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RESEARCH ARTICLE

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Improving the detection of fluorescent tracer dyes in groundwater investigations

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Abstract

Groundwater tracing with fluorescent tracer dyes is a valuable tool in many remediation projects. Three of four common dyes can be used concurrently, effectively separated, and their concentrations quantified if modern laboratory instruments and appropriate protocols are used. Unfortunately, investigators often overestimate the amount of introduced dye likely to be detected, use too little dye because of these estimates and concern that colored water might be detectable offsite, and place sampling reliance solely on grab samples of water. The common result is flawed studies that identify only some of the points to which the dyed water flows. Results are quantitatively compared for monitoring sites during periods where both water samples and granular activated carbon samplers (referred to as carbon samplers) were used. The results demonstrate that carbon samplers are superior to water samples for detecting the presence of the fluorescent tracer dyes evaluated. A technically sound and cost-effective strategy is to place primary sampling reliance on carbon samplers for detecting the presence of the dyes and secondary reliance on grab samples of water for determining dye concentrations when they are greater than the detection limits.

1 | INTRODUCTION

This article focuses on methods for improving the detection of four commonly used tracer dyes that have proven effective for groundwater tracing work at hazardous waste sites. These are eosine, fluorescein (also known as uranine), rhodamine WT, and sulforhodamine B. Common names of the dyes are used in this article, but readers are cautioned to specify dyes by both their common names and their Color Index Names and Numbers (see Exhibit 1). Investigators must also ensure that the percent of dye in the as-sold mixture is known. This percent is called "dye equivalent" and ranges widely in commercial mixtures (Aley, 2002).

Rhodamine WT and sulforhodamine B dyes have emission fluorescence peaks that are close to each other and typically should not be used together if both might be present at some sampling stations. Either of these dyes can be used concurrently with fluorescein and eosine and individually quantified, although rhodamine WT generally performs better than sulforhodamine B in groundwater tracing work (Aley, 2002; Behrens, 1986).

Fluorescent tracer dyes are valuable in groundwater characterization work because they can be detected at very low concentrations (see Exhibit 2), and because they readily adsorb onto activated carbon. The dyes can be eluted from the carbon with solutions of strong bases in an alcohol and water solution and quantified.

Separating and quantifying the tracer dyes requires laboratory analysis and is best performed by measuring fluorescence intensity in specific narrow emission wavelength ranges with a spectrofluorophotometer operated under a synchronous scan protocol (Aley, 2002). There are various instruments that can be used to test for the presence of dyes in the field; however, most field instruments (1) do not function adequately when multiple dyes are present and (2) cannot separate a fluorescence peak due to a tracer dye from background fluorescence. In the author's experience, the apparent detection of dyes by field instruments at low concentrations produces both false positive and false negatives results when samples are laboratory verified.

The fluorescence intensity of fluorescein and eosine vary with the pH of the water (Kass, 1998) as indicated in Exhibit 3. Water that is not pH adjusted prior to dye analysis and has a pH that does not provide maximum fluorescence intensity will give an inaccurately low measurement of dye concentration for fluorescein and, to a lesser extent, eosine. The fluorescence intensity of rhodamine WT and sulforhodamine B are relatively insensitive to pH at values in water typically found in the environment (Kass, 1998). At the Ozark Underground Laboratory (OUL) water samples are routinely pH adjusted by exposing them in an open container for a minimum of 2 hr to a concentrated

EXHIBIT 1 Basic information on four tracer dyes

Dye Name	Color Index Name	Color Index Number	Approximate Percent of Dye in "as sold" Mixtures Used
Eosine	Acid Red 87	45380	75
Fluorescein	Acid Yellow 73	45350	75
Rhodamine WT	Acid Red 388	None	20
Sulforhodamine B	Acid Red 52	45100	75

EXHIBIT 2 OUL instrumental detection limits for four tracer dye mixtures in carbon sampler elutants and in water samples. Reporting limits are three times the detection limits. All limits are based on the as-sold weight of the standard dye mixture

Dye Mixture	Carbon Sampler Elutant (μg/L)	Water Samples (μg/L)
Eosine	0.050	0.015
Fluorescein	0.025	0.002
Rhodamine WT	0.170	0.015
Sulforhodamine B	0.080	0.008

EXHIBIT 3 Fluorescence magnitude of eosine and fluorescein as a function of pH

Parameter	Eosine	Fluorescein
Maximum fluorescence	pH > 6.4	pH > 8.1
80% of maximum fluorescence	pH 4.0	pH 7.0
30% of maximum fluorescence	pH 2.2	pH 6.0

ammonia environment. This increases the pH of the sample but not its volume.

There are three principal reasons that the amount of dye used for groundwater traces at waste sites is often inadequate. First, most of the introduced dye is not detected at sampling points. Discussing the variety of processes involved in the low detection percentages is beyond the scope of this article. However, Exhibit 4 illustrates detection percentages under conditions where mass balance calculations using water samples were possible. These results are from springs draining karst aquifers where higher dye detection percentages should be anticipated than in most other aquifers. The data suggest that, even in karst aquifers, one should anticipate detecting only 4 to 5 percent of the dye introduced. Traces combining short travel distances and dye introductions directly into karst conduits have the highest detection percentages (Field 1999; Mull, Liebermann, Smoot, & Woosley, 1988).

A second reason for the use of inadequate amounts of tracer dye is concern that the dye may be detected off-site and color streams, springs, or wells. This is seldom a credible concern if experienced personnel are involved in the investigation design. Additionally, as shown in Exhibit 5, there is a three to almost four order of magnitude difference in dye concentrations producing color visible to a trained person under field conditions and analytical detection limits. There is a further 1.5 to 2 order of magnitude difference between dye concentrations visible to a trained person and those likely to be noticed under field conditions by the general public.

EXHIBIT 4 Percent of injected tracer dye detected at karst springs. Data from Arkansas, Kentucky, Maryland, Nevada, Tennessee, and Texas. Expanded from Aley (2016)

Dye Mixture	Amount (kg)	Straight Line Distance of Trace (km)	Injected Dye Detected (%)	Reference
Eosine	0.91	1.65	5.8	OUL data
	2.72	1.31	4.9	OUL data
	6.36	1.46	0.9	White et al. (2015)
	10.44	1.63	0.1	White et al. (2015)
	15.85	28.18	1.3	Hunt et al. (2005)
Fluorescein	0.45	0.44	45	OUL data
	0.91	2.96	15	OUL data
	4.54	1.37	0.2	White et al. (2015)
	6.81	1.42	0.01	White et al. (2015)
	11.35	22.54	0.8	Hunt et al. (2005)
Rhodamine WT	0.018	0.98	62.5	Mull et al. (1988)
	1.82	0.44	38	OUL data
	1.82	2.87	2.7	OUL data
	2.72	4.07	17.4	OUL data
	7.00	0.30	96.6-98.0	Field (1999)
Median		**1.46**	**4.9**	

Note. Hauwert, Sansom, Johns, and Aley (2004) calculated dye recovery percentages for 20 groundwater traces involving straight line travel distance of 3.2 to 30.5 km in the Barton Springs portion of the Edwards Aquifer, Texas, USA. Percent of injected dye detected at receiving springs ranged from 0% to 77% with a mean of about 16% and a median of about 4.2%. The fluorescein and eosine dye mixtures were 75% dye equivalent; the rhodamine WT mixture was 20% dye equivalent.

EXHIBIT 5 Comparison of detection limits for OUL standard dye mixtures in water with (1) laboratory analysis, (2) visually under field conditions by trained personnel, and (3) field conditions by the general public (units are micrograms per liter [μg/L])

Dye Mixture	Laboratory Analysis	Trained Personnel	General Public
Eosine	0.015	135	13,500
Fluorescein	0.002	7	140
Rhodamine WT	0.015	125	2,500
Sulforhodamine B	0.008	50	1,000

Investigators, regulators, and the public must bear in mind that tracing work is routinely used to protect public health and the environment, and that harmless amounts of dyes are being used to help characterize the behavior of compounds that have the potential to cause harm. The dyes discussed in this article have been extensively studied and their safety when used as groundwater tracers is well established (Field, Wilhelm, Quinlan, & Aley, 1995; Smart, 1984).

The third reason for failures of tracer tests to identify all sites to which the water flows, and the focus of this article, is sampling reliance on water samples rather than on carbon samplers. This article demonstrates that when sampling stations are sampled with both carbon samplers and water samples for the same sampling periods that water samples are substantially more likely to not detect the dyes than is the case for carbon samplers. It has been the author's experience that producing dye detections in studies based on water samples routinely requires the use of several times more dye (and in some cases in excess of an order of magnitude more dye) than if sampling relies on carbon samplers.

2 | METHODS

The use of carbon samplers for concentrating and visually detecting fluorescein dye was initially outlined by Dunn (1957). Since then the method has been refined and expanded by various subject matter experts to include quantitative fluorometric analysis of carbon sampler elutants for multiple dyes. All four of the dyes discussed in this article will adsorb onto activated carbon samplers and then can be eluted in the laboratory for subsequent analysis. There is no established standard method, but the approaches used by the few entities that routinely conduct professional grade tracer dye analysis are fundamentally similar.

The carbon samplers discussed in this article (see Exhibit 6) are flexible envelopes of fiberglass screening loosely containing 4.25 g of 6 to 12 mesh (3.350–1,700 mm diameter) coconut activated carbon (Calgon Product 207C; Calgon Carbon Corporation, Moon Township, Pennsylvania). Manufacturer's data show that the carbon in each sampler has a surface area of 1,150 m^2 per gram (g). A 4.25-g carbon sampler thus has a carbon surface area of 0.49 hectares (1.225 acres). Dye adsorbed onto the carbon is eluted with 15 mL of a standard solution consisting of 5 percent aqua ammonia and 95 percent isopropyl alcohol solution and sufficient potassium hydroxide to saturate the solution. The isopropyl alcohol solution is 70 percent alcohol and 30 percent water. The aqua ammonia solution is 29 percent ammonia. The eluting solution is allowed to remain in contact with the carbon for 1 hr without agitation and then poured off for analysis. The analytical protocol followed by OUL (Protem, Missouri) is detailed in Aley and Beeman (2015).

As discussed below, three primary factors affect the amount of dye adsorbed onto a carbon sampler:

- the duration of the sampling period,
- the concentration of dye in the water during the sampling period, and
- the extent of dye depletion from the water in contact with the carbon granules.

2.1 | Sampling period duration

Carbon samplers are left in place in waters being sampled for durations appropriate to the individual tracing study. At waste sites with contaminants capable of being adsorbed onto activated carbon, the sampling duration is commonly 1 week, but durations may be longer, especially if the distances being traced are longer than average and contaminant concentrations are not excessively large.

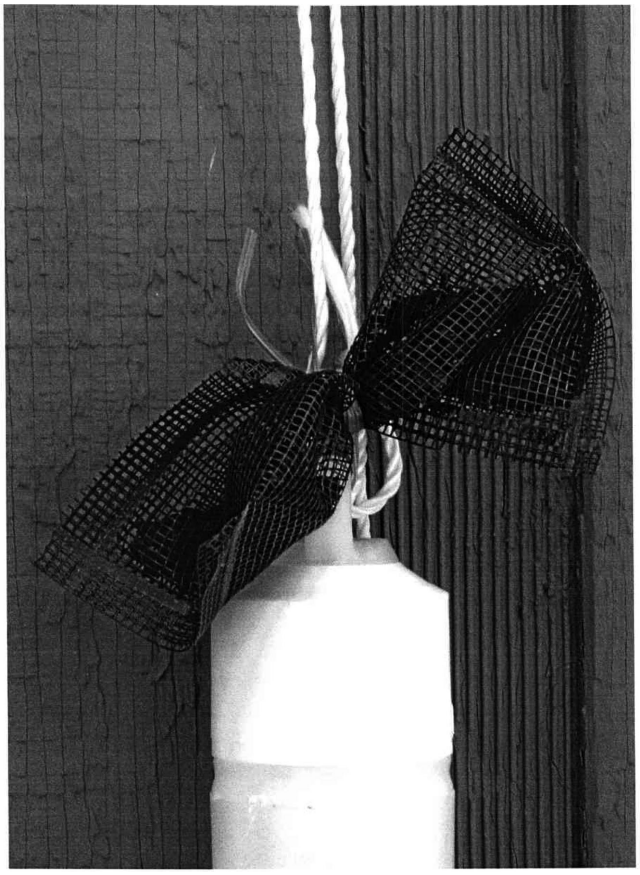

Exhibit 6 Carbon sampler on disposable bailer that is 3.81 cm in diameter. Different shaped carbon samplers are used for smaller diameter wells

For practical purposes, the carbon samplers continue to accumulate dye, if it is present, from the time the dye first reaches the sampler until the sampler is removed at the end of the sampling period. Results from carbon samplers in place for different periods of time can be normalized to compare results by dividing the total concentration in the sampler by the number of days it was in place to calculate a mean daily dye accumulation value. The reasonableness of this approach has been demonstrated by summing accumulated dye concentrations from several carbon samplers in place for short periods of time with samplers in place at the same location for the entire longer sampling period. At springs where samplers are typically placed in water flowing at 0.5 to 2.0 cm/s, the sum of dye concentrations in samples collected three or four times per week is typically about 20 percent greater than the concentration in a sampler left in place for a week. Since a much larger volume of water containing dye passes through carbon samplers in springs than in typical monitoring wells, calculating mean dye concentrations from carbon samplers per day is a reasonable way to compare results from samplers left in place for different periods of time.

2.2 | Dye concentrations in sampled water

If dye concentrations in water samples and in carbon sampler elutants are plotted against time, the shapes of the graphs are commonly similar, but different concentration scales are needed for the two types of samples. This suggests that the rate of dye adsorption onto carbon is a relatively constant percent of the dye present in the sampled water regardless of the concentration of the dye. The rate of dye adsorption onto carbon is a relatively constant percent of the dye present in the sampled water regardless of the concentration of the dye. This presumes that the dye concentration is not so great as to substantially reduce the amount of adsorbing surface area on the carbon. Extensive field experience in dye tracing at waste sites indicates that these assumption are usually reasonable.

The rate of dye adsorption onto carbon is a relatively constant percent of the dye present in the sampled water regardless of the concentration of the dye.

2.3 | Dye depletion adjacent to carbon granules

It takes about 20 min for a carbon sampler in circulating water to adsorb sufficient dye to yield a dye concentration in the eluting solution equal to the mean concentration in the water being tested. Carbon samplers placed in streams with flow velocities at the samplers of at least 1.5 cm/s maximize the adsorption of tracer dyes. Lower flow velocities reduce total dye adsorption onto activated carbon because dye is depleted from the water in immediate contact with carbon granules and water circulation is not rapid enough to replace the dye-depleted water with fresh water from which dye has not been depleted. Most monitoring wells have groundwater velocities where dye depletion in the water in contact with the carbon granules limits dye adsorption. Inherently poor water circulation around carbon samplers in wells smaller than about 5 cm in diameter enhances excessive dye depletion in the water in contact with the carbon. In contrast, carbon samplers placed at most springs or streams are unlikely to experience excessive dye depletion from the water in contact with the carbon.

While adsorption of dye or contaminants onto the carbon slightly decreases available adsorption sites, this decrease is minimal if the carbon samplers are collected and new samplers replaced at weekly intervals are not exposed to concentrations of contaminants and/or tracer dyes appreciably greater than usually encountered in groundwater at waste sites. Sampling intervals longer than about a week are sometimes appropriate, especially if concentrations of dyes and contaminants are relatively low. The most appropriate sampling intervals at monitoring wells are often determined by factors other than decreases in carbon activation sites. Additionally, while some contaminants have the potential to desorb an adsorbed dye molecule from the carbon sampler, field evidence indicates that this is a negligible problem at most waste sites.

In practice, carbon samplers function as continuous accumulators of tracer dyes present in the water being tested. The amount of dye accumulation varies with the exposure time and the concentrations of dyes in the water. The major exception is in very slow moving water where water in contact with carbon granules is depleted of dye and not replaced with water in which the dye concentration has not been depleted. This occurs in most monitoring wells.

3 | PERFORMANCE COMPARISON

Activated carbon samplers are not a replacement for water samples. Collecting both types of samples is strongly recommended for most tracer studies since the two types of samples yield different, but complimentary, data.

The OUL has a database of analysis results from approximately 150,000 carbon samplers and associated water samples. Selected data from this database were used to compare the performance of carbon samplers and grab samples of water in detecting tracer dyes. The data selected for this study are from groundwater tracing studies at sites throughout the United States. Study areas ranged from the arid west to the humid south and east. Some monitoring well data are from karst areas with springs, but most are from waste sites where the geology ranged from fractured rock to colluvium, alluvium, residuum, and glacial till. The comparison separates results for springs from those for monitoring wells. There were insufficient data for pumping wells so these wells were excluded. However, if wells are pumped most of the time and samplers are placed in the discharging water, the results are expected to be similar to those for springs.

Exhibit 7 compares tracer dye analysis results where both water samples and carbon samplers were routinely analyzed and where dye was detected in either a water sample and/or the associated carbon sampler. Sampling periods when maximum dye concentrations were unlikely to have occurred at either the beginning or end of the periods were excluded. There were a total of 1,002 sampling periods analyzed for springs and 939 for monitoring wells.

At springs, dye was detected in 98.9 percent of the carbon samplers, but in only 44.3 percent of the water samples. Sulforhodamine B was the dye least likely to be detected in water samples from springs and eosine was the most likely to be detected. The results illustrate the importance of carbon samplers in accumulating dyes and yielding positive dye detections at springs, especially when dye concentrations are below the detection limits in water samples. The few cases where dye was detected in a water sample from a spring but not in the associated carbon sampler, probably indicate that the sampler had been covered by debris or perhaps was not in the water for much of the sampling period and thus did not properly sample the water.

Exhibit 7 shows that dye was detected in 95.7 percent of the carbon samplers from monitoring wells but in only 80.9 percent of the water samples. The slow exchange of dyed water in monitoring wells as

EXHIBIT 7 Percent of sampling periods where both carbon samplers and water samples were analyzed and dye was detected in one of both kinds of samples

Dye Mixture	Total Periods	% Water Samples	% Carbon Samplers
Springs			
Mean sampling duration = 15 days			
Eosine	384	50.8	98.2
Fluorescein	277	43.0	98.6
Rhodamine WT	224	42.9	100.0
Sulforhodamine B	117	29.1	100.0
Total	1,002		
Weighted mean		44.3	98.9
Monitoring wells			
Mean sampling duration = 22 days			
Eosine	219	73.5	93.6
Fluorescein	369	84.0	99.7
Rhodamine WT	330	81.2	92.4
Sulforhodamine B	21	100	100.0
Total	939		
Weighted mean		80.9	95.7

EXHIBIT 8 Median dye concentrations when dye was detected in carbon samplers but not in associated water samples

Dye Mixture	Total Periods	Median Carbon Concentration (μg/L)	AF
Springs			
Mean sampling duration = 16 days			
Eosine	128	3.26	217
Fluorescein	106	1.51	756
Rhodamine WT	90	14.8	987
Sulforhodamine B	54	6.08	760
Total	378		
Weighted mean		5.9	656
Monitoring wells			
Mean sampling duration = 27 days			
Eosine	40	0.651	43
Fluorescein	32	2.26	1130
Rhodamine WT	38	7.49	499
Sulforhodamine B	NA	NA	NA
Total	110		
Weighted mean		3.48	517

AF = median dye concentration in carbon samplers divided by the detection limit of that dye in water.

contrasted with springs is the primary explanation for the smaller difference in detection percentages between springs and monitoring wells. OUL records do not indicate the diameter of the wells sampled, but in the author's experience many of the cases where dye was detected in water samples from wells but not in the associated carbon samplers were probably small diameter wells. The "failure rate" of a type of sample to detect dye is the percent difference between the detection percent and 100 percent. Based on the monitoring wells used in the comparisons in Exhibit 7, the failure rate of water samples to detect dye in monitoring wells when it was actually present was 19.1 percent. In contrast, the failure rate was 4.3 percent with carbon samplers. The value of sampling with carbon samplers is obvious.

Exhibit 8 provides an analysis of dye concentrations in carbon samplers in cases where dye was not detected in water samples for the same period. There were a total of 378 sampling periods at springs and 110 sampling periods at monitoring wells where tracer dyes were detectable in carbon samplers but not in any of the water samples. The data are a subset of those used for Exhibit 7 and show the extent of dye accumulation in carbon samplers when dye concentrations in the associated water are less than the detection limit. In preparing this analysis, any data for a sampling period when it was not clear that dye should have been present at both the beginning and end of the sampling period was discarded. As in the previous exhibit, data were separately analyzed for springs and monitoring wells. A ratio (called accumulation factor [AF] after Aley, 2016) was calculated by dividing the median dye concentration detected in carbon sampler elutants by the detection limit of that dye in water samples. It is likely that most dye concentrations in water samples were substantially below the detection limit and that the AF values shown in Exhibit 8 are a substantial underestimate of the true magnitude of the AF.

The ranges of concentration values and the ranges of AF values between the carbon sampler elutant concentrations and the detection limits in water are large. Exhibit 8 shows median values; mean values were routinely higher due to a few very high values. These may have reflected sampling periods when one or more short duration pulses of concentrated dye affected the spring or well.

The weighted mean AF between carbon sampler elutant concentrations and the detection limit in water samples was 656 in samples from springs and 517 in samples from monitoring wells. In both springs and monitoring wells, the activated carbon samplers detecting eosine dye appear to have performed less effectively than for the other dyes.

A common sampling frequency for dye tracing studies is approximately weekly with no sampling at less than 6, or more than 8, days. Exhibit 9 was prepared to compare the tracing results for carbon samplers and water samples for this typical sampling frequency. As in the previous exhibits, the mean AF values were greater than median values due to a few high values. There were insufficient data to assess the functioning of sulforhodamine B dye. As expected, the mean and median AF values are routinely greater for sampling durations longer than 6 to 8 days, but no exhibit was prepared to show this.

4 | CASE HISTORIES

If a groundwater tracing study is intended to identify all sampling points to which the dyed water flows, then failing to identify some locations is a serious study flaw. It is an inherent risk when sampling is

EXHIBIT 9 Accumulation factors (AF) for carbon samplers in place for periods of 6 to 8 days. There were insufficient samples for a sulforhodamine B dye assessment

Dye Mixture	Total Periods	Mean AF	Median AF
Springs			
Eosine	106	415	255
Fluorescein	70	195	102
Rhodamine WT	105	658	506
Total	281		
Weighted mean		445	311
Monitoring wells			
Eosine	93	38	5
Fluorescein	154	379	22
Rhodamine WT	136	28	11
Total	383		
Weighted mean		166	14

focused primarily or exclusively on water samples. The extent of the risk is demonstrated by the following two case studies where sampling and analysis used both activated carbon samplers and grab samples of water. If sampling in these two studies had relied only on water samples then 55 percent of the monitoring points where dye was detected would have been missed.

One case study area is in karstified limestones, the other in fractured volcanics and coarse alluvium. Both were large-scale tracing projects that involved over 100 sampling stations and relatively long monitoring periods. Both are "real-world" cases where contaminants of concern exist, where effective remediation efforts are needed, and where data resulting from groundwater tracing investigations were relied upon to identify flow paths and receptor sites as accurately and completely as possible.

4.1 | Case 1: Karst area in Frederick Valley, Maryland

White, Aley, Cobb, Weikel, and Beeman (2015) published on extensive tracer studies conducted in a karst area with gentle topography and numerous monitoring wells and springs that were sampled. The tracer dye sampling was focused on an area about 3.5 km long by 1.8 km wide. Solutional openings decreased with depth but extended to 96.8 m below ground surface.

In 1995, tracing at the site involved shallow dye introductions, 139 sampling stations, and lasted for 13 weeks with 17 additional weeks at some selected stations. For the 1995 tracing a total of 15.5 kg of tracer dye mixtures (3.18 kg eosine, 2.27 kg fluorescein, and 4.54 kg rhodamine WT) were introduced at five separate points in the upper portions of the karst aquifer. The length of the assessed portion of the aquifer is about 2 km; the longest straight-line distance traced was about 1.8 km and the mean straight-line distance traced was about 1.3 km. Fluorescein was detected in carbon samplers from two monitoring wells and six springs; it was detected in water samples from only one of the monitoring wells and four of the springs. Eosine was detected in carbon samplers from five monitoring wells and six springs; it was detected in water samples from only two monitoring wells and six springs. No rhodamine WT was detected during the 1995 sampling period.

For the 2013 study a total of 127 stations were sampled. A total of 17.2 kg of fluorescein and eosine dye mixtures was introduced into two wells screened in deep portions of the aquifer. The longest straight-line distance traced was 1.4 km and the mean distance was about 1.0 km. Fluorescein from the 2013 introduction was detected in carbon samplers from five monitoring wells and two springs; it was detected in water samples from four of the monitoring wells and from both of the springs. Eosine from the 2013 tracing was detected in carbon samplers from 11 monitoring wells and six springs; it was detected in water samples from five of the monitoring wells and two of the springs. Residual eosine and rhodamine WT from the 1995 tracing were detected during the 2013 tracing; there may have been residual fluorescein present, but there had been disposal of this dye within the area and actual sources for residual amounts of fluorescein were uncertain.

Results from the 1995 tracing showed that water samples contained detectable dye concentrations at 83 percent of the springs where dyes were detected in carbon samplers. Water samples contained detectable dye concentrations in 43 percent of the monitoring wells where dyes were detected in carbon samplers.

Results from the 2013 tracing showed that water samples contained detectable dye concentrations at 50 percent of the springs where dyes were detected in carbon samplers. Water samples contained detectable dye concentrations in 56 percent of the monitoring wells where dyes were detected in carbon samplers. In addition, in 2013 rhodamine WT derived from the 1995 dye introductions was detected in numerous carbon samplers from eight springs; water samples failed to detect rhodamine WT dye at any of these locations.

Combining results from the 1995 and 2013 tracing (including the detection of rhodamine WT from the 1995 tracing during 2013), water samples contained detectable dye at 50 percent of the springs where dyes were detected in carbon samplers and at 52 percent of the monitoring wells where dyes were detected in carbon samplers. If sampling had relied exclusively on water samples, the conclusions from the study would have been quite erroneous.

4.2 | Case 2: Site in fractured volcanics and alluvium

This case study involved a large-scale groundwater tracing study with sampling that lasted for over 2 years and included over 100 sampling stations. All four of the dyes discussed in this article were used and the total mass of dye introduced into the groundwater system at four different locations equaled about 75 kg. Well depths ranged from 30 to 270 m below ground surface. Sampling for tracer dyes was focused on an area approximately 6.5 km by 2.8 km. The length of the assessed portion of the aquifer was about 5 km. Traced travel distances between dye introduction and dye detection points averaged over 2.2 km with the longest straight-line distance traced being almost 4.5 km.

One or more of the tracer dyes was detected in one or more of the carbon samplers from 14 wells. These wells were also monitored by collecting grab samples of water each time the carbon samplers were

collected and new samplers placed. Water samples were analyzed for the beginning and end of each sampling period that yielded a positive dye detection in a carbon sampler. Positive dye detections in water samples occurred in only 2 of the 14 wells, although a third well had several dye detections slightly lower than the reporting limit (which was three times the detection limit). If this well is included as a positive detection site, then dye was detected in water samples from 21 percent of the wells where it was detected in carbon samplers. At one of the wells where dye was detected in both carbon samplers and water samples, the date of first dye arrival at the well, based on water samples, was 3 months after it was first detected in activated carbon samplers. Based on carbon sampler data for wells sampled with both carbon samplers and grab samples of water, each of the four tracer dyes was detected in at least one well. In contrast, only one of the four dyes was detected in these wells based on water samples. There were a number of multiport wells where only water samples could be collected. Dye was detected in two of these wells. Dyes were detected in 16 percent of the wells sampled with both carbon samplers and grab samples of water but in only 5 percent of the wells sampled exclusively with grab samples of water.

5 | SUMMARY

Groundwater tracing with fluorescent tracer dyes is a tool that can be used in multiple ways in groundwater investigations and remediation projects. This article has focused on the value of tracing programs that use activated carbon samplers in concert with grab samples of water. It is not the intention of this article to suggest that all groundwater tracing should use this strategy. Some tracer studies need to rely on water samples to address the specific issues of concern. However, the high failure rate of water samples in detecting dyes, as demonstrated in this article, shows the fallacy of suggesting that all tracer studies should be based on quantitative analysis of water samples.

The use of activated carbon samplers for detecting fluorescent tracer dyes is routinely the most dependable and cost-effective approach available. It is superior to introducing much larger masses of dye in an effort to obtain more quantitatively precise results and reduce the failure-to-detect rate associated with the exclusive use of water samples. Furthermore, the risk of producing unacceptably colored water is much less for studies that depend upon carbon samplers rather than water samples.

In summary, carbon samplers are routinely more effective than water samples for detecting the presence of tracer dyes at sampling stations. Carbon samplers are continuous and accumulating samplers, and can adsorb and accumulate dyes even if the dyes are only intermittently present. Since carbon samplers accumulate dyes, they can demonstrate positive traces even when dye concentrations are below detection limits in water samples. The net result is more dependable sampling for tracer dyes than is provided by water samples. In addition, the use of carbon samplers decreases the amount of tracer dyes needed and thereby lessens concern about dye creating off-site issues such as colored water. Furthermore, the use of smaller amounts of dye decreases residual dye concentrations that may complicate future tracing using the same dyes. In most cases, the use of carbon samplers decreases sampling and analytical costs because it minimizes sampling frequency as contrasted with sampling based on water samples.

Water samples can be used to determine dye concentrations at particular times or at selected intervals if automatic pumped samplers are used. If one needs to plot a "breakthrough curve" of dye concentrations versus time, or do a mass balance calculation of dye detection at a sampling station, then water samples are necessary. The use of automatic pumped samplers at most or all sampling stations is logistically impractical for large scale investigations such as the two case histories used in this article.

If monitoring wells have very low yields they provide little water circulation through carbon samplers, and this results in very little accumulation of dye in the sampler. Under these conditions it is appropriate to routinely analyze both water and carbon samplers.

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