A review of some tracer-test design equations for tracer-mass estimation and sample-collection frequency

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Abstract Determination of necessary tracer mass, initial sample-collection time, and subsequent sample-collection frequency are the three most difficult aspects to estimate for a proposed tracer test prior to conducting the tracer test. To facilitate tracer-mass estimation, 33 mass-estimation equations have been developed over the past century. These 33 equations are reviewed here, 32 of which were evaluated using previously published tracer-test design examination parameters. Comparison of the results produced a wide range of estimated tracer mass, but no means is available by which one equation may be reasonably selected over the others. Each equation produces a simple approximation for tracer mass. Most of the equations are based primarily on estimates or measurements of discharge, transport distance, and suspected transport times. Although the basic field parameters commonly employed are appropriate for estimating tracer mass, the 33 equations are problematic in that they were all probably based on the original developers experience in a particular field area and not necessarily on measured hydraulic parameters or solute-transport theory. Suggested sampling frequencies are typically based primarily on probable transport distance, but with little regard to expected travel times. This too is problematic in that tracer sampling remains a haphazard process that tends to result in false negatives or data aliasing. Simulations from the recently developed efficient hydrologic tracer-test design methodology (EHTD) were compared with those obtained from 32 of the 33 published tracer-mass estimation equations and suggested sampling frequencies. EHTD applies functional relationships developed from hydrologic measurements in a solute-transport model to develop a preliminary tracer-breakthrough curve that has been shown to reasonably predict actual tracer-test results.

Keywords Sampling frequencies · Tracer-mass estimation · Tracer-test design

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Introduction

Quantitative hydrological tracer testing is one of the most reliable methods for establishing solute-transport trajectories and for defining solute-transport parameters. Determining the necessary tracer mass to release, when to start collecting samples, and at what frequency all subsequent samples should be collected can be very difficult to estimate, especially in karstic terranes. In most tracing studies in karstic terranes, design efforts are focused on predicting where tracer will arrive and where best to release tracer. The tracer mass released is typically a guess utilizing the experience of the practitioner. While attempting to predict where the tracer will arrive and where best to release the tracer is an important and valuable aspect of conducting a tracer test, guessing the appropriate tracer mass to release is a fallacious practice that almost assures that too much or too little tracer will be released.

To facilitate the determination of necessary tracer mass for a successful tracer test, 33 tracer-mass estimation equations have been developed over the last century primarily for karstic aquifers. Although a considerable improvement over the typical method of guessing an appropriate tracer mass to release, these equations are also problematic. This is because, with the exception of two equations, they were all developed on the false assumption that a simple algebraic expression that appears to function adequately for a selected hydrological setting will then adequately function in all hydrological settings. In addition, these equations fail to properly account for the important effects of axial dispersion and solute-transport theory (Field 2001a).

Tracer test sample-collection frequency in karstic terranes is typically a haphazard procedure based on expected transport distance and supposed travel time. The haphazardness of sample collection is further exacerbated when qualitative tracing tests are conducted. In general, a preliminary sample-collection frequency is predetermined before the tracing test is initiated, but is subject to revision during the tracer test as time passes with or without tracer recovery.

In this paper, the 33 tracer-mass estimation equations are briefly reviewed, 32 of which were evaluated using previously published tracer-test design examination parameters. For this review, unless otherwise indicated, the published tracer-mass estimation equations were all probably intended to estimate the mass of tracer on an "as sold basis", which often necessarily includes a large quantity of diluent. In addition, conventional sample-collection frequency determinations are briefly reviewed. The results of the review and examination of the 33 mass-estimation equations and the typical sampling frequencies are compared with the recently developed efficient hydrologic tracer-test design (EHTD) method that has been shown to be theoretically sound and more reliable than previous methods.

Tracer-mass estimation and sampling frequencies

Hydrological tracing requires that an appropriate mass of tracer be released such that detectable concentrations of the tracer may be recovered at the sampling stations. Commonly, an estimate of the mass of tracer to release consists of nothing more than a guess that is sometimes based on the general experience of particular individuals (Alexander and Quinlan 1992, p. 19; Aley 1999, p. 14) or prior experience at the location to be traced (e.g., Meigs and Beauheim 2001). Other times, the guess refers to what sounds "good" at the time. In rare instances, a tracer-mass estimation equation may be utilized to determine the appropriate tracer mass to release. Although general tracing experience is beneficial for determining tracer quantities to release and specific site experience is better, neither approach may be regarded as scientifically rigorous. Worse, the former suggests only select individuals are adequately qualified to assess tracer needs whereas the latter suggests the possibility of numerous tracer-release efforts at a site before success may be obtained.

Tracer-mass estimation by conjecture

There are four reasons beyond practical experience that may explain why a guess is used to estimate the necessary tracer mass to release. The first is the over reliance on qualitative tracing in karstic terranes using common fluorescent dyes. Qualitative tracing commonly consists of the use of packets of activated carbon (commonly known as "detectors" or "bugs" in North America and "fluocapteurs" in France) or surgical cotton to sorb the fluorescent dye as it exits the underground. Occasionally, qualitative tracing may consist of visual observation of dyed water. Use of dye detectors is believed to facilitate karst tracing in that the detectors can be distributed throughout the area where tracer dye is expected to exit the subsurface and may be collected when convenient. Sorption onto detectors is further desirable because some studies have suggested that dye detectors allow for reduced tracer-dye concentrations due to the reported increases in tracer-dye concentrations of 100 to 400 times the concentration in water by activated carbon (Aley 1999, p. 21), although published research suggests that dye concentration by activated carbon is probably three to four times the concentration in water, but may be as high as 1,000 times the concentration in water (Käss 1998, pp. 100–103). More recent studies have suggested that, however, quantitative tracing using water samples actually allows for much lower dye concentrations than do dye detectors (G. Davies, personal communication). Also, although qualitative tracing using detectors is commonly applied in Great Britain and the United States, the method is scientifically untenable because false positive results (Lutz and Parriaux 1988; Gunn and Lowe 2000) and false negative results (Smart and others 1986) are common.

Unfortunately, activated carbon also enhances background fluorescence (fluorescent dyes and other similarly-appearing compounds), which may be advantageous for visual determination of dye, but adversely affects the signal-to-noise ratio of modern analytical instruments (S. Worthington, personal communication). Smart and Friederich (1982) document considerable difficulties related to background fluorescence and fluorometric determination of dye elutant. Excess sorption of background concentrations requires that the estimated tracer-dye concentration to be released exceed background concentrations at the sampling stations by ten times to ensure detection (N. Crawford, personal communication), an undesirable practice from both an aesthetic and ecological perspective (Smart and Karunaratne 2001). Excessive and extensive background sorption also causes ambiguous results erroneously suggesting tracer recovery at most or all the sampling stations (McCann and Krothe 1992) because the method does not lend itself to establishing that the sorbed and "identified" compound is in fact the fluorescent dye of interest.

More recent research suggests that fluorescent dye sorption by detectors may not be as straightforward as once thought. Research at the University of Minnesota (G. Davies, personal communication) suggests that the occurrence of false negatives and false positives may occur far more frequently than has previously been recognized primarily because of the vagaries of fluorescent dye sorption–desorption by the detectors. For example, sodium fluorescein [uranin (45350 C.I. Acid Yellow 73)] was found to be readily sorbed by activated carbon, but it was also desorbed almost immediately. Rhodamine WT (C.I. Acid Red 388), however, was not readily sorbed and was difficult to elute. The rapid sorption–desorption of short-wavelength dyes and slow sorption and difficult elution of

Table 1
Average dye manufacturers purities for selected powder dyes

Color index generic name	Common name	Color index constitution no.	Average purity range[a] (%)
Acid Red 9	erioglaucine	42090	73–75
Acid Red 52	Sulpho-rhodamine B	45100	85–90
Acid Red 87	eosin	45380	65–70
Acid Red 388	Rhodamine WT		82–85
Acid Yellow 73	Na-fluorescein	45350	75
Basic Violet 10	Rhodamine B	45170	90
Fluorescent Brightener 351	Tinopal CBS-X		60
Solvent Green 7	pyranine	59040	80

[a] The listed values are for the "crude" form of the dyes only

long-wavelength dyes compromises the use of activated carbon for detection (Smart and Simpson 2001). Other peculiarities related to sorption by activated carbon and sample handling (Smart and Friedrich 1982; Smart and Zabo 1997) also prevent replication of the results, a basic requirement of any scientific endeavor. The difficulties are further exacerbated by the fluorescence spectra shift caused by the high *p*H of the elutants (Käss 1998, p. 102). In addition, specific tracer-types may result in varying sorptive behaviors (Sutton and others 2001).

The second reason that the tracer mass to be released is guessed stems from the lack of knowledge regarding the volume and degree of spreading necessary for estimating the extent of tracer dilution. Sorptive characteristics of the transport medium and tracer are also typically unknowns. While surface water volume and degree of spreading can be reasonably estimated, aquifer volume and degree of spreading remain virtual unknowns until a quantitative tracer test is conducted and computationally evaluated. Understanding tracer losses due to tracer sorption generally requires extensive testing and analysis using a selected tracer and specific materials, the results of which are not readily transferable.

A third reason why necessary tracer masses are guessed may relate to the relative purities of various fluorescent dyes supplied by different manufacturers. Table 1 lists the average dye manufacturers purities of some common fluorescent dyes used for hydrological tracing and Table 2 lists the average percent pure dye content of these dyes supplied by one distributor. This range of fluorescent dye purities complicates the determination of dye mass to release.

Lastly, the fourth reason that the tracer mass to release is guessed is because of the relative obscurity, confusing nature, and inconsistency surrounding the use of existing tracer-mass estimation equations. In general, these equations have been found to be less exact than is commonly desired (Käss 1998, p. 323).

Tracer-mass estimation by mathematical equation

Many equations for calculating the amount of tracer material to release into a flow system have been published. Thirty-three empirically determined equations are considered here (Table 3, also see the Appendix section). It will be noted that some of the equations listed in Table 3 do not appear in original form as they have been modified for consistency of units, correct publication errors in secondary references, and to yield mass in grams. An examination of these equations reveals little about each except that most rely, to some extent, on volumetric-flow rate (discharge; Table 3). Presumably, the reliance on discharge by the originators of the equations was intended to address probable dilution effects. The 33 equations listed in Table 3 were developed empirically so maintaining mass balance appears not to have been an important consideration. Although not apparent from Table 3, five of the 33 listed equations incorporate different systems of measurement in their original form.

Sources for each of the equations were not always specific about which type of tracer a particular equation was meant for in the design or if it even matters, but most were probably designed for the fluorescent dye Na-fluorescein. Also, it is not always clear if an equation was intended for visual tracer detection, instrument detection in water samples, or sample collectors designed to enhance tracer concentrations (e.g., carbon sorption of fluorescent dyes via detectors).

Some equations require a "fudge-factoring" constant that takes into consideration the relative detectability of the

Table 2
Percent pure dye content for selected fluorescent dyes. The values listed are specific to one manufacturer – crude dye stocks can and will vary significantly with manufacturer

Tracer dye (Common name)	Powder dye[a] Content %[b]	Liquid dye[a] Content %[b]
erioglaucine[c]	74.0	37.0
Sulpho-rhodamine B	90.0–92.0	18.0
eosin	86.0	26.0
Rhodamine WT[d]	85.0	17.0
Na-fluorescein	60.0	30.0
Rhodamine B[e]	90.0	45.0
Tinopal CBS-X	60.0	
pyranine	80.0	

[a] Values listed are within ±5.0%

[b] $\% = \frac{C_0 A_{b_d}}{C_0 A_{b_s}} \times 100$

[c] Erioglaucine is also sold with a Food, Drug and Cosmetic (FD&C) purity equal to 92.0%

[d] Rhodamine WT is not commercially available in powder form and rarely exceeds 18% purity in liquid form

[e] Rhodamine B as a liquid is mixed with glacial acetic acid

Table 3
Some equations for estimating tracer injection mass

Number	Equation[a]	Secondary reference	Primary reference
1a	$M = 0.56\left(\frac{QC_p t_p}{1000}\right)^{0.91}$		(Worthington, personal communication)
1b	$M = 0.56\left(\frac{QC_p L}{1000\upsilon_p}\right)^{0.91}$		(Worthington, personal communication)
2	$M = 17\left(\frac{QC_p L}{3.6\times10^6}\right)^{0.93}$		(Worthington, personal communication)
3	$M = \frac{T_{C_1} L}{10}$	(Parriaux and others 1988, p. 7)	(UNESCO 1973–1983)
4	$M = T_{C_2}\left(\frac{QL}{8.64\times10^4\upsilon}\right) + \frac{V}{5.0\times10^4}$	(Parriaux and others 1988, p. 7)	(UNESCO 1973–1983)
5a	$M = \frac{T_{C_3} QL}{3600}$	(Parriaux and others 1988, p. 8)	(Bendel 1948)
		(Zötl 1974, p. 54)	(Bendel 1948)
		(Käss 1998, p. 323)	(Dienert 1913)
5b	$M = \frac{T_{C_4} QL}{3600}$	(Milanović 1981, p. 276)	(Dienert ?)[b]
6	$M = \frac{t_d C_p Q A_{d_1} S_f}{2000}$	(Parriaux and others 1988, p. 8)	(Leibundgut 1974)
		(Gaspar 1987, p. 49)	(Leibundgut 1974)
			(Leibundgut and Wernli 1982)
7a	$M = \frac{bW[2LC_p + A_{d_2}(2L-W)]}{3731}$	(Parriaux and others 1988, p. 8)	(Leibundgut 1981)
		(Käss 1998, p. 326)	
7b	$M = \frac{bL\theta[2LC_p + A_{d_2}(2L-W)]}{2g}$	(Käss 1998, p. 325)	(Leibundgut and Wernli 1982)
8	$M = \frac{QL}{3600}$	(Milanović 1981, p. 276)	(Martel 1940)[b]
		(Gaspar 1987, p. 49)	(Martel 1940)[b]
		(Bögli 1980, p. 139)	(Thurner 1967)[b]
9	$M = \frac{T_{C_4} QL}{q}$	(Milanović 1981, p. 276)	(Guillard ?)[b]
		(Gaspar 1987, p. 49)	(Guillard ?)[b]
10	$M = T_{C_5} L$	(Käss 1998, p. 325)	(Siline-Bektchourine 1951)
11	$M = LT_{C_6} T_{C_7}$		(Käss 1998, p. 327)
12	$M = L\left[\left(1 + \frac{Q}{1.8\times10^4}\right) + \frac{Q}{3600}\right]$	(Milanović 1981, p. 276)	(Stepinac 1969)[b]
		(Gaspar 1987, p. 49)	(Stepinac 1969)[b]
13	$M = \left(\frac{Q^2 L}{3600q}\right)$	(Gaspar 1987, p. 49)	(Heys 1968)
14	$M = \frac{t_d QPS_f}{8.64\times10^4}$		(Gaspar 1987, p. 50)
15	$M = \frac{T_{M_1} Q}{3600}$	(Sweeting 1973, p. 228)	(Jenko ?)[b]
16	$M = \frac{T_{M_2} q}{3600}$	(Sweeting 1973, p. 228)	(Jenko ?)[b]
17	$M = \frac{QL}{40}$	(Davis and others 1985, p. 101)	(Drew and Smith 1969)
18	$M = \frac{C_p T_\rho QL}{2500\upsilon}$	(Aley and Fletcher 1976, p. 7)	(Dunn 1968)
19	$M = 5.0Q$		(Haas 1959)
20	$M = 9.5VL$		(Haas 1959)
21	$M = \frac{QL}{366}$	(Aley and Fletcher 1976, p. 30)	(Haas 1959)
22	$M = 1478\sqrt{\frac{QL}{3.6\times10^6\upsilon}}$		(Aley and Fletcher 1976, p. 9)
23	$M = \frac{QC_p t_p T_\rho}{3398}$		(Rantz 1982, p. 237)
24	$M = \frac{QC_p \bar{t} T_\rho T_p}{747.23}$		(Kilpatrick and Cobb 1985, p. 8)
25	$M = \frac{QC_p T_\rho t_2}{1000}$		(Rathbun 1979, p. 26)
			(Rantz 1982, p. 236)
			(Kilpatrick and Cobb 1985, p. 17)
26	$M = \frac{QC_p \bar{t} T_\rho T_p}{498.15}$		(Mull and others 1988, p. 37)
27	$M = \frac{C_p T_\rho T_p}{2.94}\left(\frac{Q\bar{t}}{149.53}\right)^{0.94}$		(Kilpatrick and Wilson 1989, p. 14)
28	$M = \frac{QL}{20}$		(Käss 1998, p. 324)
29	$M = \frac{T_{M_3} LIA_{pp}}{1000}$		(Alexander and Quinlan 1992, p. 19)
30	$M = S_m L$	(Käss 1998, p. 324)	(Timeus 1926)[b]
31	$M = \frac{S_m V}{100}$	(Käss 1998, p. 324)	(Timeus 1926)[b]
32	$M = \frac{V}{200}$		(Kilpatrick 1993, p. 14)
33	$M_p = Qt_p P_h$	(Käss 1998, p. 327)	(Kinnunen 1978)

[a] Some equations slightly modified for simplification and to allow consistency of units
[b] Primary reference not always properly identified or readily available. Secondary references do not always correctly reproduce the original equations

tracer to be used, the residence time within the aquifer, the type of sampling done, the method of sample collection, and/or the method of analysis. Specifics, such as tracer type, methods of sampling and analysis, and fudge-factor multipliers, should generally be regarded as inappropriate when calculating necessary tracer mass unless a clear scientific basis for such can be established (e.g., solution conduit sinuosity ≤ 1.5).

Review of tracer-mass estimation equations

S. Worthington (personal communication) examined more than 3,000 tracer tests and was able to fit a straight line through a double logarithmic plot in two separate instances. In the first instance a double-logarithmic plot of *Mass* injected versus *Time* × *Discharge* × *Concentration* showed a clear relationship defined by Eqs. (1a), (1b) (see Table 3). In the second instance a double-logarithmic plot of *Mass* injected versus *Length* × *Discharge* × *Concentration* also resulted in a clear relationship defined by Eq. (2) (see Table 3). Equations (1a)–(2) (see Table 3) provide a means for estimating the mass of dye to be injected such that positive tracer recoveries are likely.

Equations (3)–(7a) (see Table 3) were published by Parriaux and others (1988) in a tracing guide that was intended to be practical, but is obscure and difficult to obtain. Equation (7b) (see Table 3) is a slightly more complicated form of Eq. (7a). According to Parriaux and others (1988), citing Zötl (1974, p. 60), Eqs. (3)–(7a) (see Table 3) were developed for Na-fluorescein, but may be used for tracing with *Lycopodium* spores by using 1.5–2.0 times the weight of Na-fluorescein. Zötl further suggests that higher amounts can only be advantageous. Equations (3)–(5b) (see Table 3) also include an aquifer and/or tracer-dependent coefficient T_{Ci} (Table 4) intended to adjust the tracer mass to be injected. Equation (4) is valid for Na-fluorescein, but for eosin (45380 C.I. Acid Red 87), five to ten times more dye is required (Parriaux and others 1988, p. 7). Zötl (1974, p. 54) suggests that while Eq. (5a) is appropriate for Na-fluorescein sorption onto detectors, 2.5 to 3.5 times more dye is required for water samples [Parriaux and others (1988, p. 8) incorrectly quotes Zötl as stating two to three times more dye]. Although not stated, Zötl was probably referring to visual detection of fluorescent dye in water when detectors are not being used. Equation (5b) appears similar to Eq. (5a), but the full citation and primary reference are not provided in Milanović (1981, p. 276) and includes a tracer-dependent coefficient T_{C4} that may be a misprint or is an incorrect reproduction from Zötl (1974, p. 54).

Equations (6)–(7b) (see Table 3) include a sorption coefficient A_{di} intended to increase tracer mass to be injected for which units are either not clearly provided [Eq. (6)] or are inconsistent with common application [Eqs. (7a), (7b)]. For Eq. (6) Parriaux and others (1988, p. 8) recommend $t_d=3\ L/v$ suggesting that the tracer test duration is expected to be three times the mean residence time distribution $\bar{t}$. For Eqs. (7a), (7b) $A_{d2}=1.0$ mg m^{-3} for Na-fluorescein and $A_{d2}>1.0$ mg m^{-3} for all other dyes depending on their respective sorption characteristics (Käss 1998, p. 325).

Equations (7a), (7b) includes an additional "safety factor" S_f which is not intended to protect human health or the environment from excessive tracer-mass releases. Rather, S_f is intended to ensure adequate tracer-mass injection by acting as a fudge-factor multiplier to increase the mass of tracer to be released. Equation (7b) is the equivalent of Eq. (7a) adjusted for some tracer-entrance angle other than 30°. The original form of Eq. (7b) listed in Käss (1998, p. 325) includes what appears to be some time value multiplied by gravitational acceleration g, but these parameters are not identified and no units are provided. It is probable that Eq. (7b) required multiplication by g^{-1} in suitable units. For this review, Eq. (7b) has been appropriately adjusted.

Equations (8)–(28) (see Table 3) are generally similar to Eqs. (3)–(7b) (see Table 3). Equation (8) was intended for visual detection of Na-fluorescein. Equations (9), (10), and (11) each include an aquifer and/or tracer-dependent coefficient T_{Ci} (Tables 4, 5, 6, and 7). Equation (12) is listed as being valid only when $Q \leq 5.0$ m^{3}s^{-1} and $L \geq 12$ km. Equation (13) utilizes a ratio of swallet inflow to spring discharge Q/q although this reasoning is not explained. Equation (13) is expected to overestimate tracer mass for predominantly vadose systems >1 km (Gaspar 1987, p. 49).

Equation (14) is intended for use with In-EDTA and also includes a loss coefficient P=1–3 and safety factor $S_f < 2$. The loss coefficient P represents the ratio of mass injected to the mass recovered and is justified on the reasoning that some mass of the tracer will be retained in the system (Gaspar 1987, p. 50). Setting $S_f<2$ is not explained.

Equations (15) and (16) rely on a set amount of Na-fluorescein to be injected per rate of spring discharge or swallet inflow, respectively. These two equations are probably intended for visual detection and reportedly reduced amounts of fluorescent dye could be released if detectors are used for dye sorption (Sweeting 1973, p. 228).

Table 4
Aquifer and tracer-dependent coefficients T_{C1}–T_{C4}[a]

Aquifer	Tracer	T_{C_i}
Tracer-dependent coefficient, T_{C_1}		
Clay		5–20
Sand		2–10
Fractured rock		2–20
Karst		2–10
Tracer-dependent coefficient, T_{C_2}		
Porous media		5.0×10^2
Fractured rock		3.0×10^3
Tracer-dependent coefficient, T_{C_3}		
Very permeable aquifers	Na-fluorescein	2.5×10^{-1}
Slightly permeable aquifers		1.0×10^0
	NaCl	2.5×10^2
Tracer-dependent coefficient, T_{C_4}		
	Na-fluorescein	2.5×10^{-9}

[a]Source: modified from Parriaux and others (1988)

Table 5
Aquifer and tracer-dependent coefficient T_{C5}[a]

Tracer dye	Clay stone	Sandstone	Fractured rock	Karst
Na-fluorescein	0.5–2.0	0.2–1.0	0.2–2.0	0.2–1.0
eosin	0.5–2.0	0.2–1.0	0.2–2.0	0.2–1.0
erthrosine	1.0–4.0	1.0–3.0	1.0–4.0	1.0–4.0
congo red	2.0–8.0	2.0–6.0	2.0–8.0	2.0–8.0
Methyl blue	2.0–8.0	2.0–6.0	2.0–8.0	2.0–8.0
Spirit blue	2.0–8.0	2.0–7.0	2.0–8.0	2.0–8.0
Ponceau red	1.0–4.0	1.0–3.0	1.0–4.0	1.0–4.0

[a]Source: modified from Käss (1998, p. 325)

Table 6
Tracer-dependent coefficient T_{C6}[a]

Tracer material	T_{C_6}
Na-fluorescein	1.0×10^{0}
eosin	5.5×10^{0}
Sulpho-rhodamine G	2.0×10^{0}
Rhodamine B	1.5×10^{1}
Sulpho-rhodamine B	4.0×10^{0}
Rhodamine WT	2.0×10^{1}
pyranine	5.5×10^{0}
Na-napthionate	1.5×10^{1}
Tinopal	3.0×10^{0}
NaCl	2.0×10^{4}
KCl	1.0×10^{4}
LiCl	1.0×10^{3}
spores	1.5×10^{0}
surfactants	2.0×10^{1}
phages (particle count)	1.0×10^{13}
Serratia marcescens	1.0×10^{13}
microspheres	1.0×10^{12}
indium	1.0×10^{-1}

[a]Source: modified from Käss (1998, p. 327)

Table 7
Prevailing test conditions coefficient T_{C7}[a]

Prevailing condition	T_{C_7}
Rapid flow in channels	0.1–0.9
Photosensitive decay	2.0–4.0
Surface-water flow $Q > 3.6 \times 10^{6}$	2.0–4.0
River-bank filtration $Q \leq 1.8 \times 10^{4}$	2.0–4.0
Ground-water flow $K < 3.6$	2.0–4.0
Fractured rock studies with $\psi > 60°$	2.0–4.0
Unsaturated zone 1–30 m thick	2.0–4.0
Low tracer-background levels	2.0–4.0
Turbid samples or sample with natural fluorescence	2.0–4.0
Unsaturated zone >30 m thick	5.0–10.0
Soil zone with cohesive soils	5.0–10.0
Studies near a ground-water divide	5.0–10.0
Multiple recovery stations likely	5.0–10.0

[a]Source: modified from Käss (1998, p. 328)

Equations (18), (21), and (22) were published by Aley and Fletcher (1976) in a tracing guide also intended as practical. Equation (18) is listed as being applicable for surface water and was intended for time-of-travel studies using Rhodamine WT. It includes an unidentified multiplier that may be a unit conversion factor although this is not clear. The original form of Eq. (18) is reported as a volume with units of milliliters (Aley and Fletcher 1976, p. 7), but this requires that the unidentified multiplier be a unit conversion factor representing tracer density. The multiplier appears much too large to solely represent tracer density so it is likely that it is a combined conversion factor representing density and a fudge factor. Equation (18) is a modification of the original equation by Aley and Fletcher (1976, p. 7) to obtain mass in grams on the assumption that the original equation really was intended to yield a volume in milliliters.

Equations (19)–(21) (see Table 3) represent a progression in development as technology improved (Haas 1959). Equation (19) was intended for visual detection and relates a specific amount of tracer-dye mass to discharge and distance. Equation (20) was intended for ultraviolet-light enhancement and relates tracer-dye mass to system volume and distance. Equation (21) was intended for adsorption onto activated carbon and relates tracer-dye mass to discharge and distance, but may be expected to yield excessive amounts of tracer material (Aley and Fletcher 1976, p. 9).

Equation (22) is intended for tracing ground-water flow using Na-fluorescein and is applicable to waters of pH >5.5, transport via solution conduits, and dye sorption by detectors. Substituting Rhodamine WT for Na-fluorescein requires two to ten times more tracer dye (Aley and Fletcher 1976, p. 9). This equation supposedly results in reduced tracer quantities because it does not rely on proposed downstream C_p (Aley and Fletcher 1976, pp. 7–9), the unsuitable aspect of which is not clear.

Equations (23)–(27) (see Table 3) specifically relate to actual dye mass, mix English and metric units, and require multiplication by unidentified unit conversion factors. Each of these four equations require use of the specific tracer-dye factors of density and purity, but were primarily intended for use with liquid Rhodamine WT. Equations (23)–(25) were intended for discharge measurements in surface-water streams where Eqs. (23) and (24) represent an impulse release and Eq. (25) a long pulse release (e.g., $t_2>\bar{t}$). Equation (25) appears very differently in the three primary references (Table 3), but application of consistent units and simplification shows that the original forms of Eq. (25) are identical. Equation (26), a slight modification of Eq. (24), was intended for tracing solution conduits and includes the multiplier 1.5 to account for solution-conduit sinuosity. Equation (27) was designed for time of travel studies in surface-water streams and will produce slightly different results when compared with results obtained from Eq. (23) (Kilpatrick and Wilson 1989, p. 14) and Eq. (24).

Equation (28) is identified as a USA "rule of thumb" formula for determining the appropriate mass of *Lycopodium* spores to release. It relates a percentage of discharge with a percentage of distance to obtain the mass needed (Käss 1998, p. 325).

Equations (29)–(33) (see Table 3) are somewhat different from the majority of the previous equations. Equation (29) has also been generally considered a rule of thumb in the United States for tracing flow in solution conduits. Contrary to most of the previous 28 equations, Eq. (29) does not rely on discharge to determine the appropriate tracer mass to be used. Rather, Eq. (29) relies on mass associated with a specific tracer-dye type required for the expected travel distance (Table 8). It was originally intended for visual dye confirmation in elutant (I=1.0), but use of analytical instruments has allowed a reduction in required tracer mass (I=0.01 to I=0.1). For tracing in the Appalachians, approximately five times as much dye is needed for success (Quinlan, personal communication).

Equations (30) and (31) (see Table 3) are considered valid for tracing water flow in solution conduits using Na-fluorescein (Käss 1998, p. 324). For Eq. (30), S_m=1.0 for L>100 m up to some unspecified upper limit and S_m=2.0

Table 8
Tracer-dye mass per 1,000 m of traced distance

Tracer material	T_{M_3}, grams
Na-fluorescein	282
Rhodamine WT	280
Diphenyl brilliant flavine 7GFF	≥846
Tinopal 5BM GX	≥846
Tinopal BBH pure	≥846
Phorwite AR	1,694

for L>1,000 m also up to some unspecified upper limit. Equation (31) suggests 1 to 2 g of dye per 100 m^3 of water to be traced.

Equations (32) and (33) (see Table 3) are for different conditions than the previous 30 equations. Equation (32) was designed to estimate tracer mass for lakes and estuaries with a 1 μg L^{-1} average concentration at the expected sampling locations. Equation (33) was designed for phage tracing and includes a phage factor. It appears to be little different from the other equations in that it also relies on discharge and peak arrival. However, it utilizes a phage factor and rather than having units of mass in grams it has units of N_p m^{-3} where N_p represents the number of phage. Flow discharge is clearly the main factor for the majority of the 33 equations listed suggesting tracer-dilution estimates were an overriding concern during development. Expected transport distance or transport time are also generally common elements. All other factors included in the equations were intended to address either known complications (e.g., transport distance) or unknown complications (e.g., sorption) that are expected to influence final downstream concentrations.

It should be noted that many of the parameters listed in Table 3 require preliminary calculations. For example, $t_d=3\,\bar{t}$ (Parriaux and others 1988, p. 8) for tracer tests in solution conduits may be estimated from

$$t_d = \frac{3L}{v} = \frac{3LA}{Q} \tag{34}$$

and t_d for forced-gradient tracer tests in porous media may be estimated from

$$t_d = \frac{3L}{v} = \frac{3L^2\pi b n_e}{Q} \tag{35}$$

Such essential calculations are not immediately obvious, however.

It is also necessary to point out that any equations requiring tracer purity T_p in the calculations [e.g., Eqs. (18), (23)–(27)] will be greatly affected by minor changes in the value of T_p. For these equations, fluorescent-dye type can profoundly affect how much tracer will be recommended because of the varying concentrations of different dyes and whether they are liquids or powders.

Review of sampling frequencies

The most uncertain aspect of any tracing study is the schedule for sample collection (Kilpatrick and Wilson 1989, p. 16). Whereas much effort has gone into estimating tracer mass for a tracing study, very little appears to have been done in terms of determining sample-collection frequency. Sampling frequencies are generally based on travel distances, which suggests a direct relationship between travel distance and expected time of arrival. This relationship is obviously correct, but is ambiguous because transport velocity as a function of residence time is unknown. Transport velocities can achieve extreme ranges rendering invalid sampling schedules based on transport distances that are devoid of residence time estimates.

Tracer-test sampling frequencies are typically based on two approaches. In the first instance, for transport via solution conduits, tracer recovery from qualitative-tracing tests (e.g., sorption of fluorescent dyes onto detectors) that are sampled every few hours, days, or weeks (most commonly every 1–2 weeks; Alexander and Quinlan 1992, p. 21) serves as a basis for determining appropriate sampling frequencies for quantitative-tracing tests. Sampling schedules based on qualitative tracing tests have been found to result in false positive results (Field 2000, pp. 11–14) and false negative results (Smart and others 1986), and cannot be relied upon for predicting sampling times. In the second instance, sampling frequencies may be based on transport distances from tracer-injection points to expected tracer-recovery stations with due consideration to travel times. For surface-water streams, Kilpatrick and Wilson (1989, p. 16) suggest that

$$t_p = 2.78 \times 10^{-4}\frac{L}{v_p} \tag{36}$$

can be used to determine when to initiate sampling for detection of the tracer-leading edge and 10% of the trailing edge. Leading edge is given by (Kilpatrick and Wilson 1989, p. 18)

$$t_l = t_p - \frac{t_{d_{10}}}{3} \tag{37}$$

and 10% of the tracer-trailing edge by (Kilpatrick and Wilson 1989, p. 18)

$$t_{t_{10}} = t_p + \frac{2t_{d_{10}}}{3} \tag{38}$$

Although no criteria were specified, Kilpatrick and Wilson (1989, p. 18) suggest that the number of samples to be collected can be determined by dividing t_{d10} by 30, which will result in an appropriate sampling frequency necessary for describing the tracer-breakthrough curve (BTC).

A general sampling schedule is shown in Table 9 (Milanović 1981, p. 275; Gaspar 1987, p. 57) where sampling times are based on travel distance and daily lack of tracer recovery. A site-specific schedule is shown in Table 10 (Käss 1998, p. 333) where sampling times are based on travel distance and lack of timely recovery. In both these instances sampling frequency was initially determined as a factor of transport distance, but is iteratively adjusted to longer times as tracer recovery is delayed.

A simpler, but more realistic method uses average expected travel velocity based on current-meter measurements for surface streams. For a porous medium,

Table 9
General sampling schedule for a karst terrane[a]

Distance (km)	Sampling interval (h)					
	Day 1	Day 2	Day 3	Days 4–6	Day 6	Day 15
1	2	3	4–6	8–12	24	24
1–10	4	6	8	12	24	48
>10	12	12	12	12	24	48

[a]Source: modified from Milanović (1981, p. 275) and Gaspar (1987, p. 57)

Darcy's law may be used to gain a general sense of tracer time of arrival provided required parameters (e.g., effective porosity) are available. For solution conduits an expected average transport velocity equal to 0.02 m s^{-1} may be used as the basis for designing a sampling schedule (Gareth Davies, personal communication). This average transport velocity of 0.02 m s^{-1} was statistically determined by regression analyses of more than 3,000 tracing tests worldwide (S. Worthington, personal communication). It has been suggested that sampling frequency should not be based on average velocity because the leading edge will be missed (Kilpatrick and Wilson 1989, p. 12), but this can be overcome by recognizing that the average velocity is a rough estimate and represents a rough average travel time. The suggested sampling frequency can be appropriately adjusted to ensure that initial sample collection begins prior to likely tracer breakthrough.

Efficient hydrologic tracer-test design

To better facilitate tracer testing in hydrologic systems, a new efficient hydrological tracer-test design (EHTD) methodology has been developed (Field 2001a). Unsuccessful quantitative tracer tests using several of the tracer-mass estimation equations listed in Table 3, recommended sample-collection frequencies listed in Tables 9 and 10, and previous qualitative tracer-test results led to the development of EHTD. Application of EHTD to the study site resulted in successful tracer tests and showed that good tracer-test design can be developed prior to initiating a tracer test (Field 2000, p. 26).

Basic design of EHTD

EHTD is based on the theory that field-measured parameters (e.g., discharge, distance, cross-sectional area) can be combined in functional relationships that describe solute-transport processes related to flow velocity and times of travel. EHTD applies these initial estimates for times of travel and velocity to a hypothetical continuous stirred tank reactor (CSTR) as an analog for the hydrological flow system to develop initial estimates for tracer concentration and axial dispersion based on a preset average tracer concentration. Root determination of the one-dimensional advection–dispersion equation (ADE) using the preset average concentration then provides a theoretical basis for an estimate of necessary tracer mass. Application of the predicted tracer mass with the hydraulic and geometric parameters in the ADE allows for an approximation of initial sample-collection time and subsequent sample-collection frequency where 65 samples have been empirically determined to best describe the predicted BTC.

Range of capabilities of EHTD

While most of the tracer-mass estimation equations listed in Table 3 were designed for tracing in solution conduits in karstic terranes, there appears to be no logical reason to exclude porous media systems, which may explain why Parriaux and others (1988, p. 9) provided an example using both karstic and porous media systems. Recognizing that solute-transport processes operative in hydrological systems all follow the same basic theoretical principles suggests that an appropriate model for estimating tracer mass would function effectively for all hydrological systems. However, such a model would need to be able to account for slight differences in the nature of the flow systems (e.g., effective porosity) and the manner in which the tracer test is conducted (e.g., tracer-release mode). Breakthrough curves predicted using the tracer-test design program, EHTD, for various hydrological conditions have been shown to be very reliable (Field 2001b). The hydrological conditions used to evaluate EHTD ranged from flowing streams to porous media systems so that the range of capabilities of EHTD could be assessed. The flowing streams used to evaluate EHTD included tracer tests conducted in small and large surface-water streams, a solution conduit, and a glacial-meltwater stream. The porous-media systems used to evaluate EHTD included natural-gradient, forced-gradient, injection-withdrawal, and recirculation tracer tests. Comparisons between the actual tracer tests and the

Table 10
Site-specific sampling schedule for a karst terrane[a]

Site no.	Distance (km)	Sampling interval (h)					
		Days 1–2	Days 3–4	Days 5–7	Days 8–14	Days 15–21	Days 22–49
1	0.60	2	4	6	12	24	56
2	0.95	2	4	6	12	24	56
3	1.40	4	6	12	24	24	56
4	2.90	4	6	12	24	24	56
5	5.00	4	6	12	24	24	56
6	11.00	12	12	24	24	24	56

[a]Source: modified from Käss (1998, p. 333)

results predicted by EHTD showed that EHTD adequately predicted tracer breakthrough, hydraulic characteristics, and sample-collection frequency in most instances.

Tracer-estimation equations and sampling frequencies testing

Tracer-test design examination parameters, provided by Parriaux and others (1988, p. 9) and reprinted in Käss (1998, p. 324), have previously been applied to a small set of the 33 equations listed in Table 3. Unfortunately, only a few selected equations were examined using the test examination parameters. Although no reasons were presented as to why only a small set of equations were examined using the test parameters, it is likely that one of the reasons was that additional parameters are necessary for testing the equations.

Examination of tracer-mass estimation equations

The tracer-test design examination parameters originally listed in Parriaux and others (1988, p. 9) and reprinted in Table 11 with additional parameters were applied to 32 of the 33 equations in Table 3. Liquid Na-fluorescein is considered as the tracer material used, which is conventionally available as a 30% solution (T_p=0.3) with a density of 1.2 g cm^{-3}. Equation (33) was not evaluated because it was designed for conditions other than those listed in Table 11.

Tracer-mass estimates using the tracer-test design examination parameters and Eqs. (1a)–(32) (see Table 3) resulted in tracer-mass estimates that ranged from a fraction of a gram of tracer to tens of thousands of grams of tracer (Table 12). Large tracer-mass ranges are probable using the same equation when variable hydrologic conditions and/or tracer dependent coefficients T_{Ci} are applied. Equation (25) is expected to produce greater tracer-mass estimates than the other equations because it is based on a long-pulse release ($t_2>\bar{t}$), which will also cause a much later real value for t_p than that listed in Table 11. For perspective, the results of Eqs. (1a)–(32) (see Table 3) may be compared with similar results produced by

$$M = \frac{T_p Q 10^6}{\delta(t)} \tag{39}$$

for an impulse release and

$$M = T_p Q t_2 10^6 \tag{40}$$

for a pulse release. Although Eqs. (39) and (40) were not found in any of the references listed in Table 3, it is likely

Table 11
Tracer test design parameters[a]

Parameter	Porous media	Karst
Q (m^3 h^{-1})	7.20×10^1	3.60×10^2
L (m)	5.00×10^2	3.00×10^3
W (m)	1.00×10^2	1.00×10^2
V (m^3)	1.00×10^5	3.00×10^5
b (m)	1.00×10^1	1.00×10^2
n_e	1.00×10^{-2}	1.00×10^1
υ (m h^{-1})	4.17×10^{-1}	4.17×10^1
q^{b} (m^3 h^{-1})	7.20×10^{-1}	3.60×10^1
t_d (h)	3.60×10^3	2.16×10^2
t^c_p (h)	1.20×10^3	7.20×10^1
C_p (mg m^{-3})	1.00×10^1	1.00×10^1
A_d (mg m^{-3})	1.00×10^0	1.00×10^0
θ^{d} (rad)	5.24×10^{-1}	5.24×10^{-1}
S_f	1.00×10^0	1.00×10^0
t_e^2 (h)	1.56×10^3	9.63×10^1
T_{C1}	5.00×10^0	2.00×10^0
T_{C2}	3.00×10^3	5.00×10^3
T_{C3}	2.50×10^{-1}	2.50×10^{-1}
T_{C4}	2.50×10^{-9}	2.50×10^{-9}
T_{C5}	5.00×10^{-1}	5.00×10^{-1}
T_{C6}	1.00×10^0	1.00×10^0
T_{C7}	5.00×10^{-1}	5.00×10^{-1}
T_{M1} (g)	2.00×10^3	2.00×10^3
T_{M2} (g)	2.40×10^4	2.40×10^4
T_ρ (g cm^{-3})	1.20×10^0	1.20×10^0
T_p (g g^{-1})	3.00×10^{-1}	3.00×10^{-1}
A_{pp}	5.00×10^0	1.00×10^0
I	1.00×10^{-1}	1.00×10^{-1}
S_m	1.00×10^0	1.00×10^0

[a] Source: modified from Parriaux and others (1988, p. 9)
[b] q=Q/100
[c] $t_p=t_d/3$; assume $\bar{t}=t_p$
[d] $\theta=30°$
[e] $t_2=1.3t_p$

Table 12
Tracer-mass estimates in grams (see Table 3 for cited equations)

Equation	Porous media (g)	Karst (g)
1a	2.63×10^2	8.80×10^1
2	2.00×10^0	4.12×10^1
3	2.50×10^2	6.00×10^2
4	3.00×10^3	1.56×10^2
5a	2.50×10^0	7.50×10^1
5b	2.50×10^{-8}	7.50×10^{-7}
6	1.30×10^3	3.89×10^2
7a	2.92×10^3	1.77×10^5
7b	2.92×10^3	1.76×10^5
8	1.00×10^1	3.00×10^2
9	1.25×10^{-4}	7.50×10^{-4}
10	2.50×10^2	1.50×10^3
11	3.50×10^3	1.50×10^3
12	5.12×10^2	3.36×10^3
13	1.00×10^3	3.00×10^4
14	3.00×10^0	9.00×10^{-1}
15	4.00×10^1	2.00×10^2
16	4.80×10^0	2.40×10^1
17	9.00×10^2	2.70×10^4
18	4.15×10^2	1.24×10^2
19	3.60×10^2	1.80×10^3
20	4.75×10^8	8.55×10^9
21	9.84×10^1	2.95×10^3
22	2.29×10^2	1.25×10^2
23	3.05×10^2	9.15×10^1
24	4.16×10^3	1.24×10^2
25	1.35×10^3	4.04×10^2
26	6.24×10^2	1.87×10^2
27	4.83×10^2	1.56×10^2
28	1.80×10^3	5.40×10^4
29	7.05×10^1	8.46×10^1
30	5.00×10^2	3.00×10^3
31	1.00×10^3	3.00×10^3
32	5.00×10^2	1.50×10^3

that they are commonly used because they exhibit mass balance. However, there appears to be no reason to believe that either would yield reasonable results because Q is the only included flow-system parameter.

Porous media

Application of Eqs. (1a)–(32) (see Table 3) to the porous-media examination parameters listed in Table 11 resulted in tracer-mass estimates that ranged from 2.5×10^{-8} to 4.75×10^{8} g, or a difference of >16 orders of magnitude (Table 12). If Eqs. (5b), (9), and (20) are removed from consideration the difference is three orders of magnitude. Equations (5b) and (9) may legitimately be removed from consideration on the assumption that T_{C4} was misprinted in Milanović (1981, p. 276). Equation (20) may also include a misprint (volume rather than discharge). A range of three orders of magnitude for tracer mass is difficult to resolve without additional information or site-specific experience.

For comparison purposes, Eqs. (39) and (40) would yield 2.16×10^{7} and 3.37×10^{10} g for the impulse and pulse releases, respectively. The results of Eq. (39) appears greater than all but Eq. (20) whereas the results of Eq. (40) is greater than all 32 examined equations (Table 12). Equations (20), (39), and (40) (see Table 3) likely represent an absolute upper range of mass to release and are probably excessive and possibly harmful (Field and others 1995; Behrens and others 2001).

Karstic media

Results of the karstic-media examination parameters listed in Table 11 in Eqs. (1a)–(29) (see Table 3) produced tracer-mass estimates that ranged from 7.50×10^{-7} to 8.55×10^{9} g, a difference also of >16 orders of magnitude. Removing Eqs. (5b), (9), and (20) results in a difference of five orders of magnitude. As with the porous-media case, such a large range is difficult to resolve without additional information or site-specific experience.

Equations (39) and (40) resulted in 1.08×10^{8} and 1.01×10^{10} g for the impulse and pulse releases, respectively. Equation (39) resulted in an estimated mass greater than all but Eq. (20) (Table 12) while the results of Eq. (40) is greater than all 32 examined equations (Table 12). Similar to the porous-media estimates, Eqs. (20), (39), and (40) likely represent an upper limit for tracer mass to release and are probably excessive and possibly harmful (Field and others 1995; Behrens and others 2001).

EHTD analyses of the two types of tracer tests

Similar to the 33 equations listed in Table 3, use of the EHTD methodology requires that specific flow-system parameters be measured or reasonably estimated. Shown in Table 13 is a subset of parameters from Table 11 that represent the required parameters necessary for evaluation by EHTD. From Table 13 it is apparent that only measurable parameters related to the hydraulics of the flow system are required for EHTD analysis. The two tracer-specific parameters, retardation and decay, and the sinuosity factor are not required, however. The sinuosity factor is an adjustable multiplier ≤ 1.5 that is similar to that used in Eq. (26) except that Eq. (26) requires inclusion of S_n=1.5. It is also used by EHTD to increase the measured straight line distance by an appropriate distance because natural solution conduits are not constrained to perfectly straight channels.

Table 13
EHTD tracer test design parameters

Parameter	Porous media	Karst
Q (m^3 h^{-1})	7.20×10^{1}	3.60×10^{2}
A^a (m^2)		8.63×10^{0}
L (m)	5.00×10^{2}	3.00×10^{3}
W (m)	1.00×10^{2}	
b (m)	1.00×10^{1}	
n_e	1.00×10^{-2}	
q (m^3 h^{-1})	7.20×10^{-1}	3.60×10^{0}
C_p (mg m^{-3})	1.00×10^{1}	1.00×10^{1}
$t_2{}^b$ (h)	1.56×10^{3}	9.63×10^{1}
$S_n{}^c$		1.00×10^{0}
$R_d{}^c$	1.00×10^{0}	1.00×10^{0}
μ^c (h^{-1})	0.00×10^{0}	0.00×10^{0}

[a] For this analysis $A=Q/\upsilon$ for the karstic spring. Normally Q and A would be measured concurrently and the solution $\upsilon=Q/A$ used by EHTD

[b] Parameter required by EHTD for pulse and continuous releases

[c] These parameters not required by EHTD

Although not presented in Table 13 EHTD also requires that the type of flow system tracer test be identified, the type of release be identified, and the time for tracer injection be identified in an attempt to ensure universality. The type of flow system tracer test can simply be a flowing stream (open-channel or closed-conduit flow = surface-water stream or solution conduit) or it can be porous media. EHTD analysis of porous-media systems additionally requires consideration of any one of the following hydraulic conditions:

1. Natural gradient-tracer test.
2. Forced gradient-tracer test (extraction well).
3. Injection/withdrawal test (injection-well rate = pumping-well rate).
4. Recirculation test (injection-well rate = pumping-well rate while recirculating the tracer back to the injection well).

The tracer-test parameters listed Table 13 relate to a solution conduit tracer test and forced gradient porous-media tracer test, the latter assumed because of the relatively high discharge rate (72 m^3 h^{-1}) provided by Parriaux and others (1988, p. 9).

Type of tracer release refers to three methods of tracer injection: impulse, pulse, and continuous releases. Impulse (instantaneous) releases are the most common tracer-injection method for karstic systems whereas pulse releases (slow release over some period of time) are the most common tracer-injection method for porous media systems. Continuous releases are rarely employed in either system primarily because of cost. For the porous media and karstic tracer test parameters listed in Tables 11 and 13, impulse releases were assumed except for Eq. (22) in which a long pulse release was assumed.

Time for tracer injection only refers specifically to tracer-injection time, but also may include pre- and post-tracer injection flush water to account for additional dilution effects. Total dilution volume V_D is obtained from

$$V_D = (q + Q)\bar{t} \tag{41}$$

which should not be considered a technically correct approach. However, it does yield good approximations for dilution effects, which will usually be equal to or greater than the system volume V calculated from the total discharge for the duration of the tracer test. For this analysis V_D was of some significance because q was fairly significant.

EHTD results

Application of EHTD to the parameters listed in Table 13 resulted in tracer-mass estimates of 525 g for the impulse release and 1,950 g for the pulse release for the porous media tracer test and 102 g for the impulse release and 631 g for the pulse release for the karstic tracer test (Table 14). To obtain these results, EHTD uses an average concentration $\bar{C}$ rather than a peak concentration C_p. For this analysis, the peak concentration used in Eqs. (1a)–(32) (see Table 3) was taken as the average concentration. The effect of taking $C_p = \bar{C}$ was relatively insignificant because $R_d = 1$ and $\mu = 0$ (Field 2001a).

Hydraulic parameters from EHTD simulations of the porous media and karstic tracer tests are shown in Table 14. Tracer-breakthrough curves for impulse releases for the porous-media and karstic tracer tests are shown in Figs. 1 and 2, respectively and BTC for pulse releases for the porous-media and karstic tracer tests are shown in Figs. 3 and 4, respectively. The parameters listed in Table 14 were all calculated by EHTD using the parameters listed in Table 13. Some of the EHTD-calculated parameters listed in Table 14 approximate the same parameters listed in Table 11 (e.g., υ). However, important transport parameters such as axial dispersion D_L and Péclet number P_e are uniquely calculated by EHTD. Although these parameters may only be crudely approximated by EHTD, it has been shown that these parameter estimates are generally reasonable (Field 2001b). Also, although $\bar{t}$ remained unchanged regardless of the type of tracer release employed, t_p and C_p were greatly increased when a long-pulse release was employed (Table 14) for the respective hydrologic systems. A long pulse release also causes an earlier t_1, but a greater t_f (Table 14).

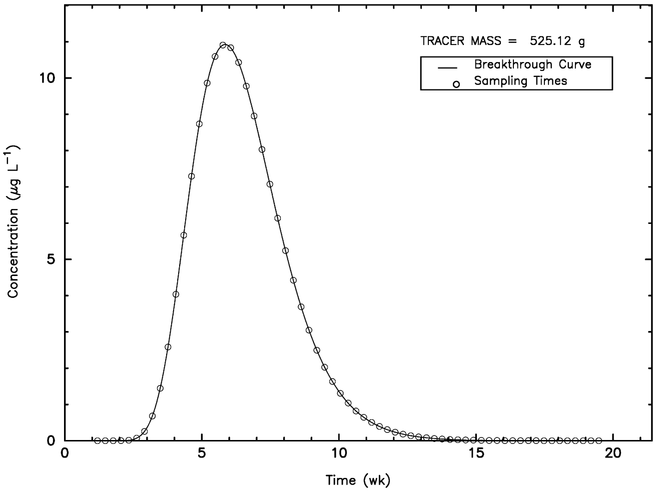

Fig. 1
EHTD results for an impulse release for the porous media test parameters

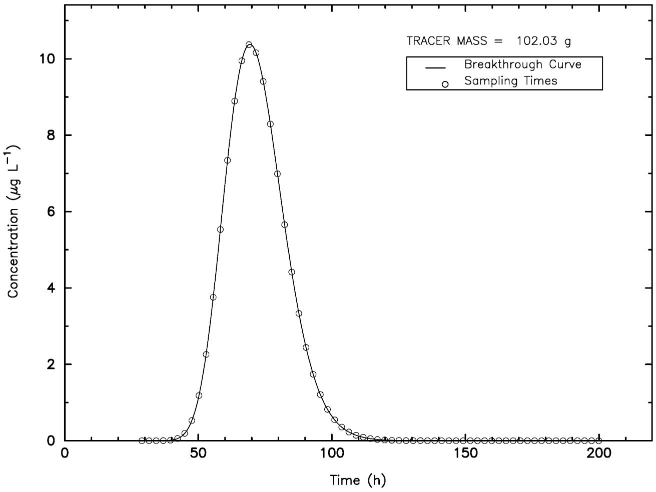

Fig. 2
EHTD results for an impulse release for the karstic test parameters

Table 14
EHTD tracer test analysis results

Parameter	Porous media	Karst
M^a (g)	5.25×10^2	1.02×10^2
M^b (g)	1.95×10^3	6.31×10^2
$\bar{t}$ (h)	1.09×10^3	7.19×10^1
$t_p{}^a$ (h)	9.82×10^2	6.90×10^1
$t_p{}^b$ (h)	1.93×10^3	1.31×10^2
υ (m h^{-1})	4.58×10^{-1}	4.17×10^1
$\upsilon_p{}^a$ (m h^{-1})	5.09×10^{-1}	4.35×10^1
$\upsilon_p{}^b$ (m h^{-1})	2.59×10^{-1}	2.30×10^1
$D_L{}^a$ (m^2 h^{-1})	7.99×10^0	1.52×10^3
$D_L{}^b$ (m^2 h^{-1})	2.09×10^1	2.44×10^3
α^a (m)	1.74×10^1	3.64×10^1
α^b (m)	4.56×10^1	5.86×10^1
$P_e{}^a$	2.87×10^1	8.25×10^1
$P_e{}^b$	1.10×10^1	5.12×10^1
$t_1{}^a$ (h)	1.92×10^2	2.90×10^1
$t_1{}^b$ (h)	2.16×10^2	1.80×10^1
$t_f{}^a$ (h)	4.80×10^1	3.00×10^0
$t_f{}^b$ (h)	9.60×10^1	5.00×10^0
$t_d{}^a$ (h)	3.27×10^3	2.00×10^2
$t_d{}^b$ (h)	6.56×10^3	3.41×10^2
$C_p{}^a$ (mg m^{-3})	1.09×10^1	1.04×10^1
$C_p{}^b$ (mg m^{-3})	1.63×10^1	1.87×10^1
V_D (m^3)	7.93×10^4	2.61×10^4
V (m^3)	7.85×10^4	2.59×10^4

It will be noted that $V = 7.85 \times 10^4$ and $V = 2.59 \times 10^4$ for the porous media and karstic tracer tests, respectively. These

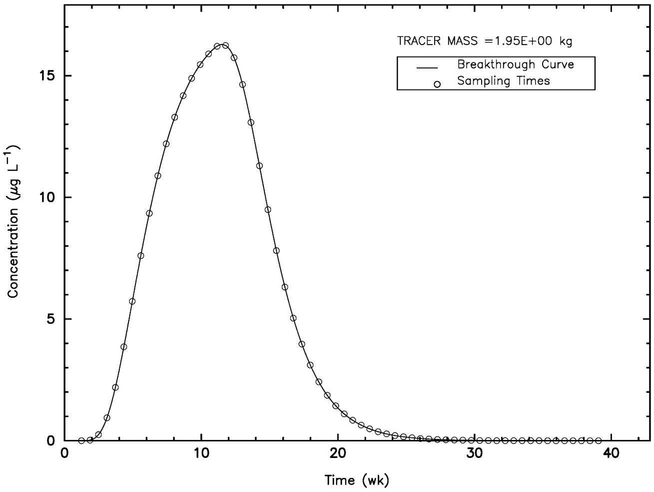

Fig. 3
EHTD results for a pulse release for the porous media test parameters

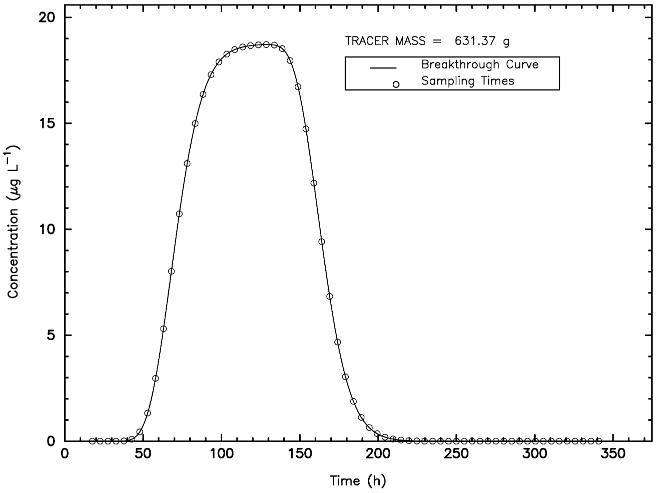

Fig. 4
EHTD results for a pulse release for the karstic test parameters

volumes are much greater than the volumes listed in Table 11. The difference is a result of arbitrarily choosing of V (Parriaux and others 1988, p. 9) as opposed to calculating V using an accepted approach such as

$$V = \frac{QL}{v} \qquad (42)$$

Applying Eq. (42) results in V=8.64 × 10^4 m^3 and V=2.59 × 10^4 m^3 for the porous-media and karstic tracer tests, respectively. Utilizing these recalculated volumes in the equations listed in Table 3 did not significantly change the results of Eq. (4), but caused a slight decrease in the results of Eqs. (20) and (31) and a substantial decrease in the results of Eq. (32) (Table 15). Although not expected, the estimated mass using Eq. (32) with the improved estimates for V was in better agreement with the EHTD-predicted mass for the karstic media tracer test.

Table 15
Tracer-mass estimates in grams (see Table 3 for cited equations)

Equation	Porous media (g)	Karst (g)
4	3.00×10^3	1.51×10^2
20	4.10×10^8	7.38×10^8
31	8.64×10^2	2.59×10^2
32	4.32×10^2	1.30×10^2

EHTD porous media analysis results

Comparison with EHTD-estimated tracer mass for the impulse release for the porous media tracer test suggests that only Eqs. (12), (18), (23), (26), (30), and (32) (see Table 3) can reasonably be considered for estimating tracer mass. Of these, only Eq. (26) was greater than the EHTD-estimated tracer mass, the others being relatively low. Interestingly, Eq. (12) is considered invalid for these conditions (L<12 km) whereas Eq. (30) is considered valid for tracing solution conduits. Equations (18), (23), (26), and (32) were all intended for tracing surface water. For the pulse release, Eq. (25) underestimated M slightly relative to EHTD probably as a result of the lack of consideration for additional dilution effects caused by q.

EHTD karstic media analysis results

Comparison with EHTD-estimated tracer mass for the karstic tracer test suggests that only Eqs. (1a), (4), (5a), (18), (22), (23), (26), (27), and (29) (see Table 3) reasonably estimate the appropriate mass of tracer to release. Equations (1a), (5a), and (29) are low relative to the EHTD-estimated tracer mass while Eqs. (4), (18), (22), (23), (26), and (27) are relatively high. Equations (4), (5a), and (29) all require the use of multipliers representing tracer-dependent factors controlled by aquifer conditions. These multipliers may also assume a range of values, but only Eq. (29) is reasonably specific regarding the multiplier value to use for the given conditions. Similar to the porous media tracer test, the pulse release described by Eq. (25) underestimated M slightly relative to EHTD, again probably as a result of the lack of consideration for additional dilution effects caused by q.

Mass required as related to sorption by detectors

Several of the 33 equations listed in Table 3 [e.g., Eqs. (5a), (21), (22), and (29)] were specifically intended for sorption onto detectors allowing for reduced tracer-dye concentrations. For the porous media tracer test, Eqs. (5a), (19), (22), and (29) all resulted in a lower estimated tracer mass than the mass suggested by EHTD. For the karstic tracer test, Eqs. (5a), (19), (20), (21), and (22), (29) all resulted in greater tracer-mass estimates than suggested by EHTD. In general, the vast majority of the 32 of 33 equations listed in Table 3 and tested resulted in much greater tracer-mass estimates than suggested by EHTD for either the porous media system or the karstic system. Tracer-dye concentration enhancement by activated carbon should allow for much lower tracer-mass estimates than predicted by EHTD. However, the lack of a measurable and distinct BTC that is normally obtained when water samples are collected and analyzed prevents clear determination that the dye of interest has been recovered.

Travel times and sampling frequencies

Typically, users of Eqs. (1a)–(33) (see Table 3) would initiate sample-collection frequencies according to flow rates estimated using Darcy's law for porous media aquifers. Unfortunately, because hydraulic conductivity, hydraulic gradient, and effective porosity may not be available, Darcy's law is difficult to apply. For karstic aquifers, weekly or biweekly sample-collection schedules for qualitative tracer tests are conventionally employed. Alternatively, Tables 9 and 10 may be considered if water samples are to be collected. Rarely, an assumed karstic flow velocity of 0.02 $m\ s^{-1}$ may be considered in defining a sampling schedule.

Travel times

The suggested time of arrival for peak concentration t_p for the tracer-test design examination parameters (Table 11) of 50 days and 72 h for the porous and the karstic media case, respectively really represent $\bar{t}$. Because of the difficulty in estimating t_p prior to conducting a tracer test, $t_p \approx \bar{t}$ was taken as a necessary approximation. EHTD predicted t_p=41 and 81 days for the impulse and pulse releases for the porous media tracer test, respectively and t_p=70 h (3 days) and 131 h (6 days) for the pulse and impulse releases for the karstic media tracer test, respectively (Table 14). Clearly t_p was very well approximated by EHTD for both example tracer tests.

Using t_d=3 L/υ suggests expected tracer tests durations of 150 and 9 days for the porous-media and karstic system tracer tests, respectively (Table 11). EHTD, however, suggested 136 and 8 days for the porous media and karstic system tracer tests, respectively, for an impulse release (Figs. 1 and 2) and 274 and 14 days for the porous media and karstic system tracer tests, respectively, for a pulse release (Figs. 3 and 4, Table 14). These differences occurred because EHTD employs a slightly different process for estimating t_d. These latter times are relatively insignificant.

Sampling times

EHTD suggests appropriate sampling frequencies based on the type of flow system and the type of release. In all instances, sampling frequency suggestions are determined by the expected times of travel and the need to adequately define the BTC. Early detection of tracer breakthrough requires that sampling be initiated prior to initial tracer breakthrough. Sixty-five samples are recommended for adequate BTC definition, especially for instances in which BTCs may be multimodal or long tailed (Field 2001a). Application of weekly or biweekly sampling schedules or the sampling schedules listed in Tables 9 and 10 would fail to adequately define either BTC. Collecting samples for the EHTD-suggested durations t_d, listed in Table 14, would clearly define the entire BTC should the tracer tests conform to the ADE. If tracer recoveries were still strong beyond the EHTD-suggested durations, sampling analyses could continue unimpeded at the EHTD-suggested frequencies.

Porous media sampling times

Figures 1 and 3 depict the recommended sampling times for 65 samples that correspond, for impulse and pulse releases, respectively for the porous media case. Suggested sampling frequencies were 48 h for the impulse case and 96 h for a pulse release (Table 14). Initial suggested sample-collection times were 8 and 9 days after tracer injection for the impulse and pulse releases, respectively (Table 14).

Karstic media sampling times

Recommended sampling times for the karstic test, for impulse and pulse releases are shown in Figs. 2 and 4. Suggested sampling frequencies were 3 h for the impulse case and 5 h for a pulse release (Table 14). Initial suggested sample-collection times were 29 and 18 h after tracer injection for the impulse and pulse releases, respectively (Table 14).

Conclusions

Thirty-three tracer-mass estimation equations and the computer program, EHTD, were reviewed and tested using published test criteria. Testing 32 of the 33 equations and EHTD produced extreme ranges in the results. EHTD is the only method that was developed using established solute-transport theory. The other 33 equations were all developed empirically. Although the review and testing described does not provide a means for determining the best tracer-mass estimation method and sampling frequency method to employ, recent tracer-testing successes using EHTD suggests that EHTD may be more reliable than the other methods (Field 2000).

Sample-collection schemes were also reviewed and shown to be difficult to implement and unreliable because they are of such a haphazard nature. Application of Darcy's law for porous media cases was not applied because of insufficient test data, but Darcy's law is believed to be a reasonable model for designing a sampling schedule provided that difficult to obtain parameters (e.g., effective porosity) can be adequately estimated. For karstic media, application of an assumed average velocity equal to 0.02 $m\ s^{-1}$ for designing a sampling schedule can be effective provided tracer release and transport occur via solution conduits. Given the complexities and difficulties associated with the published 33 tracer-mass estimation equations and conventional sampling schemes, continued use of any of these tracer-mass estimation equations and/or sampling schemes must remain suspect at best. As shown by EHTD, these previously developed equations/methods fail to yield consistent results. Application of the more scientifically sound method developed in EHTD is more likely to assure successful tracer-test results (Field 2001a) and is suggested as a more reliable alternative.

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Appendix

Notation

A	Cross-sectional area of a spring (m^2)
A_{bd}	Absorptivity of dye sample (dimen.)
A_{bs}	Absorptivity of dye at 100% strength (dimen.)
A_{d1}	Tracer adsorption coefficient >1.0 ($mg\ m^{-3}$[?]) (note: adsorption is normally identified as a distribution coefficient in $mL^3\ g^{-1}$)
A_{d2}	Tracer adsorption coefficient ≥1.0 ($mg\ m^{-3}$) (note: adsorption is normally identified as a distribution coefficient in $mL^3\ g^{-1}$)
A_{pp}	Multiplier for Appalachian karst =5.0
α	Dispersivity $=\frac{D}{\upsilon}$ (m)
b	Aquifer thickness (m)
C_o	Initial (stock) dye concentration ($g\ L^{-1}$)
C_p	Expected peak tracer concentration ($mg\ m^{-3}$)
$\delta(t)$	Dirac delta (unit impulse) function with respect to time (h^{-1}) [Note: $\int_0^\infty \delta(t)\ dt=1$]
D_L	Axial dispersion ($m^2\ h^{-1}$)
g	Gravitational acceleration =978.039 at 0° latitude[?] ($cm\ s^{-2}$[?])
I	Multiplier for instrumental analysis =0.01–1.0
K	Aquifer hydraulic conductivity ($m\ h^{-1}$[?])
L	Expected tracer transport distance (m)
M	Calculated tracer mass to inject (g)
M_p	Number of phage to be release ($N_p\ m^3$)
n_e	Effective porosity (dimen.)
θ	Expected tracer entrance angle for transverse spread (degrees)
P_e	Péclet number $=\frac{\upsilon L}{D}$ (dimen.)
P	Expected ratio of injected tracer to recovered tracer (In-EDTA) representing tracer loss =1.0–3.0 (dimen.)
P_h	Phage factor and count $\approx 2.0 \times 10^{10}$ to 5.0×10^{10} (dimen.)
ψ	Tracer scattering angle (degrees)
q	Inflow rate at injection point ($m^3\ h^{-1}$)
Q	Well or spring discharge ($m^3\ h^{-1}$)
R_d	Tracer retardation (dimen.)
S_f	Safety factor to ensure adequate peak concentration for detection (dimen.)
S_m	Multiplier for tracer mass =1.0–2.0 (dimen.)
S_n	Sinuosity factor =1.0 × to 1.5 × (dimen.)
$\bar{t}$	Mean tracer travel time (h)
t_d	Expected duration of tracer test (h)
t_{d10}	Expected tracer test duration at 10% of the peak concentration (s)
t_1	Time for first sample to be collected (h)
t_2	Tracer injection time for a pulse injection (h)
t_f	Time interval for sample collection (h)
t_p	Expected time to peak tracer arrival (h)
t_{t10}	Trailing edge to 10% level (h)
T_{Ci}	Aquifer and tracer-dependent coefficients (Tables 4, 5, 6, and 7) (dimen.)
T_{M1}	Tracer-dye (fluorescein) mass to inject per spring discharge $=2.0 \times 10^3$ to 5.0×10^3 (g)
T_{M2}	Tracer-dye (fluorescein) mass to inject per inflow rate at injection point $=2.4 \times 10^4$ (g)
T_{M3}	Tracer-dye (Table 8) mass for 1,000 m transport distance (g)
T_p	Tracer purity $= \frac{C_o A_{b_d}}{C_o A_{b_s}} \times 100$ ($g\ g^{-1}$)
T_ρ	Tracer density ($g\ cm^{-3}$)
μ	Tracer decay (h^{-1})
υ	Mean velocity for tracer migration ($m\ h^{-1}$)
υ_p	Expected velocity for peak-tracer migration ($m\ s^{-1}$)
V	Flow system volume (m^3)
V_D	Dilution volume for a spring or well (m^3)
W	Transverse spread of tracer (m)

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