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Assessing Aquatic Ecotoxicological Risks Associated with Fluorescent Dyes Used for Water-Tracing Studies

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ABSTRACT

Hydrological tracer testing is the most reliable diagnostic technique available for identifying and quantifying hydrodispersive transport processes. As such, hydrologic tracing is an essential tool that is commonly used to establish flow trajectories, to understand solute-transport processes, and to develop human health and ecological risk assessments. Unfortunately, the use of anthropogenic materials to trace the flow of water may also impart another source of risk to human health and the environment. In general, attempts are usually made to deliberately release tracer agents at concentrations far below their recognized toxic levels. Ecotoxicologically safe levels for injection concentrations of fluorescent tracer agents are generally set at levels far below that which are necessary to maintain measurable downstream concentrations. Appropriate tracer test design is important, because incorrect tracer-mass estimates may result in the release of larger tracer masses than are necessary and that exceed expected environmental concentrations (EECs). To maintain tracer concentrations at or below accepted levels, optimal tracer-test design is essential and may be achieved using the Efficient Hydrologic Tracer-Test Design methodology. By applying an optimal tracer-test design, it is more likely that downstream tracer EECs will be maintained at or below accepted concentrations while maintaining sufficiently high downstream EECs necessary for positive tracer detection.

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1. INTRODUCTION

Flow tracing using anthropogenic tracers, such as fluorescent dyes, is a well-documented diagnostic tool commonly employed in experimental investigations of chemical, biological, and physical systems (Weinstein and Duduković, 1975; Levenspiel, 1999; Schudel et al., 2002; and Flury and Wai, 2003). An anthropogenic tracer is any substance foreign to the environment of interest that adequately labels the flow medium for later detection. Tracers are typically applied to flow systems of interest in which simple flow connections need to be established or in which the use of a tracer will yield important hydrological information that would otherwise be difficult or impossible to acquire.

Determining when, where, and at what concentrations a tracer will arrive is at the heart of all tracer experiments. Brouyère (2003, p. 10) addresses the when, where, and how much in terms of contaminants, but the principle may be applied to the use of a tracer as well (Figure 1). As is the case with release of pollutants in the environment, there are three practical questions regarding the release of a tracer that need to be addressed and that are most succinctly stated as follows (Figure 1):

1. How long will it take for the tracer to reach the downgradient receptor?
2. At what concentration level(s) will the tracer be recovered?
3. For how long will the tracer persist?

The results of tracer tests can then be evaluated directly or they can be evaluated numerically to elucidate specific transport properties (Field, 2002d). It should be noted in Figure 1 that concentration (C), first arrival time (t_1), and final arrival time (t_f) are somewhat ambiguous in that their level of importance depends greatly on perception and practical limitations. The concern for C depends on what is considered a significant risk for the particular tracer, such as peak concentration (C_p), while the values for t_1 and t_f depend on a selected concentration and instrument sensitivity. Figure 1 may also be

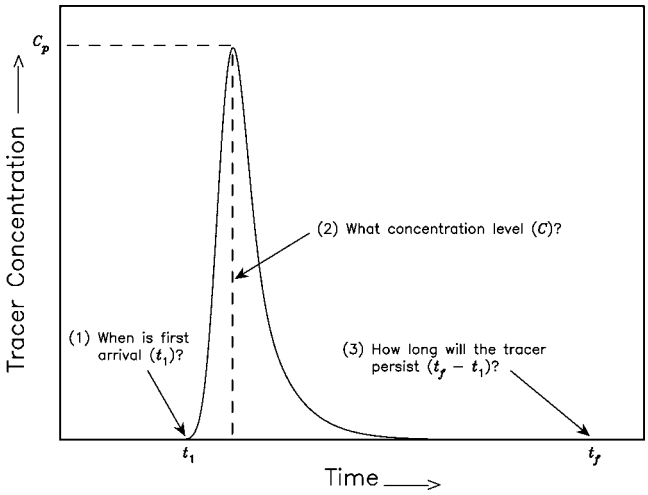

Figure 1. Three practical questions regarding contamination (after Brouyère, 2003, p. 10).

viewed from a tracer release perspective at the injection point.

When a tracing agent is applied to a specific system, a certain amount of consequent human health risks associated with the tracer will be attendant. Ecotoxicological risks will also be of concern should the tracer be released in the environment. The benefits associated with the use of a tracer must then be weighed against the potential risks. For example, digestive disorders in the human gastrointestinal tract are often evaluated by using an ingested barium tracer, because it is believed that the benefits of using such a tracer outweigh the potential harm that may be caused by the short-term ingestion of barium. A similar principle applies to the use of vaccines, in which case instead of protecting some individuals from specific diseases, the vaccines sometimes cause the diseases.

According to Schudel and others (2002, p. 10), tracer tests using fluorescent dyes may result in unwanted side effects, such as colored drinking water, and may adversely affect sensitive enterprises that use water in their production, such as bottled-water suppliers. Schudel and others (2002, pp. 59–61) provide a procedure for predicting the zone of risk, but again, only for water coloration, probably because of the rather low human health and ecotoxicological risks associated with the fluorescent dyes commonly used for hydrologic tracing. The purpose of this article is to provide an updated discussion of some of the ecotoxicological risks associated with the fluorescent dyes commonly used for tracing hydrologic systems and the importance of using an optimal tracer-test design developed using the Efficient Hydrologic Tracer-test Design (EHTD) method (Field, 2003) to minimize expected environmental concentrations (EECs) and the associated ecotoxicological risks.

2. REVIEW OF PREVIOUS STUDIES ON TRACER RISKS

Numerous reviews of toxicity studies of various fluorescent dyes have been published in the past few decades (Käβ, 1998). Most of the previous studies associated with hydrologic tracer testing address fluorescent dyes, because fluorescent dyes are inexpensive, commonly applied tracing agents, some of which have been used for over 100 years (Käβ, 1998, p. 23). However, the type of tracer applied, from the relatively harmless (e.g., sodium chloride and fluorescein) to the relatively toxic (e.g., tritium), is insignificant. As stated by Paracelsus (1493–1541), ''All substances are poisons; there is none which is not a poison. The right dose differentiates a poison . . . .'' The actual mass of tracer released and its EECs are the most significant aspects related to the safe use of tracers.

2.1. Fluorescent Dye Tracer Toxicities

Toxicities of fluorescent dyes used for water tracing have been infrequently investigated over the past 40 years. Many of the earlier studies (ca. ~1960–1975) were reviewed by Smart and Laidlaw (1977) as part of a larger general evaluation of fluorescent dyes for hydrologic tracing.

Later, Smart (1982) significantly expanded on the Smart and Laidlaw review by specifically evaluating 12 commonly used fluorescent dyes for hydrologic tracing studies for toxicities using existing literature sources. Smart (1984) updated the 1982 review and incorporated additional material not previously considered in the previous review.

Median lethal concentration (LC_{50}) tests on various aquatic organisms indicated only minor adverse effects for the 12 dyes reviewed by Smart (1984). As reported by Smart, concentrations of 1–10 mg/L for Rhodamine B, Rhodamine WT, and fluorescein (depending on the test organism) did not affect development or cause mortality in shellfish eggs or larvae after 48 hours of exposure.

Field and others (1995) expanded on Smart (1982, 1984) and included one additional dye-intermediate, amino G acid, and included estimates for the 96-hour median effective concentration (EC_{50}) for green algae. To overcome a lack of basic toxicity measurement data, a limitation of Smart's studies (1982, 1984), Field and others used the method of Quantitative Structure Activity Relationships (QSARs) (Wagner et al., 1995) to develop a more comprehensive understanding of the toxicities associated with the fluorescent dyes reviewed. The original study by Field and others (1995) consisted of a Structure Activity Relationships (SARs) analysis for human health and a QSAR analysis for ecotoxicity. The QSAR models have been shown to be a valid choice for

Table 1. *Summary of human health concerns based on a Structure Activity Relationships (SARs) analysis (after Field et al., 1995).*

Dye Type	Chemical Formula	Skin Absorption	Oral Uptake	Carcinogenicity	Oncogenic Effects	Mutagenic Effects
Fluorescein	$C_{20}H_{10}Na_2O_5$	None	Limited	Little concern	None	Little concern
Eosin	$C_{20}H_6Br_4Na_2O_5$	None	Limited	Inadequate data	Some concern	Some concern
Rhodamine B	$C_{28}H_{31}ClN_2O_3$	None	Limited	Inadequate data	Little concern	Little concern
Rhodamine WT	$C_{29}H_{29}N_2NaO_5$	None	Limited	Inadequate data	Little concern	Little concern
Sulpho-Rhodamine G	$C_{25}H_{26}N_2O_7S_2$	None	None	Little concern	Little concern	Little concern
Sulpho-Rhodamine B	$C_{27}H_{29}N_2NaO_7S_2$	None	None	Little concern	Little concern	Little concern
Tinopal CBS-X	$C_{28}H_{20}N_{12}Na_2O_8S_2$	None	None	Little concern	Little concern	Little concern
Tinopal 5BM GX	$C_{38}H_{38}N_{12}Na_2O_6S_2$	None	None	Little concern	Little concern	Little concern
Phorwite BBH Pure	$C_{40}H_{44}N_{12}O_{10}S_2$	None	None	Inadequate data	Little concern	Little concern
Diphenyl Brilliant Flavine 7GFF	$C_{42}H_{22}N_6Na_6O_{18}S_6$	None	None	Little concern	Little concern	Little concern
Lissamine Flavine FF	$C_{26}H_{18}K_2O_6S_2$	None	None	Little concern	Uncertain	Uncertain
Pyranine	$C_{16}H_7Na_3O_{10}S_3$	Negligible	Negligible	Little concern	Little concern	Little concern
Amino G acid	$C_{10}H_9NO_6S_2$	None	None	Little concern	Some concern	Some concern

estimating aquatic toxicities when toxicity testing data are lacking (Wagner et al., 1995). They are widely applied throughout the United States and Europe (Freidig, 2000, p. 9) and are recommended in a European Union white paper (Papa et al., 2005).

A QSAR study consists of (1) a detailed review of available toxicity data; (2) a detailed review of available test data on analogous or similar substances and/or potential metabolites; and (3) mathematical expressions for biological activity. Based on the QSAR analysis developed by U.S. Environmental Protection Agency (U.S. EPA) Office of Toxic Substances, Field and others (1995) concluded that few, if any, human health effects are likely (Table 1) and that ecological effects are generally insignificant (Table 2). As a result of the lack of any significant adverse effects from any of the fluorescent dyes tested, Field and others (1995) recommended downstream EECs be maintained at or below 1–2 mg/L, which was determined to be adequately protective of human health and the environment while maximizing the probability of detection. By setting fluorescent dye EECs at or below 1–2 mg/L, more flexibility in designing and implementing tracer tests is allowed than may be accomplished using the previously recommended EEC of 10 μg/L (Wilson et al., 1986, p. 8). The recommended allowable downstream concentration of 1–2 mg/L was supported by Flury and Wai (2003).

Käβ (1998) has suggested a different kind of risk that needs serious consideration: limitation of selected dyes, specifically fluorescein (uranine), because of high background fluorescence levels. Fluorescein is used so extensively (e.g., in automobile antifreeze) that it is now

Table 2. *Summary of ecological toxicity based on a Quantitative Structure Activity Relationships (QSARs) analysis (after Field et al., 1995).*

Dye Type	Fish 96-hour LC_{50} (mg/L)	Cladocera 48-hour LC_{50} (mg/L)	Green Algae 96-hour EC_{50} (mg/L)	Additional Information
Fluorescein	2,200	165	<10	Algae EC_{50} based on 7-day EC_{100} = 10 mg/L
Eosin	>1,000	>100	>10	Daphnid LC_{50} based on fish acute value. Algae EC_{50} based on 7-day NOEC = 10 mg/L
Rhodamine B	314	>29	<10	Algae EC_{50} based on 7-day EC_{100} = 10 mg/L
Rhodamine WT	>320	170	20	Algae NEC = 0.2 mg/L based on acid dyes as a class
Sulpho-Rhodamine G	>500	88	20	Algae NEC = 0.2 mg/L based on acid dyes as a class
Sulpho-Rhodamine B	1,200	139	20	Algae NEC = 0.2 mg/L based on acid dyes as a class
Tinopal CBS-X	158	>100	20	Daphnid LC_{50} based on fish acute value. Algae NEC = 0.2 mg/L based on acid dyes as a class
Tinopal 5BM GX	>100	>100	20	Algae NEC = 0.2 mg/L based on Acid Yellow 7 acid dyes as a class
Phorwite BBH Pure	>1,000	>100	10	Daphnid LC_{50} based on fish acute value. Algae NEC = 0.2 mg/L based on acid dyes as a class
Diphenyl Brilliant Flavine 7GFF	158	>100	>10	Daphnid LC_{50} based on fish acute value. Algae NEC = 0.2 mg/L based on acid dyes as a class
Lissamine Flavine FF	>1,000	>1,000	20	Algae NEC = 0.2 mg/L based on acid dyes as a class
Pyranine	>500	>100	20	Daphnid LC_{50} based on fish acute value. Algae NEC = 0.2 mg/L based on acid dyes as a class
Amino G acid	1,400	386	20	Algae NEC = 0.2 mg/L based on acid dyes as a class

Table 3. *Efficient Hydrologic Tracer-Test Design (EHTD) tracer test design parameters.*

Parameter	Units	Porous Media	Karst Aquifer
Q	m^3/hour	7.20×10^1	3.60×10^2
A[1]	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/hour	7.20×10^{-1}	3.60×10^0
C_p	mg/L	1.00×10^1	1.00×10^1
t_0[2]	hour	1.56×10^3	9.63×10^1
C_i[3]	mg/L	0.00×10^0	0.00×10^0
γ_1[3]	—	0.00×10^0	0.00×10^0
γ_2[3]	—	0.00×10^0	0.00×10^0
S_f[3]	—	—	1.00×10^0
R_d[3]	—	1.00×10^0	1.00×10^0
μ[3]	per hour	0.00×10^0	0.00×10^0

[1]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.
[2]Parameter required by EHTD for pulse and continuous releases.
[3]These parameters not required by EHTD but must be listed in the input file.

somewhat ubiquitous and can adversely influence the results of water tracing tests by indicating positive recoveries when really there are none (Käβ, 1998, p. 30). This type of risk, a false positive, can lead to major judgmental errors when deciding on appropriate human health and environmental protections to implement as a result of the tracer test results.

Another similar type of risk appears to occur when using any of the numerous rhodamines available for water tracing. Independent laboratories have confirmed that the rhodamines readily degrade to lower wavelengths by a process known as deaminoalkylation (Käβ, 1998, pp. 33–34), although degradation rates and causes have not yet been quantified. Use of any of the rhodamines in conjunction with or without other fluorescent dyes with lower wavelengths (e.g., fluorescein, eosin) may cause false positives and/or false negatives and potentially major judgmental errors when decisions are made with regard to the appropriate human health and environmental protections to implement.

Lastly, Behrens and others (2001) reported on recent investigations on the human toxicity and ecotoxicity of 17 selected tracer agents. Based on their analyses of ecotoxicity, Behrens and others suggested that Rhodamine WT, Rhodamine B, and Rhodamine 6G may be unsafe for environmental tracing and that sulpho-Rhodamine B is probably ''ecotoxicologically unsafe.'' Fluorescein, eosin, Amido-Rhodamine G, sodium napthionate, pyranine, Tinopal CBS-X, Tinopal ABP liquid, fluorescent polystyrene microspheres, and dyed clubmoss spores are probably safe. Lithium salts, strontium salts, bromides, and activatable isotopes may be acceptable, but with restrictions.

Unfortunately, because neither the data nor a detailed description of the test methods used by Behrens and others (2001) was provided, additional analyses are warranted (Valcovic, 2001). However, until more comprehensive studies are conducted, the QSAR method of analysis described by Field and others (1995) may be more useful for estimating mutagenicity and other toxic end points (Cronin et al., 2003).

3. EXPECTED ENVIRONMENTAL CONCENTRATIONS AND HAZARD QUOTIENTS

As previously noted, the actual measured concentrations that various organisms are exposed to determine the extent of the risk (e.g., the dose makes the poison). When addressing risks, typically the risk assessor is concerned with the EEC (Burns, 2004, p. 1), which may be any concentration selected by the risk assessor, but is typically either the average concentration ($\bar{C}$) or the peak concentration (C_p) at the receptor location. In terms of risks associated with tracer agents, the EECs determined in the selected medium need to be compared with appropriate measures of risk (e.g., LD_{50}). For this analysis, C_p is taken as the EEC of interest. This may be regarded as a conservative approach, because the time duration of C_p is typically very short for most tracer tests, whereas the time duration of $\bar{C}$ is much longer.

Optimal estimates for the mass of tracer to release in a porous medium and karstic aquifer were determined using the design criteria shown in Table 3 and the EHTD method. The choice of a porous medium and a karstic aquifer reflect the two main types of flow in the environment, in which the karstic aquifer is represented by a solution conduit with a flowing stream similar to a surface water stream. The design parameters have been previously used for test criteria (Parriaux et al., 1988; Field, 2003), and EHTD has been shown to reasonably estimate necessary tracer masses and transport parameters (Field, 2002a, 2002b, 2002c, 2003). For this evaluation, no initial concentrations, production, decay, or retardation effects were assumed in the simulations.

3.1. Sampling Station EECs

To compare the EECs with ''safe concentrations'' and ''allowable concentrations,'' tracer-mass estimates (Table 4) were developed using selected tracer-mass estimation equations (Field, 2002c), the parameters listed in Table 3, and some additional design criteria (Field, 2002c) to calculate peak concentrations at downstream sampling stations. The tracer-mass estimates shown in Table 4 were entered into EHTD to estimate downstream concentrations. EHTD estimates tracer mass by

Table 4. *Tracer-mass estimates in grams. Equation numbers refer to equation numbers presented in Field (2002c).*

Equation	Porous Media (g)	Karst Aquifer (g)
(1a)	2.63×10^{2}	8.80×10^{1}
(2)	2.00×10^{0}	4.72×10^{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^{2}	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}
(39)	2.16×10^{7}	1.08×10^{8}
(40)	3.37×10^{10}	1.01×10^{10}

application of the advection-dispersion equation using either a predetermined user-set average tracer concentration or tracer mass.

Comparisons of the estimated EECs need to be made with the average tracer concentration set by the user in EHTD (10 μg/L) and allowable peak concentration of 1–2 mg/L recommended by Field and others (1995) to determine the extent that tracer-mass estimates exceed the safe and allowable concentration levels. In addition, comparing the estimated tracer concentrations with the 96-hour LC_{50} for fish for Tinopal 5BM GX (100 mg/L) the 48-hour LC_{50} for cladocera for Rhodamine B (29 mg/L) and the 96-hour EC_{50} for green algae for Rhodamine B (<10 mg/L) allows for greater insight into the potential for adverse effects on aquatic biota. LC_{50}'s for Tinopal 5BM GX and Rhodamine B were chosen because these are the two fluorescent dyes that exhibit the greatest effect on the test organisms, with the exception of algae (Table 2). The green algae EC_{50} for Rhodamine B was included in this analysis, even though the estimated EC_{50} for green algae is primarily for shading effects and is thus not relevant; in general, shading effects only occur when dye concentrations in surface waters and springs receiving ground water are high enough (e.g., ~10 mg/L) to restrict sunlight penetration.

Table 5. *Sampling stations expected environmental concentrations (EECs), as determined from the Efficient Hydrologic Tracer-Test Design (EHTD) and tracer-mass estimates listed in Table 4.*

	Impulse Release		Pulse Release	
Equation	Porous Media EEC (μg/L)	Karstic Aquifer EEC (μg/L)	Porous Media EEC (μg/L)	Karstic Aquifer EEC (μg/L)
EHTD	1.04×10^{1}	1.02×10^{1}	1.88×10^{1}	2.02×10^{1}
(1a)	5.32×10^{0}	8.87×10^{0}	2.16×10^{0}	2.61×10^{0}
(2)	8.19×10^{1}	9.65×10^{3}	3.32×10^{1}	2.84×10^{3}
(3)	5.05×10^{0}	6.04×10^{1}	2.05×10^{0}	1.78×10^{1}
(4)	6.07×10^{1}	1.57×10^{1}	2.46×10^{1}	4.62×10^{0}
(5a)	5.05×10^{-2}	7.56×10^{0}	2.05×10^{-2}	2.22×10^{0}
(5b)	5.05×10^{-10}	7.56×10^{-8}	2.05×10^{-10}	2.22×10^{-8}
(6)	2.62×10^{1}	3.92×10^{1}	1.06×10^{1}	1.15×10^{1}
(7a)	5.90×10^{1}	1.78×10^{4}	2.39×10^{1}	5.24×10^{3}
(7b)	5.90×10^{1}	1.78×10^{4}	2.39×10^{1}	5.23×10^{3}
(8)	2.02×10^{-1}	3.02×10^{1}	8.19×10^{-2}	8.89×10^{0}
(9)	2.53×10^{-6}	7.56×10^{-5}	1.02×10^{-6}	2.22×10^{-5}
(10)	5.05×10^{0}	1.51×10^{2}	2.05×10^{0}	4.45×10^{1}
(11)	7.07×10^{1}	1.51×10^{2}	2.87×10^{1}	4.45×10^{1}
(12)	1.03×10^{1}	3.38×10^{2}	4.19×10^{0}	9.96×10^{1}
(13)	2.02×10^{1}	3.02×10^{3}	8.19×10^{0}	8.89×10^{2}
(14)	6.06×10^{-2}	9.07×10^{-2}	2.46×10^{-2}	2.67×10^{-2}
(15)	8.08×10^{-1}	2.01×10^{1}	3.28×10^{-1}	5.93×10^{0}
(16)	9.70×10^{-2}	2.42×10^{0}	3.93×10^{-2}	7.11×10^{-1}
(17)	4.55×10^{0}	2.72×10^{1}	1.84×10^{0}	8.00×10^{0}
(18)	8.38×10^{0}	1.25×10^{1}	3.40×10^{0}	3.69×10^{0}
(19)	7.28×10^{0}	1.81×10^{2}	2.95×10^{0}	5.34×10^{1}
(20)	9.60×10^{6}	8.61×10^{8}	3.89×10^{6}	2.53×10^{8}
(21)	1.99×10^{0}	2.97×10^{2}	8.05×10^{-1}	8.75×10^{1}
(22)	4.63×10^{0}	1.26×10^{1}	1.87×10^{0}	3.72×10^{0}
(23)	6.17×10^{0}	9.22×10^{0}	2.50×10^{0}	2.71×10^{0}
(24)	8.41×10^{0}	2.10×10^{2}	3.41×10^{0}	6.17×10^{1}
(25)	2.72×10^{1}	4.07×10^{1}	1.10×10^{1}	1.20×10^{1}
(26)	1.26×10^{1}	3.15×10^{2}	5.11×10^{0}	9.26×10^{1}
(27)	9.77×10^{0}	2.21×10^{2}	3.96×10^{0}	6.50×10^{1}
(28)	3.64×10^{1}	5.44×10^{3}	1.47×10^{1}	1.60×10^{3}
(29)	1.42×10^{0}	8.52×10^{0}	5.77×10^{-1}	2.51×10^{0}
(30)	1.01×10^{1}	3.02×10^{2}	4.09×10^{0}	8.89×10^{1}
(31)	2.02×10^{1}	3.02×10^{2}	8.19×10^{0}	8.89×10^{1}
(32)	1.01×10^{1}	1.51×10^{2}	4.09×10^{0}	4.45×10^{1}
(39)	4.37×10^{5}	1.09×10^{7}	1.77×10^{5}	3.20×10^{6}
(40)	6.81×10^{8}	1.02×10^{9}	2.76×10^{8}	3.00×10^{8}

The EHTD was initially used to determine an optimized tracer mass to release, such that downstream EECs would occur at the user-set average tracer concentration of 10 μg/L. In addition, the tracer-mass estimates listed in Table 4 were used to override the user-set average tracer concentration in EHTD to estimate downstream EECs (Table 5), based on the estimated tracer masses.

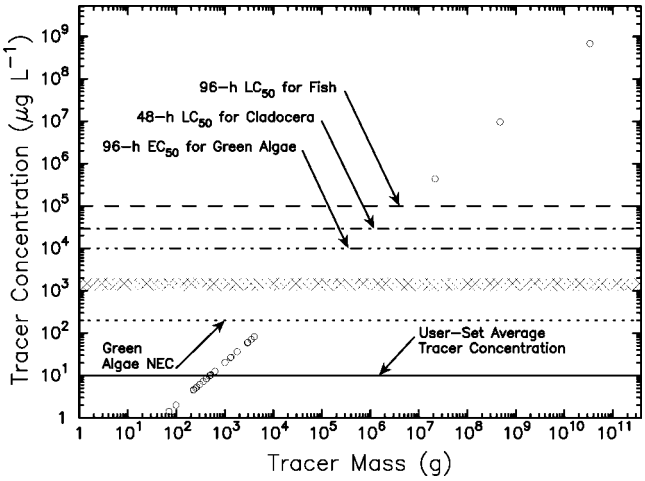

Figure 2. Plot of sampling stations EECs, ordered from least to greatest, as determined from selected tracer-mass estimation equations for an impulse release in a porous medium. Cross-hatched pattern represents the allowable range for downstream EECs. (Tracer masses $<$ 1.0 g and/or EECs $<$ 1.0 μg/L not plotted.)

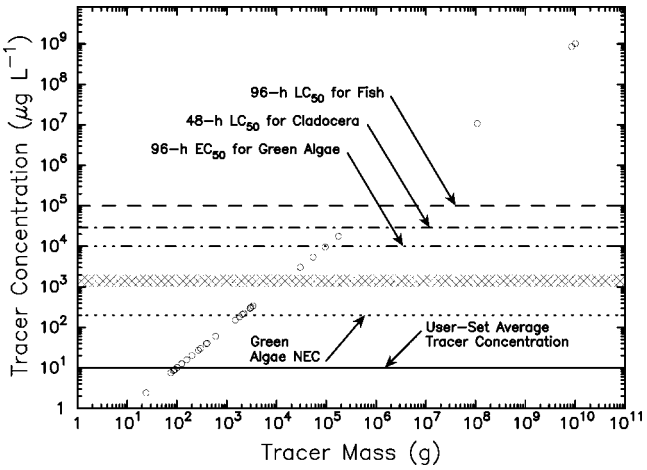

Figure 4. Plot of sampling stations EECs, ordered from least to greatest, as determined from selected tracer-mass estimation equations for an impulse release in a karstic aquifer. Cross-hatched pattern represents the allowable range for downstream EECs. (Tracer masses $<$ 1.0 g and/or EECs $<$ 1.0 μg/L not plotted.)

3.1.1. Porous Media Sampling Station EECs

For an impulse release, EHTD estimated that 516.54 g would result in the desired downstream (500-m) EEC. For a pulse release, EHTD estimated that 2,297.20 g would result in the desired downstream tracer EEC. A pulse release typically requires larger quantities of tracer to be released to form a concentration plateau, rather than the sharp concentration peak that occurs from an impulse release.

Figures 2 and 3 show that, with the exception of three tracer-mass estimates (see eqs. 20, 39, and 40 in Field [2002c]), all downstream EECs occur below the LC_{50}'s for fish and cladocera and below the EC_{50} for green algae. Although fish and cladocera are not truly representative of subsurface porous-media biota, such a comparison is useful because ground water does eventually discharge to surface water. In addition, except for the same three tracer-mass estimates, all EECs lie below the allowable range of 1–2 mg/L (Field et al., 1995). Several occur above the EHTD user-set average tracer concentration of 10 μg/L but below the green algae no effect concentration (NEC).

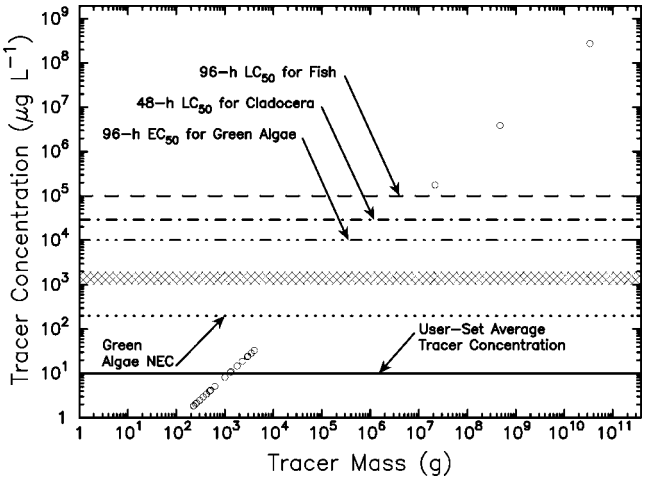

Figure 3. Plot of sampling stations EECs, ordered from least to greatest, as determined from selected tracer-mass estimation equations for a pulse release in a porous medium. Cross-hatched pattern represents the allowable range for downstream EECs. (Tracer masses $<$ 1.0 g and/or EECs $<$ 1.0 μg/L not plotted.)

3.1.2. Karstic Aquifer Sampling Station EECs

The EHTD was again used to initially determine an optimized tracer mass to release so that an average tracer concentration of 10 μg/L would be achieved. For an impulse release, EHTD estimated that 101.43 g would result in the desired downstream (3-km) EEC. It was also estimated that 681.65 g would result in the desired downstream tracer EEC for a pulse release.

Figures 4 and 5 show that, with the exception of three tracer-mass estimates (see eqs. 20, 39, and 40 in Field [2002c]), all downstream EECs occur below the LC_{50}'s for fish and cladocera. However, in addition to the same three tracer-mass estimates, four additional EECs occur above the allowable range of 1–2 mg/L for the impulse release (Figure 4), and two EECs lie above the allowable range of 1–2 mg/L for the pulse release (Figure 5). Several EECs occur above the EHTD user-set average tracer concentration of 10 μg/L, with most also falling below the green algae NEC. Two EECs lie on or slightly above the EC_{50} for green algae for the karstic aquifer when an impulse release is realized.

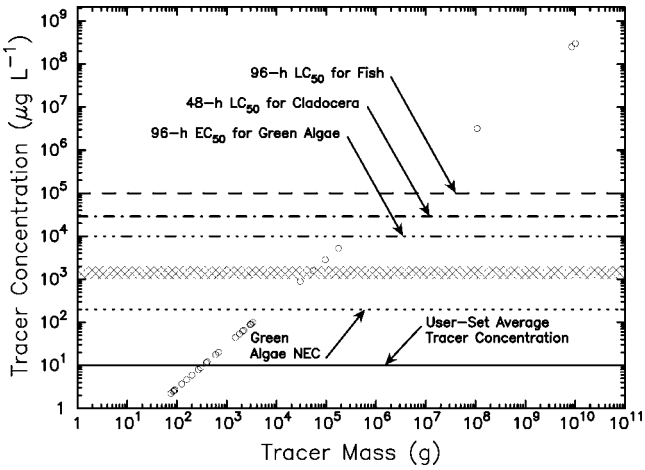

Figure 5. Plot of sampling stations EECs, ordered from least to greatest, as determined from selected tracer-mass estimation equations for a pulse release in a karstic aquifer. Cross-hatched pattern represents the allowable range for downstream EECs. (Tracer masses < 1.0 g and/or EECs < 1.0 µg/L not plotted.)

3.2. Injection Site EECs

Comparison of EECs with safe concentration levels at downstream sampling locations provides no indication of the actual injection site EECs, which, by necessity, will be significantly greater than the downstream EECs. To assess the level of environmental risk at the injection site, EHTD was used to estimate injection site EECs (Table 6) using the tracer-mass estimates listed in Table 4.

For this simulation, the longitudinal distance (L) and/or transverse distance (W) were adjusted to represent the actual injection sites. Because the transport distances are insignificant, longitudinal dispersion is also insignificant and $\bar{C} = C_p$ for the impulse releases only. These assumptions allow for consideration of an immediate point source. EHTD was initially run using the previously estimated optimal tracer-mass estimates to provide for an examination of the effect of the EHTD estimates as well as the estimates listed in Table 4.

The estimated EECs were not compared with the EHTD user-set average tracer concentration (10 µg/L) or the allowable peak concentration of 1–2 mg/L, because these concentrations were intended only for downstream EECs (Field et al., 1995). Instead, the EECs were compared with the recommended maximum concentration at the injection point of 100 µg/L (Perler, 1988) (this arbitrarily determined low concentration is generally ignored). Injection site EECs were also compared with the 96-hour LC_{50} for fish for Tinopal 5BM GX (100 mg/L), the 48-hour LC_{50} for cladocera for Rhodamine B (29 mg/L), and the 96-hour EC_{50} for green algae for Rhodamine B (<10 mg/L), which are the only true measures that can be used at the injection sites.

Table 6. *Injection site expected environmental concentrations (EECs), as determined from Efficient Hydrologic Tracer-Test Design (EHTD) and tracer-mass estimates listed in Table 4.*

	Impulse Release		Pulse Release	
Equation	Porous Media EEC (µg/L)	Karstic Aquifer EEC (µg/L)	Porous Media EEC (µg/L)	Karstic Aquifer EEC (µg/L)
EHTD	1.33×10^{8}	6.62×10^{6}	2.04×10^{1}	2.02×10^{1}
(1a)	6.78×10^{7}	5.75×10^{6}	2.34×10^{0}	2.61×10^{0}
(2)	1.04×10^{9}	6.26×10^{9}	3.61×10^{1}	2.84×10^{3}
(3)	6.44×10^{7}	3.92×10^{7}	2.23×10^{0}	1.78×10^{1}
(4)	7.74×10^{8}	1.02×10^{7}	2.67×10^{1}	4.63×10^{0}
(5a)	6.44×10^{5}	4.90×10^{6}	2.23×10^{-2}	2.23×10^{0}
(5b)	6.44×10^{-3}	4.90×10^{-2}	2.23×10^{-10}	2.23×10^{-8}
(6)	3.34×10^{8}	2.54×10^{7}	1.15×10^{1}	1.15×10^{1}
(7a)	7.53×10^{8}	1.15×10^{10}	2.60×10^{1}	5.24×10^{3}
(7b)	7.52×10^{8}	1.15×10^{10}	2.60×10^{1}	5.24×10^{3}
(8)	2.58×10^{6}	1.96×10^{7}	8.90×10^{-2}	8.90×10^{0}
(9)	3.20×10^{1}	4.90×10^{1}	1.11×10^{-6}	2.23×10^{-5}
(10)	6.44×10^{7}	9.79×10^{7}	2.23×10^{0}	4.45×10^{1}
(11)	9.02×10^{8}	9.79×10^{7}	3.12×10^{1}	4.45×10^{1}
(12)	1.32×10^{8}	2.19×10^{8}	4.56×10^{0}	9.97×10^{1}
(13)	2.58×10^{8}	1.96×10^{9}	8.90×10^{0}	8.90×10^{2}
(14)	7.73×10^{5}	5.88×10^{4}	2.67×10^{-2}	2.67×10^{-2}
(15)	1.03×10^{7}	1.31×10^{7}	3.56×10^{-1}	5.94×10^{0}
(16)	1.24×10^{6}	1.57×10^{6}	4.27×10^{-2}	7.12×10^{-1}
(17)	5.80×10^{7}	1.76×10^{7}	2.00×10^{0}	8.01×10^{0}
(18)	1.07×10^{8}	8.12×10^{6}	3.69×10^{0}	3.69×10^{0}
(19)	9.28×10^{7}	1.18×10^{8}	3.20×10^{0}	5.34×10^{1}
(20)	1.22×10^{14}	5.58×10^{14}	4.23×10^{6}	2.54×10^{8}
(21)	2.53×10^{7}	1.93×10^{8}	8.76×10^{-1}	8.76×10^{1}
(22)	5.90×10^{7}	8.19×10^{6}	2.04×10^{0}	3.72×10^{0}
(23)	7.86×10^{7}	5.98×10^{6}	2.72×10^{0}	2.72×10^{0}
(24)	1.07×10^{8}	1.36×10^{8}	3.70×10^{0}	6.17×10^{1}
(25)	3.47×10^{8}	2.64×10^{7}	1.20×10^{1}	1.20×10^{1}
(26)	1.61×10^{8}	2.04×10^{8}	5.56×10^{0}	9.27×10^{1}
(27)	1.25×10^{8}	1.43×10^{8}	4.30×10^{0}	6.51×10^{1}
(28)	4.64×10^{8}	3.53×10^{9}	1.60×10^{1}	1.60×10^{3}
(29)	1.82×10^{7}	5.52×10^{6}	6.28×10^{-1}	2.51×10^{0}
(30)	1.29×10^{8}	1.96×10^{8}	4.45×10^{0}	8.90×10^{1}
(31)	2.58×10^{8}	1.96×10^{8}	8.90×10^{0}	8.90×10^{1}
(32)	1.29×10^{8}	9.79×10^{7}	4.45×10^{0}	4.45×10^{1}
(39)	5.57×10^{12}	7.05×10^{12}	1.92×10^{5}	3.21×10^{6}
(40)	8.68×10^{15}	6.60×10^{14}	3.00×10^{8}	3.00×10^{8}

3.2.1 Porous Media Injection Site EECs

EHTD was used to assess the effect of the optimal tracer mass for the porous medium for both the impulse release (516.54 g) and for the pulse release (2,297.20 g) at the point of injection. Figure 6 shows that all plotted EECs exceed all measures of risk when an impulse injection is realized. Only the EEC developed from Eq. 5b (Tables 4 and 6) can be considered acceptable from an ecotoxicological point of view, but not from a downstream detection point of view. Because the EEC produced by Eq. 5b is so small (6.44×10^{-3} µg/L), it could not be plotted on Figure 6. Such a small EEC is well below the maximum

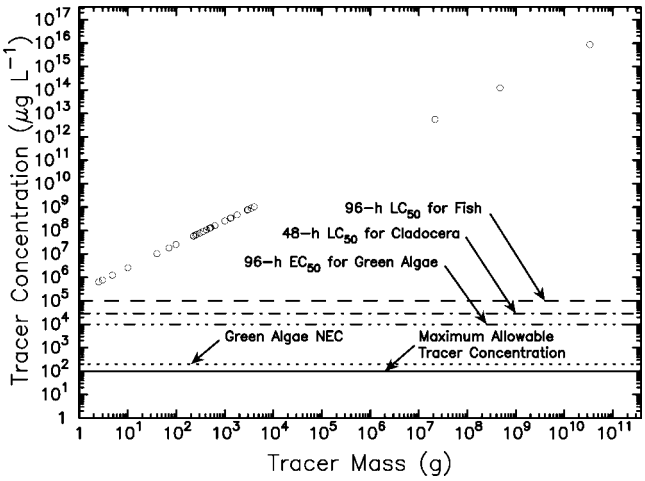

Figure 6. Plot of injection stations EECs, ordered from least to greatest, as determined from selected tracer-mass estimation equations for an impulse release in a porous medium. (Tracer masses < 1.0 g and/or EECs < 1.0 μg/L not plotted.)

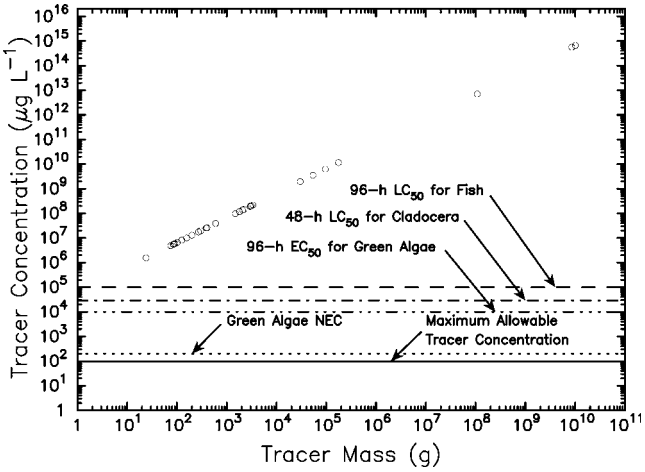

Figure 8. Plot of injection sites EECs, ordered from least to greatest, as determined from selected tracer-mass estimation equations for an impulse release in a karstic aquifer. (Tracer masses < 1.0 g and/or EECs < 1.0 μg/L not plotted.)

levels allowed, but it is also likely to result in inadequate downstream detection levels.

Figure 7, however, shows that only three of the EECs exceed all measures of risk when a pulse injection is realized. This effect occurred because the rate of flow, Q, was sufficiently high, and the rate of injection, q, was sufficiently low. This large difference between injection and discharge rates allowed the tracer to move away from the injection site at a velocity that prevented extreme EECs.

3.2.2. Karstic Aquifer Injection Site EECs

EHTD was also used to evaluate the effect of the optimal tracer mass for the karstic aquifer for both the impulse release (101.43 g) and for the pulse release (681.65 g). Figure 8 shows that all the EECs exceed all measures of risk when an impulse injection is realized. Again, only Eq. 5b (Tables 4 and 6) can be considered acceptable from an ecotoxicological point of view, but not from a downstream detection point of view, because the EEC produced by Eq. 5b is so small (4.90×10^{-2} μg/L) and could not be plotted on Figure 8.

As with the porous-media simulation, Figure 9 shows that only three of the EECs exceed all measures of risk when a pulse injection is realized. However, four estimates exceed the green algae NEC (0.2 mg/L), and four estimates approximately equaled the maximum allowable concentration (100 μg/L) (Tables 4 and 6). It would

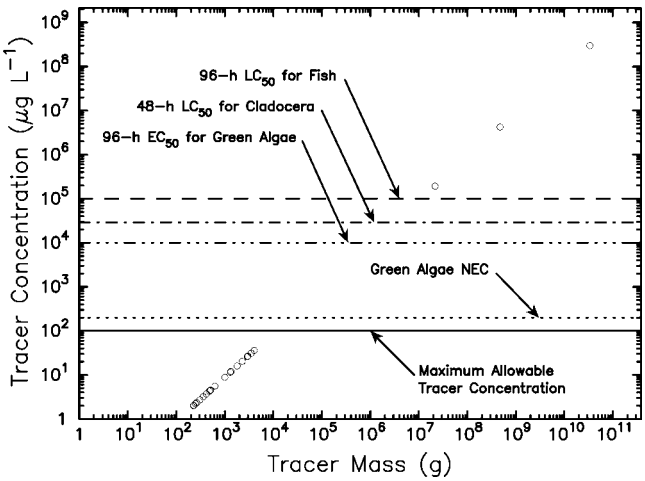

Figure 7. Plot of injection sites EECs, ordered from least to greatest, as determined from selected tracer-mass estimation equations for a pulse release in a porous medium. (Tracer masses < 1.0 g and/or EECs < 1.0 μg/L not plotted.)

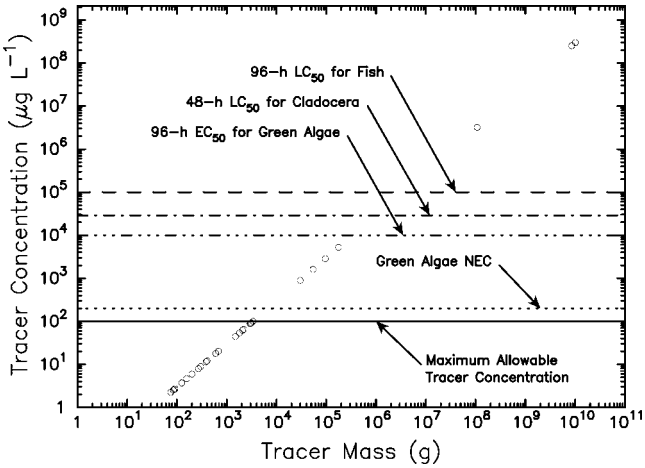

Figure 9. Plot of injection sites EECs, ordered from least to greatest, as determined from selected tracer-mass estimation equations for a pulse release in a karstic aquifer. (Tracer masses < 1.0 g and/or EECs < 1.0 μg/L not plotted.)

Table 7. *Hazard quotients (HQs) exceeding one (HQ > 1.0) for green algae at sampling stations.*

	Impulse Release		Pulse Release	
Equation	Porous Media HQ (dimen.)	Karstic Aquifer HQ (dimen.)	Porous Media HQ (dimen.)	Karstic Aquifer HQ (dimen.)
(2)	—	4.83×10^{1}	—	1.42×10^{1}
(7a)	—	8.90×10^{1}	—	2.62×10^{1}
(7b)	—	8.89×10^{1}	—	2.61×10^{1}
(12)	—	1.69×10^{0}	—	—
(13)	—	1.51×10^{1}	—	4.45×10^{0}
(20)	4.80×10^{4}	4.31×10^{6}	1.94×10^{4}	1.27×10^{6}
(21)	—	1.49×10^{0}	—	—
(24)	—	1.05×10^{0}	—	—
(26)	—	1.57×10^{0}	—	—
(27)	—	1.11×10^{0}	—	—
(28)	—	2.72×10^{1}	—	8.00×10^{0}
(30)	—	1.51×10^{0}	—	—
(31)	—	1.51×10^{0}	—	—
(39)	2.18×10^{3}	5.44×10^{4}	8.84×10^{2}	1.60×10^{4}
(40)	3.40×10^{6}	5.09×10^{6}	1.38×10^{6}	1.50×10^{6}

Table 8. *Hazard quotients (HQs) exceeding one (HQ > 1.0) for green algae at injection sites.*

	Impulse Release		Pulse Release	
Equation	Porous Media EEC (dimen.)	Karstic Aquifer EEC (dimen.)	Porous Media EEC (dimen.)	Karstic Aquifer EEC (dimen.)
EHTD	6.66×10^{5}	3.31×10^{4}	—	—
(1a)	3.39×10^{5}	2.87×10^{4}	—	—
(2)	5.22×10^{6}	3.13×10^{7}	—	1.42×10^{1}
(3)	3.22×10^{5}	1.96×10^{5}	—	—
(4)	3.87×10^{6}	5.09×10^{4}	—	—
(5a)	3.22×10^{3}	2.45×10^{4}	—	—
(6)	1.67×10^{6}	1.27×10^{5}	—	—
(7a)	3.76×10^{6}	5.77×10^{7}	—	2.62×10^{1}
(7b)	3.76×10^{6}	5.76×10^{7}	—	2.62×10^{1}
(8)	1.29×10^{4}	9.79×10^{4}	—	—
(10)	3.22×10^{5}	4.90×10^{5}	—	—
(11)	4.51×10^{6}	4.90×10^{5}	—	—
(12)	6.60×10^{5}	1.10×10^{6}	—	—
(13)	1.29×10^{6}	9.79×10^{6}	—	4.45×10^{0}
(14)	3.87×10^{3}	2.94×10^{2}	—	—
(15)	5.15×10^{4}	6.53×10^{4}	—	—
(16)	6.18×10^{3}	7.84×10^{3}	—	—
(17)	2.90×10^{5}	8.81×10^{4}	—	—
(18)	5.34×10^{5}	4.06×10^{4}	—	—
(19)	4.64×10^{5}	5.88×10^{5}	—	—
(20)	6.12×10^{11}	2.79×10^{12}	2.11×10^{4}	1.27×10^{6}
(21)	1.27×10^{5}	9.63×10^{5}	—	—
(22)	2.95×10^{5}	4.09×10^{4}	—	—
(23)	3.93×10^{5}	2.99×10^{4}	—	—
(24)	5.36×10^{5}	6.79×10^{5}	—	—
(25)	1.74×10^{6}	1.32×10^{5}	—	—
(26)	8.05×10^{5}	1.02×10^{6}	—	—
(27)	6.23×10^{5}	7.16×10^{5}	—	—
(28)	2.32×10^{6}	1.76×10^{7}	—	8.01×10^{0}
(29)	9.08×10^{4}	2.76×10^{4}	—	—
(30)	6.44×10^{5}	9.79×10^{5}	—	—
(31)	1.29×10^{6}	9.79×10^{5}	—	—
(32)	6.44×10^{5}	4.90×10^{5}	—	—
(39)	2.78×10^{1}	3.53×10^{10}	9.61×10^{2}	1.60×10^{4}
(40)	4.34×10^{13}	3.30×10^{12}	1.50×10^{6}	1.50×10^{6}

EEC = expected environmental concentration; EHTD = Efficient Hydrologic Tracer-Test Design.

appear that injection site EECs indicate that pulse releases might be a more acceptable manner by which tracer agents should be released into hydrologic systems.

3.3. Aquatic Hazard Quotients (HQs)

A typical measure of aquatic risk is to develop HQs by comparing the predicted exposure concentration (PEC) to a representative predicted no effect concentration (PNEC) (HQ = PEC/PNEC). Unfortunately, the only PNEC available for the dyes of interest is the 0.2 mg/L NEC for algae (Table 2). The NEC listed in Table 2 is concerned with shading effects and does not represent a true ecotoxicological risk. However, it does represent a level of concern.

It is also appropriate to point out that the HQ does not represent a true risk when the HQ exceeds 1.0 (Volosin and Cardwell, 2002), as is commonly assumed. The relationship of PEC to PNEC is a ratio of exposure to effect and is generally considered to be just an indicator of concern, one that requires more investigation, primarily because of the large number of uncertainties (Volosin and Cardwell, 2002) associated with the measured data.

3.3.1. Sampling Station HQs

For this analysis, the PECs are considered equal to the EECs. Comparing the sampling station PECs with the green algae PNECs produced a set of instances with HQs greater than 1.0. Only those equations that produced an HQ greater than 1.0 are listed in Table 7.

For the given set of conditions and the very low PECs used, it is apparent from Table 7 that an impulse release in a karstic aquifer is more likely to result in HQs greater than 1.0. However, eqs. 20, 39, and 40 (Volosin and Cardwell, 2002) warrant the greatest concern, regardless of hydrologic regime or type of release, because of their large HQ values.

3.3.2. Injection Site HQs

Comparing the injection site PECs with the algae PNECs produced a larger set of instances with HQs greater than 1.0. Only Eqs. 5b and 9 resulted in HQs less than 1.0 for both flow regimes and tracer release methods. However, only a few equations resulted in HQs greater than 1.0 for pulse releases (Table 8).

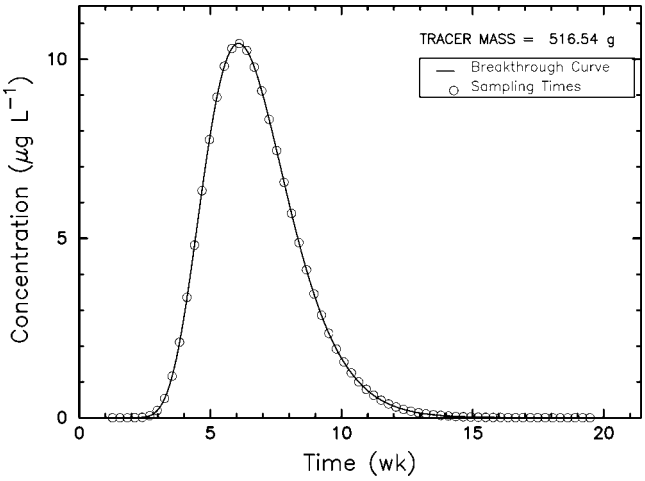

Figure 10. EHTD results for an impulse release for the porous-media test parameters for the downstream sampling station.

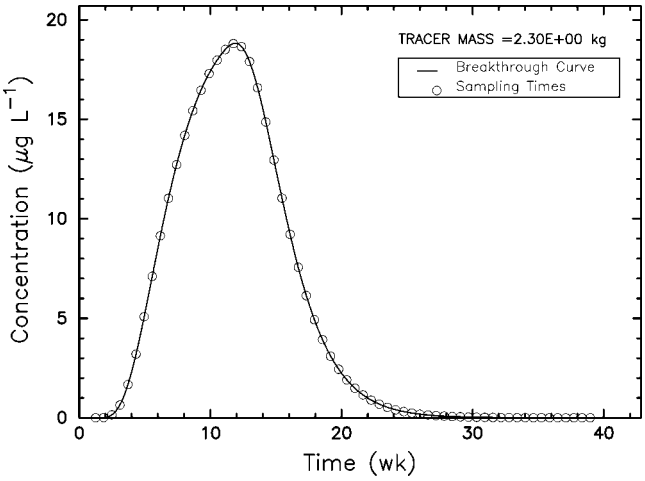

Figure 12. EHTD results for a pulse release for the porous-media test parameters for the downstream sampling station.

For the given set of conditions and the very low PECs used, it is apparent from Table 8 that an impulse release in either the porous media or the karstic aquifer is more likely to result in HQs greater than 1.0 at the injection sites. However, as with the sampling station PECs, only eqs. 20, 39, and 40 (Volosin and Cardwell, 2002) warrant significant concern, regardless of hydrologic regime, because of their large HQ values.

4. EXPOSURE ASSESSMENT OF TRACER RELEASES

Comparisons of the tracer EECs with safe and with allowable concentrations provide only one measure of risk. Figures 6 and 8 indicate a potentially serious risk to aquatic biota at the injection sites when impulse releases are implemented. However, it should be noted that conditions other than those used in the simulations might affect the downstream sampling stations using either an impulse or pulse release (e.g., background concentration, decay, etc.). It can be expected that excessive tracer-mass estimates or inadequate tracer-mass estimates will occur as a result of specific circumstances and/or mistakes in parameter estimates.

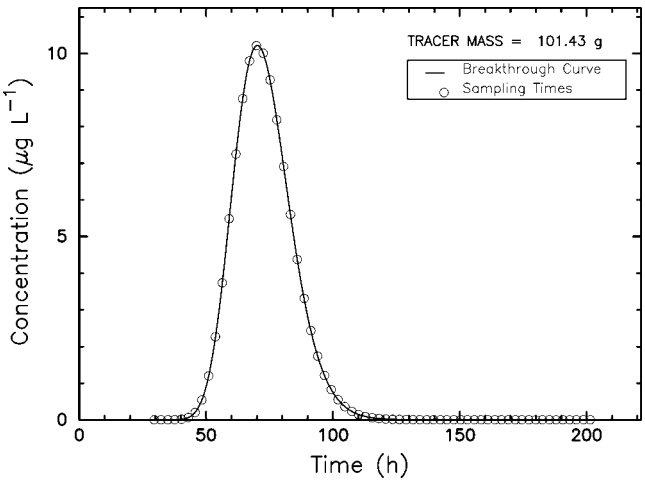

Figure 11. EHTD results for an impulse release for the karstic test parameters for the downstream sampling station.

High EECs do not necessarily translate into adverse effects on aquatic biota. The amount of time an organism is exposed is a significant parameter that must be considered. This is evident from the fact that basic aquatic toxicity tests are based on exposure time (e.g., 48-hour LC_{50} test, 96-hour LC_{50} test, 96-hour EC_{50} test, etc.)

4.1. Effective Exposure Time for Sampling Station EECs

Downstream breakthrough curves (BTCs) for the four simulations (porous media, karstic aquifer, and impulse and pulse tracer releases) were developed using EHTD for the downstream sampling stations (Figures 10–13). Breakthrough curves for the impulse releases are depicted in Figures 10 and 11 and indicate relatively restricted exposure times when compared with the BTCs for the pulse releases depicted in Figures 12 and 13. Longer exposure times are expected for pulse releases compared with impulse releases.

The significance of the BTCs in terms of exposure time may also be assessed by examining selected parameters. Tables 9 and 10 list the most relevant parameters for assessing the exposure at the downstream sampling stations. Most significant is the time difference (Δt) between earliest realistic arrival time (t_1) and the latest realistic arrival time (t_f) ($\Delta t = t_f - t_1$). (Measured concentrations earlier and later than realistic are so low that instrument noise must be a consideration.)

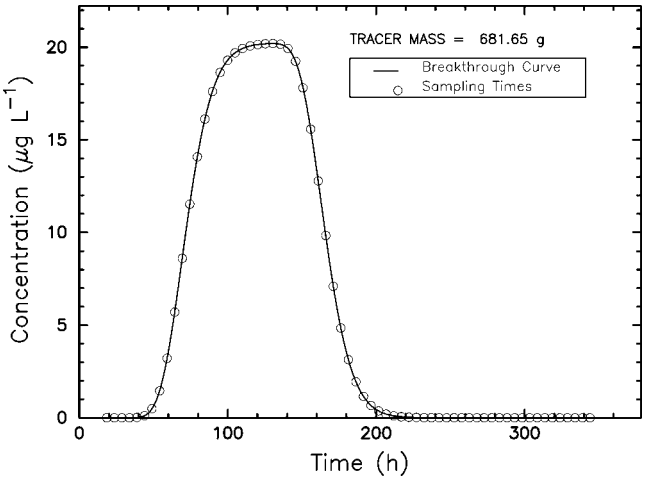

Figure 13. EHTD results for a pulse release for the karstic test parameters for the downstream sampling station.

Examining the range of the EECs exhibited by the BTC rather than relying solely on the peak concentration as being representative of an EEC is also appropriate, because the total time for the occurrence of the peak concentration may be extremely short. In the case of an impulse release, the time of exposure for C_p is immeasurably small.

For the impulse release for the porous medium, EHTD estimated that $\Delta t = 127$ days, and for the karstic aquifer that $\Delta t = 7$ days. For the pulse release for the porous medium, EHTD estimated that $\Delta t = 264$ days, and for the karstic aquifer that $\Delta t = 14$ days.

4.2. Effective Exposure Time for Injection Site EECs

Injection site BTCs for the four simulations (porous media, karstic aquifer, and impulse and pulse tracer releases) were also developed using EHTD (Figures 14–17). Breakthrough curves for the impulse releases depicted in Figures 14 and 15 indicate extremely restricted exposure times when compared with the BTCs for the pulse releases depicted in Figures 16 and 17. Again, such an occurrence is to be expected when impulse releases are compared with pulse releases.

Tables 11 and 12 depict the relevant parameters for assessing exposure, with Δt representing the most significant parameter. For the impulse releases for the porous medium, EHTD estimated that $\Delta t = 2.4$ seconds, and for the karstic aquifer that $\Delta t = 1.8$ seconds. For the pulse releases for the porous medium, EHTD estimated that $\Delta t = 64$ days, and for the karstic aquifer that $\Delta t = 4$ days. While the pulse releases do not result in excessively high EECs at the injection sites, the impulse sites have the opposite effect. In addition, the extremely high EECs for the impulse releases occur over such a short time interval (2.4 seconds for a porous medium and 1.8 seconds for

Table 9. *Efficient Hydrologic Tracer-Test Design (EHTD) analysis of sampling station results for impulse releases.*

Parameter	Units	Porous Media	Karst Aquifer
M	g	5.17×10^2	1.01×10^2
$\bar{t}$	hour	1.09×10^3	7.19×10^1
t_p	hour	1.02×10^3	7.05×10^1
υ	m/hour	4.58×10^{-1}	4.17×10^1
υ_p	m/hour	4.58×10^{-1}	4.26×10^1
D_L	m^2/hour	7.99×10^0	1.52×10^3
α	m	1.74×10^1	3.64×10^1
P_e	—	2.87×10^1	8.25×10^1
t_1	hour	2.12×10^2	2.95×10^1
t_f	hour	4.78×10^1	2.69×10^0
Δt	hour	3.27×10^3	2.01×10^2
$\bar{C}$	μg/L	1.00×10^1	1.00×10^1
C_p	μg/L	1.04×10^1	1.02×10^1
V	m^3	7.93×10^4	2.61×10^4

Table 10. *Efficient Hydrologic Tracer-Test Design (EHTD) analysis of sampling station results for pulse releases.*

Parameter	Units	Porous Media	Karst Aquifer
M	g	2.30×10^3	6.82×10^2
$\bar{t}$	hour	1.09×10^3	7.19×10^1
t_p	hour	1.98×10^3	1.31×10^2
υ	m/hour	4.58×10^{-1}	4.17×10^1
υ_p	m/hour	2.53×10^{-1}	2.30×10^1
D_L	m^2/hour	2.09×10^1	2.44×10^3
α	m	4.56×10^1	5.86×10^1
P_e	—	1.10×10^1	5.12×10^1
t_1	hour	2.08×10^2	1.85×10^1
t_f	hour	1.04×10^2	5.09×10^0
Δt	hour	6.55×10^3	3.44×10^2
$\bar{C}$	μg/L	1.00×10^1	1.00×10^1
C_p	μg/L	1.88×10^1	2.02×10^1
V	m^3	7.93×10^4	2.61×10^4

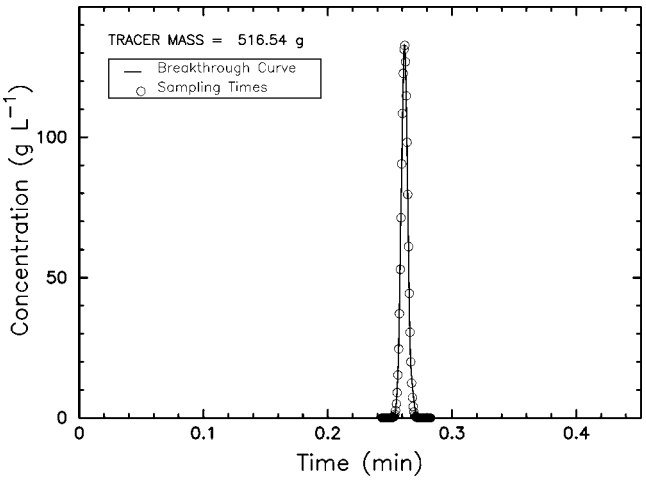

Figure 14. EHTD results for an impulse release for the porous-media test parameters for the injection site.

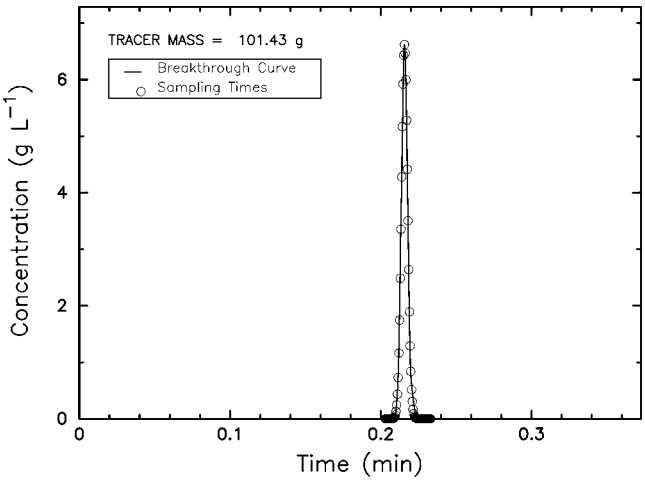

Figure 15. EHTD results for an impulse release for the karstic test parameters for the injection site.

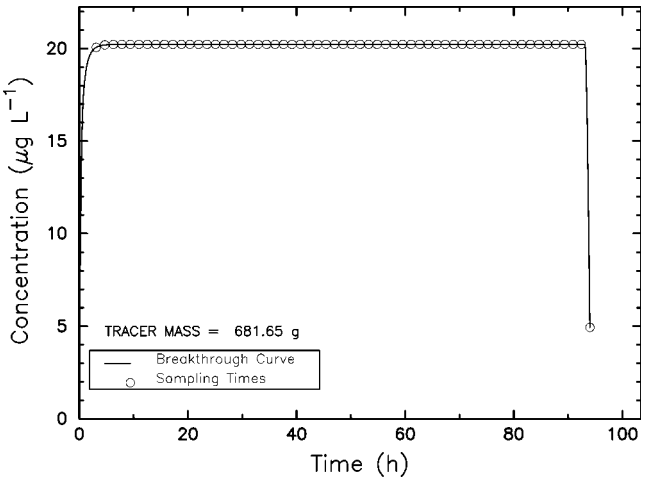

Figure 17. EHTD results for a pulse release for the karstic test parameters for the injection site.

a karstic aquifer) that there is essentially no effective exposure time (EET) at the highest concentrations.

5. SUMMARY AND CONCLUSIONS

Aquatic risks are conditioned on relevant EECs and exposure times. All anthropogenic substances are toxic at some concentration, so measures of risk depend on the EECs and EETs, both of which may be influenced by the tracer design.

Tracer-mass estimation equations produce a wide range of tracer-mass estimates (Table 4) (Field, 2002c), which translate into a wide range of downstream EECs (Table 5). In most instances, downstream EECs will occur below safe and allowable concentrations, regardless of hydrologic system or type of tracer release. However, injection site EECs (Table 6) generated from impulse releases occur at much greater levels than safe and maximum allowable concentrations, indicating a potentially serious aquatic risk. This noted aquatic risk is emphasized by the extent to which several EECs resulted in HQs much greater than 1.0.

The significance of the aquatic risks posed at injection sites is greatly ameliorated when EETs are included in the assessment. The EET is a vanishingly small amount of time for impulse releases and is reasonably short for pulse releases. Although relatively longer exposure times occur when pulse releases are realized, the reduced EECs associated with pulse releases render the relatively longer exposure times a lesser concern.

Large EECs and/or long EETs require that well-designed tracer tests be properly developed. Optimal tracer-test design is recognized as a difficult undertaking; compared with analyses of tracer-test results, very little research has been conducted regarding good tracer-test

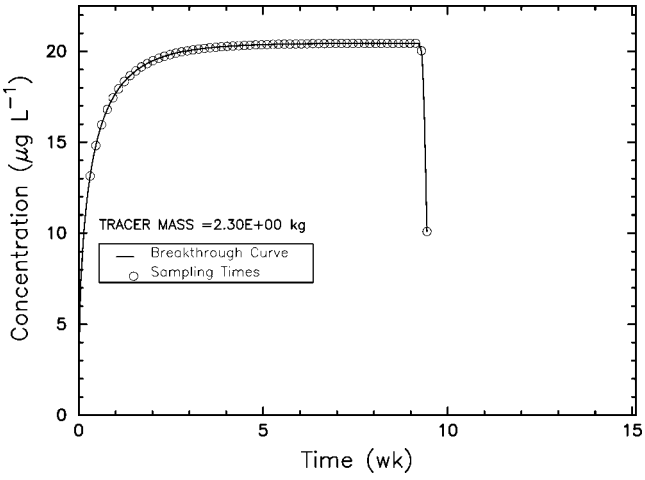

Figure 16. EHTD results for a pulse release for the porous-media test parameters for the injection site.

Table 11. *Efficient Hydrologic Tracer-Test Design (EHTD) analysis of injection site results for impulse releases.*

Parameter	Units	Porous Media	Karst Aquifer
M	g	5.17×10^{2}	1.01×10^{2}
$\bar{t}$	hour	4.36×10^{-3}	3.60×10^{-3}
t_p	hour	4.36×10^{-3}	3.60×10^{-3}
υ	m/hour	2.29×10^{2}	4.17×10^{1}
υ_p	m/hour	2.29×10^{2}	4.17×10^{1}
D_L	m^2/hour	1.11×10^{-2}	2.79×10^{-4}
α	m	4.86×10^{-5}	6.68×10^{-6}
P_e	—	2.06×10^{4}	2.24×10^{4}
t_1	hour	4.06×10^{-3}	3.39×10^{-3}
t_f	hour	4.71×10^{-3}	3.88×10^{-3}
Δt	hour	1.02×10^{-5}	7.79×10^{-6}
$\bar{C}$	µg/L	1.33×10^{8}	6.62×10^{6}
C_p	µg/L	1.33×10^{8}	6.62×10^{6}
V	m^3	3.17×10^{-1}	1.31×10^{0}

Table 12. *Efficient Hydrologic Tracer-Test Design (EHTD) analysis of injection site results for pulse releases.*

Parameter	Units	Porous Media	Karst Aquifer
M	g	2.30×10^{3}	6.82×10^{2}
$\bar{t}$	hour	4.63×10^{-3}	3.60×10^{-3}
t_p	hour	1.54×10^{3}	4.42×10^{1}
υ	m/hour	2.29×10^{2}	4.17×10^{1}
υ_p	m/hour	6.48×10^{-4}	3.39×10^{-3}
D_L	m^2/hour	4.01×10^{6}	6.05×10^{2}
α	m	1.75×10^{4}	1.45×10^{1}
P_e	—	5.71×10^{5}	1.04×10^{-2}
t_1	hour	5.20×10^{1}	1.58×10^{1}
t_f	hour	1.59×10^{3}	3.51×10^{2}
Δt	hour	2.60×10^{1}	1.57×10^{0}
$\bar{C}$	µg/L	1.72×10^{-1}	2.03×10^{0}
C_p	µg/L	2.05×10^{1}	2.02×10^{1}
V	m^3	3.17×10^{1}	1.31×10^{0}

design. The EHTD methodology was developed with optimal tracer-test design as its main focus. It can be used to assist in designing tracer tests that will minimize risks to aquatic biota while maximizing the likelihood of obtaining positive tracer recoveries at downstream sampling stations. Obtaining positive tracer recoveries can be as important as minimizing risks, depending on the importance of the tracer test. Increasingly, regulatory agencies are relying on the results of tracer tests for the development of human health and environmental protection strategies (e.g., U.S. EPA, 2000, p. 30,224). Inadequate detection of tracer agents at all downstream sampling stations can result in inadequate protection decisions that may persist for decades. Comprehensive tracer testing using good design strategies can lead to improved human health and environmental protection decisions while minimizing the risks posed by the tracer agents.

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NOTATION

A spring cross-sectional area (L^2)
b aquifer thickness (L)
C tracer concentration (M/L^3)
$\bar{C}$ mean tracer concentration (M/L^3)
C_p peak tracer concentration (M/L^3)
D_L axial dispersion (L^2/T)
γ_i dimensionless exponential production (growth) constants for the production value problem [i = 1,2]
L transport distance (L)
M solute mass recovered (M)
n_e effective porosity (dimen.)
P_e Péclet number (dimen.)
q injection discharge (L^3/T)
Q spring or pumping well discharge (L^3/T)
R_d solute retardation (dimen.)
S_f sinuosity factor (dimen.)
$\bar{t}$ mean residence time (T)
t_0 solute release time (T)
t_1 first measured arrival time (T)
Δt time difference between first tracer detection and final tracer detection (T)
t_f last measured arrival time (T)
t_p peak time of arrival (T)
υ mean flow velocity (L/T)
υ_p peak velocity (L/T)
μ solute decay (T)
V flow system volume (L^3)
W width of solute-migration zone (L)

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