time, D_L = longitudinal dispersion coefficient, v = effective flow velocity, and x = longitudinal distance. This equation can be solved for a range of initial and boundary conditions. Kreft & Zuber (1978) proposed an analytical solution for porous media:

$$C(x,t) = \frac{M}{Qt_0\sqrt{4\pi P_D \left(\frac{t}{t_0}\right)^3}} \exp\left(-\frac{\left(1-\frac{t}{t_0}\right)^2}{4P_D\frac{t}{t_0}}\right)$$

where M = tracer mass, Q = discharge, t_0 = mean transit time P_D = dispersion parameter, a normalised form of the dispersion coefficient ($D_L/(v \cdot L)$) allowing for increasing dispersion with flow paths length (L) and flow velocity (v).

Adsorption results in a retardation of the tracer cloud, i.e. transport velocity of the adsorbed tracer is less than for the fluid or a conservative tracer:

$$v_R = \frac{v_x}{R_D}$$

where v_R = retarded flow velocity, v_x = conservative flow velocity, R_D = retardation factor.

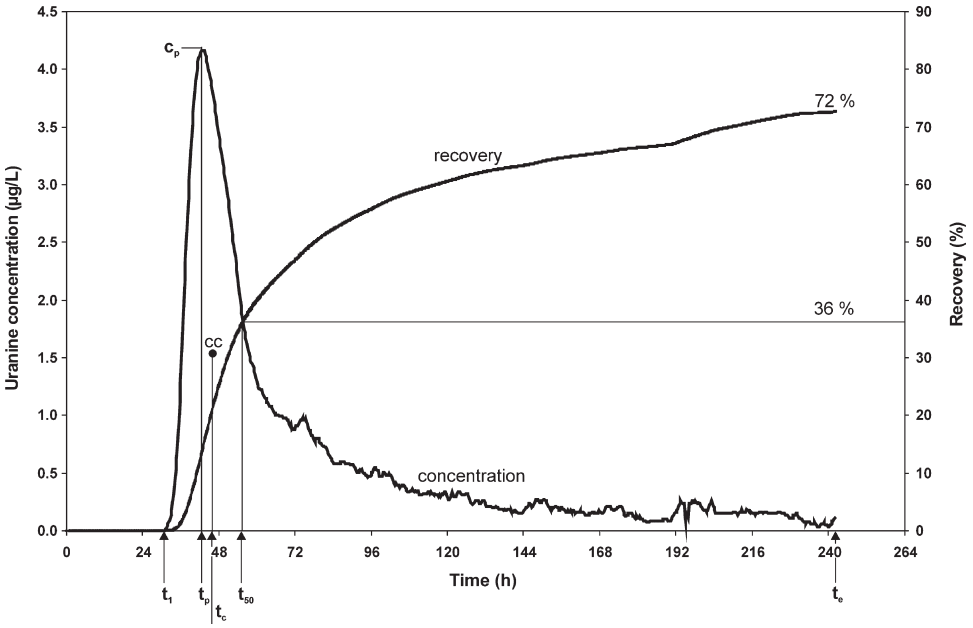

Figure 8.7. Tracer breakthrough curve resulting from an instantaneous injection. The main features are: time of first detection (t_1), time and concentration of the peak (t_p, c_p), time of the concentration centroid cc (t_c), time where half of the recovered tracer has passed (t_{50}), end of the observation period (t_e). The recovery curve shows cumulatively the fraction of injected tracer that arrived at the sampling point. In this case, the total recovery at the end of the observation period is 72%, so t_{50} is the time with a 36% recovery.

Biodegradation is a complex process, but may be approximated by:

$$c_t = c_0 \cdot e^{-\lambda \cdot t}$$

a decline analogous to radioactive decay, where c_t = concentration of the degradable tracer at time t, c_0 = concentration of the conservative tracer, λ = constant of decay.

8.4.4 Breakthrough curves

The definitive product of quantitative tracing is a time-concentration tracer breakthrough curve (Fig. 8.7) generated by online monitoring or analysis of water samples. It represents the behaviour of the injected tracer in the flow route. The magnitude of the breakthrough is determined by the tracer mass and volumetric flow (i.e. dilution). This former effect is readily removed by dividing all concentrations by the injected mass or (in the case of particulates) injected numbers. Breakthrough curves from entirely different systems are best compared using a dimensionless form generated by dividing time by a reference time (typically mean transit time or time to peak concentration) and concentration by the peak concentration.

The primary features of a breakthrough curve are the premonitory background (if present), the rising limb, the peak, and the recession. Asymmetry is caused by dispersion,

storage and other transport processes. The time delay of the breakthrough curve of a conservative tracer is determined by length of the flow path and flow velocity. Its breadth arises from dispersion and increases with time. In a karst aquifer, the breakthrough curve reflects the structure of the flow paths and may also be influenced by temporal variation of recharge. Retardation shifts the curve towards higher transit times, while degradation reduces all concentration values, mainly on the falling limb, as the degradation is time-dependent.

8.4.5 Travel time and transport velocity

A number of transport statistics can be derived from the breakthrough curve. The first arrival time depends on the analytical detection limit and background stability; it is thus more correct to speak of first detection. In contrast, the time and concentration of the peak are readily determined from a continuous data record. If discrete sampling fails to define a peak, then a peak may be estimated using adjacent values. The time of last detection is difficult to determine, as it strongly depends on the analytical detection limit and on the duration and resolution of the monitoring. An exponential fit can be used to extrapolate tracer tails.

The mean transit time cannot be directly read from the curve. In most cases, the mean transit time lies between the time of maximum concentration and the time at which 50% of the tracer has passed. The concentration centroid of the breakthrough curve provides a good approximation of the mean transit time. The mean transit time can be computed statistically (e.g. Smart 1988b) or by solution of the advection-dispersion equation for the measured data. Where the breakthrough curve is ill-sampled or contains errors, the time of peak provides the most robust estimate of travel time.

Travel times can be converted to respective velocities if a relevant travel distance is available. In karst systems, the travel path may have been explored by speleologists in caves or inferred from geology. Where it is unknown, the straight-line distance between the points of injection and recovery can be used to obtain a linear velocity. The flow velocities corresponding to the different times are the maximum flow velocity (first detection), the dominant or modal flow velocity (peak), the effective flow velocity (mean transit time) and the mean velocity (half of the recovered tracer mass) (Schulz 1998). Flow velocities in karst aquifers span a wide range from a few metres up to several hundred metres per hour (Ford & Williams 1989, Gospodaric & Habic 1976, Morfis & Zojer 1986, Behrens et al. 1992).

8.4.6 Mass recovery

The fraction of the injected tracer mass passing a sampling point provides valuable information on the system hydrology and the tracer performance. Mass recovery requires high-resolution discharge and concentration data at each site. If discharge is constant, the recovered tracer mass is the integral of the breakthrough curve times the discharge. For variable discharge, the recovered tracer mass M_R is calculated by integration of the tracer load (concentration-discharge product) over the time:

$$M_R = \int_{t=0}^{\infty} (Q \cdot c)dt$$

The cumulative tracer recovery (mass or %) is often presented in the same diagram as the breakthrough curve to show that the recovery curve approaches an asymptotic final value, and to allow definition of the time at which half of the recovered tracer has passed (Fig. 8.7).

The mass recovery is often significantly less (and rarely more) than 100%, due to tracer storage (e.g. in the karst matrix) or delivery to non-monitored springs (e.g. under water or in other catchments). The tracer may also have been lost to adsorption or decomposition. Sometimes, sampling or measurement errors are responsible for poor recovery. Significant losses may imply dye storage within the aquifer, thus compromising further tracing.

8.4.7 Characterisation of conduit networks

Tracer results can be negative, poorly defined, well defined or fully configured. Negative results where the tracer is not detected are ambiguous. Poorly defined results occur when the tracer is detected only intermittently, or at levels close to background. Such results indicate a possible linkage perhaps with intermittent dilution (e.g. sampling incompletely mixed flow from a local tributary), but may also arise from technical problems. Such data cannot be rigorously analysed. Well-defined tracer results rise well above background levels and show a characteristic breakthrough curve allowing more rigorous analysis. Fully configured tracer results constitute a breakthrough curve with concurrent discharge data and high overall recovery.

The primary application of tracer tests is in defining underground linkages and this is often obtained with charcoal detectors or occasional grab sampling. Greater resolution of karst conduit networks is possible with fully configured tests where the injection tracer mass and discharge can be compared to the recovered mass and discharge (Fig. 8.8). Conservative tracers are preferred for this type of interpretation.

When the discharge at the injection point is similar to that at the sampling point, and when the recovery rate is close to 100% (case A), there is a direct connection between the two points, without flow divergence or convergence. Conceptually and comparatively, it is useful to determine the geometry of an equivalent conduit connecting the two points, assuming that it is straight, water-filled and has a constant cross-sectional area. The conduit volume (V) can be estimated by integrating the discharge from the injection time to the mean transit time or centroid time:

$$V = \int_{t=0}^{t_c} Q dt$$

The equivalent conduit cross-sectional area can be computed by dividing the volume by the travel distance, and the radius of the conduit can be computed from simple geometry.

In most cases, however, the discharge rate at the sampling site will be different than at the injection point, and the recovery rate will be smaller than 100%, indicating flow divergence and/or flow convergence between the two points (cases B–F).

The form of the tracer breakthrough curve may allow additional resolution of underground conditions. A single peak suggests a single conduit that can be characterised in general using appropriate interpretative models. Multiple peaked curves may indicate multiple flow routes (case I). Tracer passing through a conduit may be directed into storage. The storage may be an off-line (case G) or an in-line void (case H). Storage in such sites is often driven by varying flow, and may cause surprising disappearance or apparently spontaneous appearance of tracer. Sustained tails on a breakthrough curve can result from storage but may also result from unresolved multiple peaks (Werner 1998a), or matrix or dead-zone

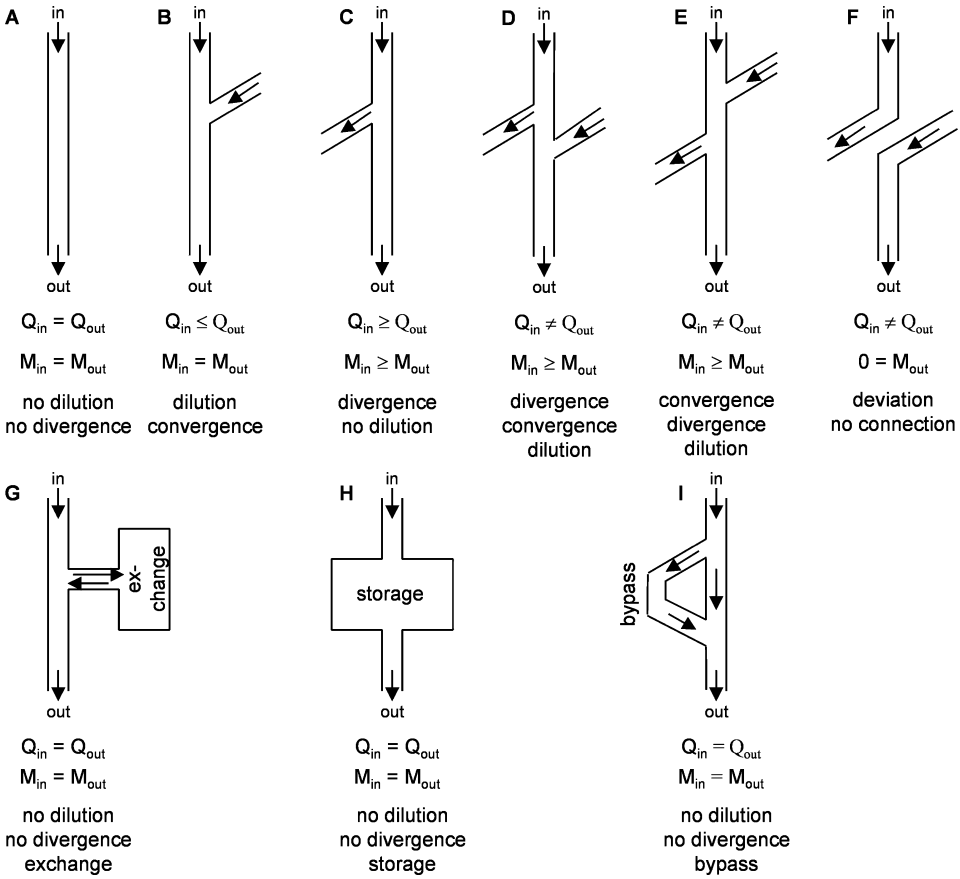

Figure 8.8. Karst network configurations based upon the measurement of input (in) and output (out) discharge and tracer recovery under steady flow conditions. Q: discharge, M: tracer mass. A to F represent different configurations where flow converges or diverges and tracer transport will occur straight on to the outlet or will be redirected. G, H and I represent special cases, which can be deduced from the shape of the breakthrough curve (peak, tailing): G has off-line storage, H has in-line storage, I is a system with bypass. The complexity of real karst systems makes it difficult to resolve to clear configurations (modified after Ashton 1966, Atkinson et al. 1973, Brown & Ford 1971, Brown & Wigley 1969, Smart 1988a).

storage (Hauns et al. 2001). Modelling of such storage is difficult. More general dead zone models have been developed to describe the effect of temporary storage in simple uniform channels (e.g. Davis et al. 2000, Field and Pinsky 2000).

It is sometimes possible to resolve relatively complex underground flow systems, if the data from several tracer tests are combined with geological, speleological and hydrological observations (e.g. Smart 1988a), and with hydrochemical and isotopic (i.e. natural tracer) data (Pronk et al. 2006).

Replication of tracer tests under different flow conditions may reveal changes in underground routing and velocity that are of considerable importance in water resource management. The relationship between parameters like conduit volume and discharge reveals

the extent of storage changes and the dynamic and static storage in a system (Smart 1988b). The travel-time discharge relationship reveals whether a system is open channel or closed conduit flow (Stanton & Smart 1981), or even where overflow routing develops (Smart 1997). Multiple peaked breakthrough curves at higher discharge may indicate more rapid overflow routing (Stanton & Smart 1981). When multiple springs are under investigation, the relative yield of water and tracer and breakthrough curves can be evaluated to identify spring families that show close or more distant relationships. Changes in these relationships with discharge are indicative of underground routing and hydraulic change (Smart 1988a).

Tracing during varying flow leads to complications of interpretation. For example, travel time is generally faster on rising than falling stage. Water and tracer can also be redirected into storage, or delayed or divided without necessarily following two physical routes.

8.4.8 Quantification of transport parameters using analytical models

Chapter 10 of this book deals with modelling. This section only provides a brief overview of how analytical models can help to better interpret tracer test results and determine transport parameters. Karst aquifers are difficult to model because as aquifers they are heterogeneous and anisotropic, and as conduit networks they have unsteady open (vadose) and closed (phreatic) channels of varying scale. There are two main types of models: global and distributed models. Distributed models subdivide the aquifer into homogeneous sub-units with water and tracer transfer between these sub-units. Global or lumped parameter models transform an input signal into an output signal using an analytical equation that substitutes for the physical properties of the aquifer. It is also possible to use a known output signal in order to determine physical parameters of the aquifer (inverse modelling). This is usually done by means of a best-fit approach, i.e. the physical parameters are systematically varied until the modelled curve fits to the measured data series. These parameters may then be applied to forward prediction of aquifer response.

Common modelling tools for the interpretation of tracer tests are based on fitting an analytical transport equation (e.g. equation 2 on page 164) to a measured breakthrough curve. For advective-dispersive transport, two fitting parameters are required, the first representing advection (e.g. mean transit time or effective flow velocity) and the second representing dispersion. Several computer codes are available for this type of interpretation, such as TRACI (Werner 1998a,b) or CXTFIT (Toride et al. 1999). The QTRACER2 program can also be used for the evaluation of tracer breakthrough curves (Field 2002).

Multiple-peak breakthrough curves produced from single tracer injections under steady flow indicate the presence of different flow paths in the aquifer. The Multi-Dispersion-Model assumes that these flow path (conduits) split directly at the injection point (swallow hole) and reunify at the sampling point (spring). Each flow paths is characterised by an individual advective flow velocity and dispersion. At the sampling point, the individual breakthrough curves superimpose to form a multi-peak curve (Maloszewski et al. 1992, Werner 1998a). Inversely, the decomposition of a multi-peak curve makes it possible to determine the individual flow velocities and dispersion of the individual flow paths (Fig. 8.9).

Karst aquifer systems are always much more complex than a model can describe. Parameters obtained from inverse modelling are useful for analysis and comparison of tracer breakthrough curves, but are greatly generalised and not representative of reality.

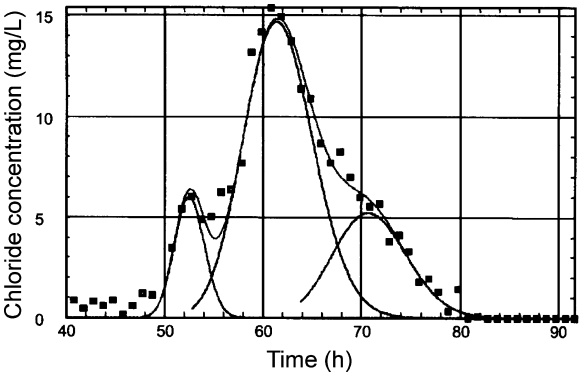

Figure 8.9. In 1877, a tracer test with NaCl proved the underground connection between the sink of the Danube and the Aach spring in the Swabian Alb, Germany (Knop 1878). More than 100 years later, Werner (1998a) modelled the breakthrough curve using a Multi-Dispersion-Model. The breakthrough curve can be decomposed into three curves with three different effective flow velocities and dispersion coefficients. However, it is not clear what constitutes an interpretable peak and what is artefact. The initial high values suggest a level of uncertainty in the data that does not support the overall fit proposed.

8.5 SUMMARY

Groundwater tracing is a method of investigating underground water and contaminant transport by labelling water with identifiable tracer substances or physical properties. It is particularly applicable to karst areas where the underground flow dominates but is not readily comprehended. The technical and environmental requirements of a tracer mean that fluorescent dyes are most widely used, along with less tractable particulate tracers.

Tracer tests are used primarily to define underground connections, spring catchment areas and contaminant origin or destination in karst areas. Such tests require rudimentary monitoring to establish the presence or absence of a tracer. More sophisticated groundwater tracing is used to determine parameters for aquifer hydraulic and geometry or contaminant transport. Simple sampling and analysis may be sufficient for the former style of investigation, but the latter require high frequency or continuous sampling and quantitative tracer analysis. Quantitative time concentration data allow travel time and dispersion statistics to be calculated. Supplementary discharge data permits mass recovery and unsteady flow effects to be studied. A number of models are available for tracer breakthrough and aquifer analysis. They provide valuable guidance on possible configuration of the aquifer, although they remain much simplified.