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Using Activated Carbon Samplers to Improve Detection of Fluorescent Tracer Dyes in Groundwater Remediation Studies

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ABSTRACT: Fluorescent tracer dyes are commonly used in designing and evaluating groundwater remediation projects. Activated carbon samplers, the focus of this paper, adsorb, retain, accumulate, and provide continuous sampling for fluorescent dyes including eosine, fluorescein, rhodamine WT, and sulforhodamine B. Analysis of carbon sampler elutants for the presence and concentration of tracer dyes used a laboratory-based spectrofluorophotometer set to synchronously scan excitation and emission fluorescence wavelengths with the wavelength separation selected to maximize the fluorescence intensity of the tracer dyes and minimize background fluorescence. Tracer dyes were separated from each other and quantified.

The comparative effectiveness of water and carbon samplers in detecting tracer dyes was assessed using data from 1,941 sampling periods at sampling stations where one or more of the four dyes was detectable. Tracer dyes were detected in carbon samplers at springs in 98.9% of the sampling periods, but in water samples from only 44.3% of the periods. At monitoring wells tracer dyes were detected in carbon samplers in 95.7% of the sampling periods, but in water samples in only 80.9% of the sampling periods. The accumulation factor (AF) is the accumulated dye concentration in a carbon sampler divided by the mean dye concentration in water samples for the same period. Based on sampling periods of 6 to 8 days, the weighted mean AF for eosine, fluorescein, and rhodamine WT in carbon samplers from springs was 445 and was 166 for carbon samplers in monitoring wells.

INTRODUCTION

Studies and sampling stations from which data were extracted for this paper were selected from multiple sites to characterize dye performance under a wide range of hydrogeologic and climatic conditions. Selected studies had a good database of results from both water samples and carbon samplers from multiple sampling stations. Sampling for most of the selected studies continued until dye concentrations at sampling stations were at least one order of magnitude smaller than peak concentrations. The selected studies for monitoring wells were about 50% in karst settings, 30% in fractured rock, and 20% in other settings where preferential flow routes were anticipated. All of the spring studies were in karst. Sampling and analysis approaches were as specified in Aley and Beeman (2013).

Activated carbon samplers adsorb and accumulate tracer dyes. The dyes are desorbed (eluted) by treating the carbon with an eluting solution and then analyzing this elutant on a Shimadzu RF-5301 spectrofluorophotometer operated under a synchronous scan protocol.

The settings for excitation and emission slits on the spectrofluorophotometer are narrower for carbon sampler elutants than for water samples. The rationale for using the narrower slits for carbon sampler elutants is that extraneous fluorescent material is likely to be more abundant in carbon samplers than in water samples. As a result of the difference in slit settings the detection limits for the four dyes are smaller for water samples than for carbon sampler elutants (see Table 1).

TABLE 1. Detection limits for four tracer dyes.

Dye Mixture	Carbon Sampler Elutants (µg/l)	Water Samples (µg/l)
Eosine (AR-87)	0.050	0.015
Fluorescein (AY-73)	0.025	0.002
Rhodamine WT (AR-388)	0.170	0.015
Sulforhodamine B (AR-52)	0.080	0.008

Dye quantities introduced in the selected studies varied as a function of the anticipated subsurface travel distance to the most distant potential detection site, the hydrogeologic setting, and the type of dye being used. The dye equivalents in the mixtures routinely used were 75% for eosine, fluorescein, and sulforhodamine B and 20% for rhodamine WT. The amount of dye used for a particular trace depended upon a number of factors. If a dye introduction used fluorescein the quantity was commonly between 0.45 and 2.73 kg. Traces with eosine typically used 50% more dye mixture by weight than traces with fluorescein, and traces with rhodamine WT and sulforhodamine B dyes typically used three to four times more dye mixture by weight than traces with fluorescein. All dye concentrations are based on the as-sold weight of the dye mixture used.

The performance of carbon samplers and grab samples of water was assessed independently for springs and monitoring wells. Dye accumulation on activated carbon is commonly greater at springs than in monitoring wells because water at springs circulates through the carbon samplers more rapidly. Where water movement in contact with the activated carbon is restricted the water in direct contact with the carbon particles becomes depleted of some dye and, as a result, the total amount of dye accumulated on the carbon is reduced. This is especially true for wells with low yields or in well segments where there is minimal water circulation. The amount of dye accumulated on carbon in very small diameter wells (2.54 cm or less) is reduced due to poor water circulation in and around the carbon samplers. Data in this paper represent wells that range in diameter from 2.54 to 15.24 cm.

Carbon samplers in wells were routinely placed in the middle of the screened interval or (in open-hole wells) in the middle of the saturated zone. Multiple carbon samplers are sometimes placed in open-hole wells with individual samplers set at zones of higher permeability. No wells containing multiple carbon samplers were used for the current study. Water samples from monitoring wells were typically collected by lowering a dedicated bailer to the depth where the carbon samplers were routinely placed. Wells were not purged.

UNDER-UTILIZATION OF ACTIVATED CARBON SAMPLERS

Activated carbon samplers have been under-utilized in groundwater tracing work due to at least two common misconceptions:

- That grab samples of water are better because they are more quantitative than carbon samplers.
- That much of the dye introduced for a trace will be detected at downgradient sampling stations.

Dye Quantification in Carbon Samplers. To make analysis results from activated carbon samplers quantitative and to permit comparison with water samples the Ozark Underground Laboratory (OUL) has standardized all materials and steps in the process as outlined in Aley and Beeman (2015).

The amount of tracer dye adsorbed by activated carbon samplers is a function of the concentration of dye in the water in contact with the activated carbon and the duration of this contact. Dye is removed from the passing water by adsorption, not filtration. The velocity of water passing through a sampler is an important factor when the flow rate of the water is slow enough that the water in contact with the carbon is depleted of a significant portion of its dye before being replaced by fresh water. In the experience of the OUL this is not an appreciable limitation at springs if the samplers are placed where the water velocity is at least 1.5 cm/sec. Samplers placed where flow rates are about 1.5 cm/sec adsorb about the same amount of dye as samplers placed where the velocity is about 30 cm/sec. Depletion of dye from water in contact with carbon occurs in most monitoring wells when samplers are suspended in the well bore. This does not negate the utility of activated carbon samplers in monitoring wells.

Carbon samplers are well suited to detecting short duration dye pulses in springs and monitoring wells. These pulses, which are common in karst and other heterogeneous aquifers, are subject to being missed if only grab samples of water are collected at typical sampling frequencies. Additionally, water samples frequently fail to detect the presence of small concentrations of tracer dyes. As a result water samples routinely over-estimate the time of first dye arrival, underestimate the duration of dye pulses, miss some dye detection locations, and miss locations where dyes are not continuously present.

Dye Detection Percentages. The amount of dye introduced for tracer tests is often based on the erroneous assumption that only a limited amount of dye will be detained in the aquifer during the course of the study. This erroneous assumption is compounded by concern from clients or regulators that colored water might be visible to the public and that the amount of dye used must ensure that this does not occur. The net result is that an inadequate mass of dye is introduced for many attempted traces.

Mass balance calculations can be made for dye traces where the dye discharges from one or more springs and where the flow rates and dye concentrations can both be measured in water samples. Conditions suitable for making these calculations are seldom met at hazardous waste sites, but insight into the amount of dye detained in karst or fractured rock aquifers can be gained from tracer studies where mass balance calculations are possible.

Table 2 shows the calculated percent of injected dye detected from 33 traces to karst springs. In none of the cases was there reported evidence of leakage into a deeper aquifer. One of the most important variables in detection percent is the nature of the dye introduction point. Dye introductions directly into a cave stream and detections at downstream springs (Field, 1999; Smoot et al., 1987) yielded large detection percentages whereas dye introductions into borings or monitoring wells (White et al., 2015) routinely yielded small detection percentages. Presuming that excessively large masses of dye are not used, a detection of 2 to 4% of the injected amount of tracer dye is a reasonable estimate for most karst sites that discharge from springs. The percent is routinely smaller for karst sites without obvious springs and in most non-karst aquifers.

TABLE 2. Percent of injected tracer dye detected at karst springs. Data from sites in Arkansas, Kentucky, Tennessee, Maryland, and Texas.

Dye Mixture Amount and Type	Straight Line Distance (km)	Percent of Injected Dye Detected	Reference
0.91 kg Eosine	1.65	5.8	OUL data
6.36 kg Eosine	1.46	0.9	White et al. (2015)
10.44 kg Eosine	1.63	0.1	White et al. (2015)
15.85 kg Eosine	28.18	1.3	Hunt et al. (2005)
0.45 kg Fluorescein	0.44	45	OUL data
0.91 kg Fluorescein	2.96	15	OUL data
4.54 kg Fluorescein	1.37	0.2	White et al. (2015)
6.81 kg Fluorescein	1.42	0.01	White et al. (2015)
11.35 kg Fluorescein	22.54	0.8	Hunt et al. (2005)
0.018 kg Rhodamine WT	0.91	62.5	Smoot et al. (1987)
1.82 kg Rhodamine WT	0.44	38	OUL data
1.82 kg Rhodamine WT	2.87	2.7	OUL data
7.0 kg Rhodamine WT	0.30	96.6-98.0	Field 1999

Hauwert et al. (2004) calculated dye recovery percentages for 20 groundwater traces involving straight line travel distances 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%. Types of dye varied with greater quantities for longer traces. The fluorescein and eosine dye mixtures were 75% dye equivalent; the rhodamine WT mixture was 20% dye equivalent.

FREQUENT FAILURE OF WATER SAMPLES TO DETECT TRACER DYES

Activated carbon samplers are continuously sampling and accumulating dye. In contrast, water samples provide data on the dye concentration at the instant the sample is collected. Collecting both kinds of data is recommended.

Dye analysis results were compared for water samples and carbon sampler elutants from 1002 sampling periods at springs and 939 sampling periods at monitoring wells. For each selected sampling period water samples were collected and analyzed at both the start and end of the sampling period and a carbon sampler was in place and analyzed for the entire sampling period. Results are shown in Table 3. The detection rates for water samples from springs varied by dye type from 29.1 to 50.8% with a weighted mean of 44.3%. The comparable values for monitoring wells varied from 73.5% to 100% with a weighted mean of 80.9%. In contrast, the detection rates for carbon samplers from springs varied by dye type from 98.2 to 100% with a weighted mean of 98.9%. The comparable values for monitoring wells varied from 92.4 to 100% with a weighted mean of 95.7%. Clearly carbon samplers are superior to water samples for detecting the presence of the four tracer dyes.

TABLE 3. Sampling periods at springs and monitoring wells when dye was detected in carbon and/or water samples. EOS = eosine; FLO = fluorescein; RWT = rhodamine WT; and SRB = sulforhodamine B.

Parameter	EOS	FLO	RWT	SRB	Total or Weighted Mean
SPRINGS					
Total sampling periods	384	277	224	117	1002
Mean length of sampling periods (days)	16	14	10	20	
Periods when dye was detectable in water samples	50.8%	43.0%	42.9%	29.1%	44.3%
Periods when dye was detectable in carbon samplers	98.2%	98.6%	100%	100%	98.9%
MONITORING WELLS					
Total sampling periods	219	369	330	21	939
Mean length of sampling periods (days)	13	25	26	16	
Periods when dye was detectable in water samples	73.5%	84.0%	81.2%	100%	80.9%
Periods when dye was detectable in carbon samplers	93.6%	99.7%	92.4%	100%	95.7%

White et al. (2015) reported that eosine and fluorescein were introduced into two separate wells in 2013 and subsequently detected that year in carbon samplers from 24 groundwater sampling points. Based on water samples, detectable concentrations of these dyes were found in only 13 of these locations. If both dyes were detected at the same location it was counted as two sampling points. In addition, White et al. (2015) reported that rhodamine WT introduced into the same karst groundwater system through a small sinkhole in 1995 was detected in 2013 (18 year later) in carbon samplers from 9 sampling stations but in none of the water samples from these stations. Combining data for the 1995 and 2013 dye introductions, dye was detected in activated carbon samplers from 33 sampling points but in water samples from only 13 stations. As a result, if sampling reliance had been placed on water samples rather than carbon samplers, 61% of the points where tracer dyes were detectable would have been missed. It is unlikely that the failure to detect rate would have been lowered if water samples had been collected more frequently.

The most likely explanation for the high failure to detect rate for water samples is that dye concentrations in water samples were below the detection limit. In some cases dye may be present at the sampling station in pulses and these pulses were not sampled by the grab samples of water. Loss of dye from water samples prior to analysis is unlikely since samples were kept under refrigeration between the time of collection and the time of analysis and analysis occurred within 10 working days of receipt at the laboratory. Additionally, occasional re-analysis of samples indicated that this possibility was unlikely.

As indicated in Table 3, a tracer dye is sometimes detectable in water samples but not in the associated carbon sampler. This is most common in small diameter monitoring wells and is attributed to poor circulation of dyed water around the carbon sampler or sometimes to field personnel not ensuring that the carbon sampler is submerged in the water.

ACCUMULATION FACTORS FOR CARBON SAMPLERS

The term “accumulation factor” (AF) is introduced in this paper. The AF equals the dye concentration in a carbon sampler elutant divided by the mean concentration in water samples during the period the carbon sampler was in place. If dye is not detectable in water samples the AF for a sampling period is calculated assuming that the dye concentration in the water samples equals the detection limit for that dye in water. This under estimates the AF for periods when dye is not detectable in water samples.

Table 4 presents data for all sampling periods when dye was detected in carbon samplers but not in the water samples for the beginning and end of the sampling period. Sampling periods when dye may have first arrived at a sampling station are excluded. Mean dye concentrations in carbon samplers from springs are at least two orders of magnitude larger than the detection limits for the dyes. The same applies to monitoring wells except that the mean value for eosine in carbon samplers is only about one and a half orders of magnitude greater than the detection limit.

TABLE 4. Sampling periods at springs and monitoring wells when dye was detected in carbon but not in associated water samples. EOS = eosine; FLO = fluorescein; RWT = rhodamine WT; and SRB = sulforhodamine B; NA = none available.

Parameter	EOS	FLO	RWT	SRB	Total or Weighted Mean
SPRINGS					
Total sampling periods	128	106	90	54	378
Mean length of sampling periods (days)	18	14	13	22	16
Maximum concentration in carbon samplers µg/l	15,900	54.0	914	346	
Minimum concentration in carbon samplers µg/l	0.297	0.152	0.477	0.974	
Mean concentration in carbon samplers µg/l	135	3.20	30.9	29.3	58.2
Median concentration in carbon samplers µg/l	3.26	1.51	14.8	6.08	5.9
Median concentration in carbon divided by detection limit in water.	217	756	987	760	656
MONITORING WELLS					
Total sampling periods	40	32	38	NA	110
Mean length of sampling periods (days)	19	29	34	NA	27
Maximum concentration in carbon samplers (µg/l)	37.2	39.5	115	NA	
Minimum concentration in carbon samplers (µg/l)	0.151	0.06	0.125	NA	
Mean concentration in carbon samplers (µg/l)	2.34	5.86	19.34	NA	9.24
Median concentration in carbon samplers (µg/l)	0.651	2.26	7.49	NA	3.48
Median concentration in carbon divided by detection limit in water	43	1130	499	NA	517

Mean concentrations of dyes in carbon samplers are routinely larger than median concentrations. The explanation is the common presence of a few carbon samplers with large dye concentrations. The weighted mean AF value for carbon samplers from springs is 656 and is 517 from monitoring wells.

Much of the sampling for tracer dyes is conducted at weekly intervals plus or minus one day. Table 5 indicates the percent of sampling intervals when dye was present in water samples, carbon samplers, or in both types of samples for 6 to 8 day sampling intervals. The weighted mean AF for carbon samplers in place for 6 to 8 days is 445 for spring sampling stations and 165 for monitoring wells.

TABLE 5. Accumulation Factors for carbon samplers in place for periods of 6 to 8 days. EOS = eosine; FLO = fluorescein; and RWT = rhodamine WT. There were insufficient data for an analysis of sulforhodamine B dye.

Parameter	EOS	FLO	RWT	Total or Weighted Mean
SPRINGS				
Total sampling periods	106	70	105	281
Periods when dye was detectable in water	65%	46%	45%	53%
Periods when dye was detectable in carbon	99%	99%	100%	99%
Range of AF values	3 – 6053	9 – 1217	37 – 2333	
Mean AF	415	195	658	445
Median AF	255	102	506	311
MONITORING WELLS				
Total sampling periods	93	154	136	383
Periods when dye was detectable in water	84%	84%	90%	86%
Periods when dye was detectable in carbon	91%	100%	86%	93%
Range of AF values	0.1 – 681	5 – 18804	1 – 451	
Mean AF	38	379	28	166
Median AF	5	22	11	14

When data from a number of locations are combined the range of AF values varies widely both at springs and monitoring wells. The range is routinely smaller for a single site.

Several mechanisms are responsible for the variability in AF values. Substantial short-term variations in dye concentrations in tested water is a major factor. Low AF values could result from desorption of tracer dye from carbon samplers in the presence of some groundwater contaminates, yet carbon samplers work well even in wells with substantially elevated concentrations of the most common contaminants of concern so this does not appear to be a common explanation for low AF values.

CASE STUDY

A groundwater tracing study was conducted by the OUL that provides a useful comparison of the behavior of fluorescein and rhodamine WT dyes in both water and carbon samplers. 4.5 kg of fluorescein dye mixture and 12.9 kg of rhodamine WT mixture were introduced within a few minutes of each other into the same point in a losing stream segment of a small headwaters stream. There was no natural flow of water at the dye introduction point at the time of dye introduction. A total of 81,750 L of water for the trace was hauled to the site by tanker truck in multiple loads over an 8-hour period. All introduced water disappeared into the subsurface within 12 meters of the dye introduction point. A large amount of dye was used for this trace to determine if there was a hydrologic connection between lands adjacent to the dye introduction point and large springs up to 15.5 km distant.

Dye from the trace was detected in Southeast Spring, located 320 meters from the dye introduction point and 23 meters lower in elevation. The thickness of the clay-rich cherty residuum underlying the dye introduction area was approximately 10 meters. The mean flow rate of the spring during the study was approximately 2.5 L/sec.

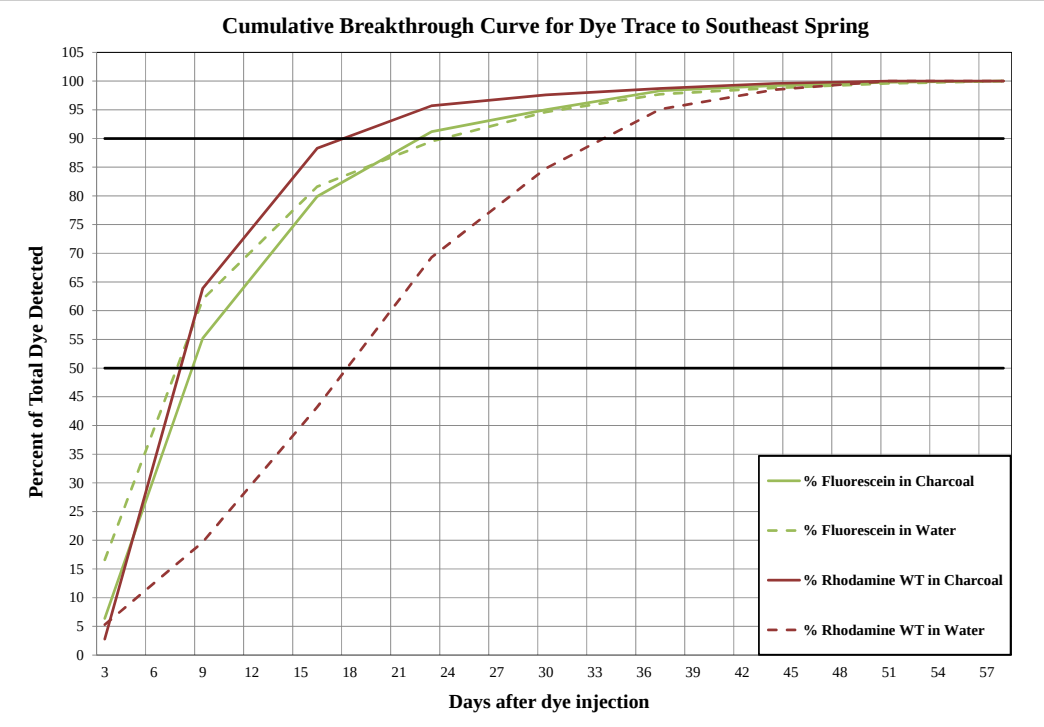

FIGURE 1. The cumulated percent of each of the dyes detected on each of the sampling dates during the 58-day study period. Results are shown for both water samples and carbon samplers. Time values that are typically most useful are: (1) time of first dye arrival; (2) time when 50% of the detected dye has arrived at the sampling station; and (3) time when 90% of the detected dye has arrived. Except for rhodamine WT in water, the graph shows that these important times are similar regardless of which dye or which sample type is used.

Based upon dye concentrations in water samples 0.612 kg of fluorescein dye mixture discharged from Southeast Spring during the 58-day study period. This was 13.5% of

the mass of fluorescein dye mixture introduced. Based upon rhodamine WT dye concentrations in water samples 0.145 kg of the rhodamine WT dye mixture introduced was detected in waters discharging from Southeast Spring during the 58-day study period. This was 1.1% of the mass of rhodamine WT mixture introduced.

On a unit weight basis 35 times more fluorescein than rhodamine WT was detected in water. This occurred for two principal reasons. First, rhodamine WT has a greater tendency to adsorb onto earth materials than does fluorescein (Aley, 2008). Second, rhodamine WT is composed of approximately equal proportions of two isomers (Sabatini and Al Austin, 1991). One of these isomers experiences substantial retardation in groundwater systems and it is likely that little if any of this isomer discharged from Southeast Spring. The mean AF for rhodamine WT was larger than the mean AF for fluorescein. This is consistent with the greater sorption tendency of rhodamine WT.

CONCLUSIONS

Activated carbon samplers are superior to water samples for detecting the presence of commonly used fluorescent tracer dyes in both springs and monitoring wells. They are especially useful in cases where dye concentrations are less than detection limits in water samples or when tracer dyes reach sampling stations in pulses and their detection may be missed by grab samples of water.

Those designing groundwater tracing studies often underestimate loss, dispersion, and retention of tracer dyes within the aquifer being tested. These underestimations, compounded by client or regulatory desires to not produce any visually colored water that might be seen by the public, frequently result in very small dye concentrations at sampling stations. If sampling for tracer dyes places primary reliance on the analysis of water samples the common result of very small dye concentrations at sampling locations is that the resulting data are biased. Specifically, (1) the time of first dye arrival at a sampling station is frequently over-estimated, (2) the duration of the dye pulse is underestimated, (3) some sampling stations receiving very small concentrations of tracer dyes are not identified, and (4) some sampling stations where dyes are present only in short-duration pulses are not identified. The risk of biased results can be substantially reduced by placing primary sampling reliance on standardized activated carbon samplers that are quantitatively analyzed. Analysis of grab samples of water collected each time carbon samplers are changed is strongly recommended for all sampling locations where tracer dyes are detected in carbon samplers.

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Improving Detection of Fluorescent Tracer Dyes In Groundwater Remediation Studies Using Activated Carbon Samplers

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Background

- Fluorescent tracer dyes are commonly used in remediation studies.
- Three types of sampling approaches
  - Field instruments.
  - Grab samples of water.
  - Activated carbon samplers.
- This is a performance assessment of activated carbon samplers and water samples.
- Premise: Activated carbon samplers are under-utilized and routinely superior to water samples.

Activated Carbon Samplers

- Continuous and accumulating samplers
- Production and analysis standardized
- Large adsorbing surface area.
- Well suited to use at waste sites.

Common Misconceptions

First, that a large percent of introduced dye will be detected, especially in karst. This routinely results in the introduction of too little dye.

Problem compounded by need to introduce more dye when sampling with water samples than when sampling with carbon samplers.

Following table from 33 groundwater traces in karst.

Dye Detection Percentages

Percent of injected tracer dye subsequently detected at springs draining karst aquifers. Data from sites in Arkansas, Kentucky, Tennessee, Maryland, and Texas.

Dye Mixture Amount and Type	Straight Line Distance of Trace (km)	Percent of Injected Dye Detected	Reference
0.91 kg Eosine	1.65	5.8	OUL data
6.36 kg Eosine	1.46	0.9	White et al. (2015)
10.44 kg Eosine	1.63	0.1	White et al. (2015)
15.85 kg Eosine	28.18	1.3	Hunt et al. (2005)
0.45 kg Fluorescein	0.44	45	OUL data
0.91 kg Fluorescein	2.96	15	OUL data
4.54 kg Fluorescein	1.37	0.2	White et al. (2015)
6.81 kg Fluorescein	1.42	0.01	White et al. (2015)
11.35 kg Fluorescein	22.54	0.8	Hunt et al. (2005)
0.018 kg Rhodamine WT	0.91	62.5	Smoot et al. (1987)
1.82 kg Rhodamine WT	0.44	38	OUL data
1.82 kg Rhodamine WT	2.87	2.7	OUL data
7.0 kg Rhodamine WT	0.30	96.6-98.0	Field 1999

Note 1: Hauwert et al. (2004) calculated dye recovery percentages for 20 groundwater traces involving straight line travel distances of 3.2 to 30.5 km. 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%. Types of dye varied with greater quantities for longer traces.

Note 2: The fluorescein and eosine dye mixtures were 75% dye equivalent; the rhodamine WT mixture was 20% dye equivalent.

Common Misconceptions

- Second, that activated carbon sampling is not quantitative.
  - It is not true.
  - All steps standardized.
  - Measure of the total amount of dye accumulated in sampling period.

The Data Base

- 1,941 sampling periods where dyes were present.
- Analysis of both carbon and water samples for all sampling periods.
- Data from 104 springs and 71 wells in 12 states with variable climate and hydrogeology.
- 50% karst, 30% fractured rock, 20% other.
- Data for wells and springs evaluated separately.

Accumulation Factor (AF)

- Dye concentration in carbon sampler elutant divided by mean dye concentration in water samples for the sampling period.
- AF expected to be greater for springs than monitoring wells.
- AF increases with increases in the sampling period duration.

Detection Percentages

Sampling periods at springs and monitoring wells when dye was detected in carbon or water samples. EOS = eosine; FLO = fluorescein; RWT = rhodamine WT; and SRB = sulforhodamine B.

Parameter	EOS	FLO	RWT	SRB	Total or Weighted Mean
SPRINGS					
Total sampling periods	384	277	224	117	1002
Mean length of sampling periods (days)	16	14	10	20	
Periods when dye was detectable in water samples	50.8%	43.0%	42.9%	29.1%	44.3%
Periods when dye was detectable in carbon samplers	98.2%	98.6%	100%	100%	98.9%
MONITORING WELLS					
Total sampling periods	219	369	330	21	939
Mean length of sampling periods (days)	13	25	26	16	
Periods when dye was detectable in water samples	73.5%	84.0%	81.2%	100%	80.9%
Periods when dye was detectable in carbon samplers	93.6%	99.7%	92.4%	100%	95.7%

Detection Failures In Water

- Water samples miss short duration pulses.
- In one karst study dye detected in carbon from 33 stations but in water from only 13. 61% failure if reliance had only been on water samples.
- Commonly need at least 10X more dye at wastes sites than amount required for carbon sampling.
- Carbon samplers more tolerant than water samples of small dye concentrations.

AF Values

- Calculated only if dye detectable in carbon samplers and in water samples at beginning and end of sampling period.
- Longer the sampling duration greater the AF up to about 3 weeks.

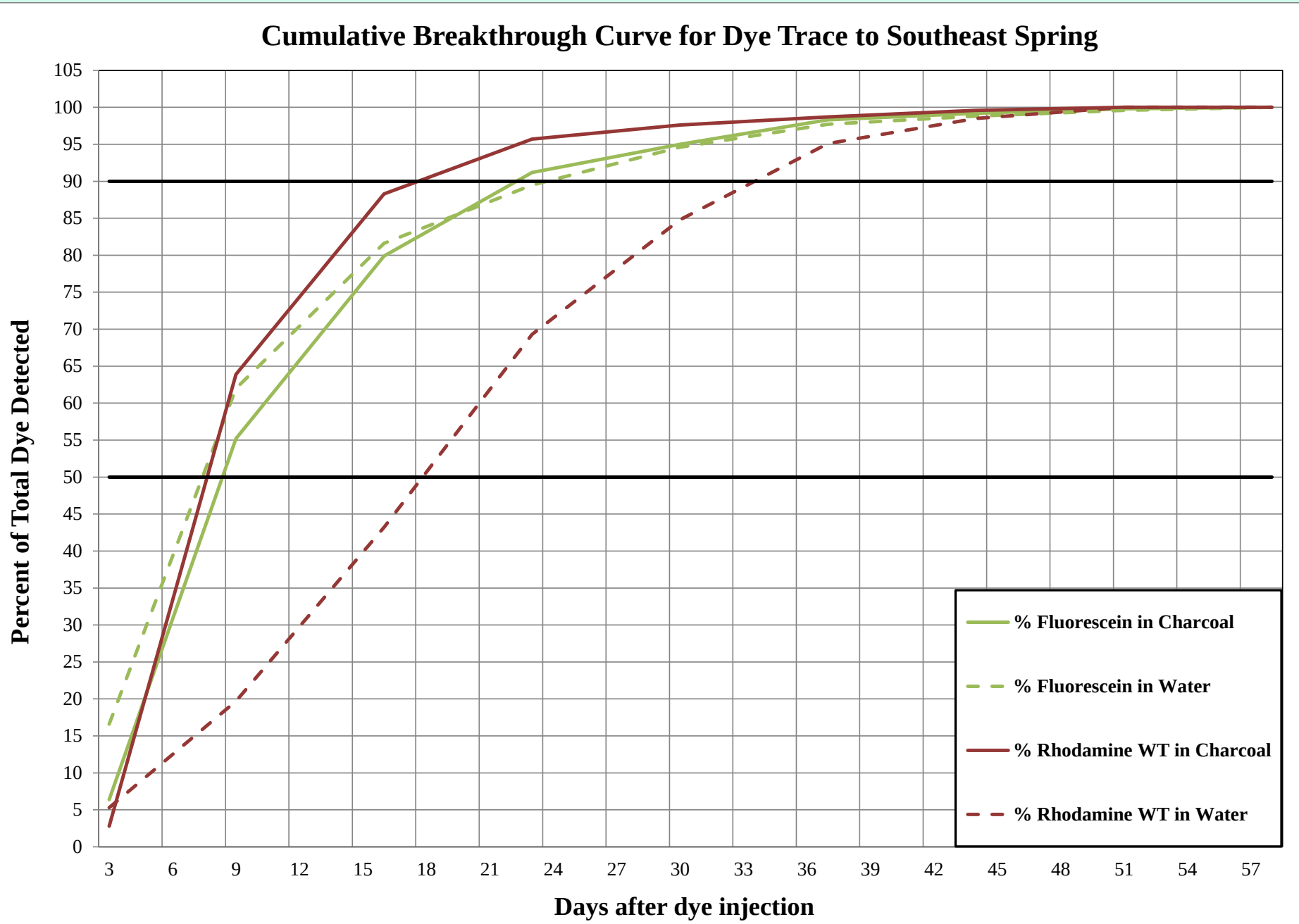
AF 6 to 8 Days Duration.

Accumulation Factors for carbon samplers in place for periods of 6 to 8 days. EOS = eosine; FLO = fluorescein; and RWT = rhodamine WT. There were insufficient data for an analysis of sulforhodamine B dye.

Parameter	EOS	FLO	RWT	Total or Weighted Mean
SPRINGS				
Total sampling periods	106	70	105	281
Percent of periods when dye was detectable in water samples	65%	46%	45%	53%
Percent of periods when dye was detectable in carbon samplers	99%	99%	100%	99%
Range of AF values	3 to 6053	9 to 1217	37 to 2333	
Mean AF	415	195	658	445
Median AF	255	102	506	
MONITORING WELLS				
Total sampling periods	93	154	136	383
Percent of periods when dye was detectable in water samples	84%	84%	90%	86%
Percent of periods when dye was detectable in carbon samplers	91%	100%	86%	93%
Range of AF values	0.1 to 681	5 to 18804	1 to 451	
Mean AF	38	379	28	166
Median AF	5	22	11	

Case Study

- 4.5 kg of fluorescein and 12.9 kg rhodamine WT introduced at same point in dry losing stream segment.
- Flushed with 81,750 L of water.
- Distance to Southeast Spring 320 m. Residuum 10 m, elevation difference 23 m.
- Spring flow 2.5 L/sec


Cumulative Breakthrough Curve for Dye Trace to Southeast Spring
Percent of Total Dye Detected
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
3
6
9
12
15
18
21
24
27
30
33
36
39
42
45
48
51
54
57
Days after dye injection
% Fluorescein in Charcoal
% Fluorescein in Water
% Rhodamine WT in Charcoal
% Rhodamine WT in Water

Case Study Results (1)

- Good comparison of water and carbon sampling and two common dyes.
- Enough dye was used for good water sample results.
- In water samples, 13.5% of fluorescein detected but only 1.1% of rhodamine WT.
- Useful to analyze both carbon and water.

Case Study Results (2)

- Mean AF for fluorescein was 285; it was 821 for rhodamine WT. Sampling was weekly.
- The rhodamine WT in water results are the least credible. The other three plots are similar.
- Fluorescein persisted longer than rhodamine WT.

Conclusions

- Failure to detect percentages are greater for water samples than carbon samplers at both springs and wells.
- Water samples routinely over-estimate time of first dye arrival, under-estimate duration of dye pulse, miss some dye detection locations, and miss locations where dyes are not continuously present.

Recommendations

- Use both carbon samples and water samples concurrently. Analyze water only if dye is detected in carbon.
- In low yield and small diameter wells routinely analyze both water and carbon samplers.
- In most cases, place primary sampling reliance on carbon samplers, secondary reliance on water.

Questions?