# Addendum #11 to Field Sampling Plan for Part 2 of the Supplemental Groundwater Remedial Investigation Former York Naval Ordnance Plant 1425 Eden Road, Springettsbury Township York, Pennsylvania

# Prepared for Harley-Davidson Motor Company Operations, Inc. October 16, 2013

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### **Groundwater Tracer Studies**

### Introduction

The Field Sampling Plan for Part 2 of the Supplemental Groundwater Remedial Investigation (FSP) (GSC, April 2012) discusses two types of groundwater tracer testing that were proposed for the site. Subsection 4.2.4.9 discusses groundwater tracer testing to investigate intermediate and deep karstic flow pathways using selected borehole pairs. Subsection 4.3.10 discusses qualitative dye tracer test involving the injection of various dyes into monitoring wells. As a result of the recent data collected, and the remaining questions concerning groundwater pathways in the karstic portion of the aquifer, plans for two separate tracer tests have been developed using dyes as tracers. The tests described herein will take the place of the conceptual plans outlined in the FSP.

### Codorus Creek Sampling Results

Section 4.3.3 of the FSP describes a work plan to sample Codorus Creek groundwater discharges. The sampling was conducted on September 22, 2013. Stream samples were collected upstream and downstream of the area of suspected groundwater discharge from the fYNOP Site. In addition, a thermistor was used to locate and identify discrete discharges of groundwater to Codorus Creek, which were subsequently sampled. Also, surface water

discharges from Johnsons Run, the York County waste water treatment plant, and the unnamed tributary from the west were sampled. **Figure 1** indicates the locations of samples. **Table 1** provides the concentrations of volatile organic compounds, priority pollutant metals, common ions and miscellaneous parameters. Following is a summary of some key findings from the surface water sampling that were pertinent to the design of the tracer testing presented in this addendum.

- Two locations were discovered that were obvious groundwater-fed springs into Codorus Creek. In both cases, these discharges were below the water level of the creek on the day of sampling. Samples collected at these locations are designated COD-SW-17 and COD-SW-15 (see Figure 1). The temperature of the water in these areas was approximately 20°F lower than the rest of the creek, characteristic of groundwater temperatures. Total alkalinity in these samples was two times higher than other samples from the creek (see Table 1), as would be expected if it were groundwater discharging from a carbonate aquifer.
- Stream samples collected upstream and downstream of the suspected area of groundwater discharge from the Site showed very low concentrations of Site-related chemicals of concern PCE, TCE and cis-1,2 DCE at estimated values of less than 0.5  $\mu$ g/l. These concentrations indicate low background concentrations in the stream upgradient of the Site, and no change in stream concentration below the Site on this sample date. In contrast,
  - COD-SW-17 had a PCE concentration of 45 μg/l, TCE concentration of 20 μg/l, and cis-1,2 DCE at 7.9 μg/l.
  - COD-SW-15 had a PCE concentration of 3.2 μg/l, TCE concentration of 3.7 μg/l, and cis-1,2 DCE at 2.1 μg/l,

suggesting these discharges may be related to or impacted by conditions in the aquifer beneath the fYNOP Site.

• Pie diagrams illustrating the ratio of chlorinated solvents in the water samples are posted near the sample locations of COD-SW-17 and COD-SW-15 on **Figure 1**. The pie diagram representing the water quality from the groundwater discharge at COD-SW-17 indicates a similar ratio to wells in the southwest corner of the West Parking Lot (SW-WPL), like CW-20. The pie diagram representing the water quality from groundwater discharging from

COD-SW-15 indicates a similar ratio to well MW-100D, which is located on the east side of the creek along the creek levee access road.

Based on these recent observations, two tracer tests are planned. **Test 1** will be performed with the groundwater extraction system in the WPL operating, and will test the ability of the existing interim groundwater extraction system to capture groundwater in the deep karst system in the SW-WPL. This is based on the similarity of the ratios between the groundwater in the SW-WPL and COD-SW-17. **Test 2** will test whether groundwater flowing beneath the Site discharges to the Codorus Creek, and is based partly on the similarity of the chemical ratios of MW-100D and COD-SW-15. **Test 2** will be conducted with the groundwater extraction system turned off.

### Matrix Interference and Background Analysis

On May 7, 2013, GSC collected matrix interference samples and background samples to assess the feasibility of tracer testing at the Codorus Creek levee area. Samples were submitted to Crawford Hydrology Laboratory of Western Kentucky University for Matrix Interference analysis and for analysis of the 6 common dyes (Tinopal CBS-X, Fluoroscein, Eosine, D&C Red #28, Rhodamine WT, Sulphorhodamine B) and to TestAmerica-Pittsburgh for analysis of bromide, chloride, and sodium ions. The results are included as **Appendix A**. The dyes fluorescein, eosine, D&C Red 28, Rhodamine WT, and sulphorhodamine B, are all at very low background concentrations, or were not detected. Tinopal dye was found in the creek at concentrations between 0.7 and 3.1  $\mu$ g/l, which are sufficiently elevated concentrations, thus Tinopal will not be used in the tracer testing to avoid possible background interference.

### Test 1 – SW-WPL Deep Karst Capture Analysis

Fluorescent dye Sulphorhodamine B will be injected into well CW-20 in the southwest corner of the West Parking Lot (SW-WPL). The dye will be injected into the aquifer while the interim groundwater treatment system is operating. This well intersects a weathered rock zone containing void between 213 and 217 feet deep, and thus represents deep karst. The objective is to determine whether intermediate to deep karstic groundwater at this location is captured by the interim groundwater extraction system. The same dye tracer Sulphorhodamine B was injected in CY2000 by Crawford Associates into MW-75S, which was completed in karstic voids from 154

feet to 173. The dye was captured by well CW-9 in 7 days, which pumps from a solution cavity at a depth of 50 to 70 feet below ground surface (BGS).

A matrix interference and background analysis will be conducted on extraction wells CW-8, CW-9, CW-13, CW-15A, and CW-17 prior to the initiation of **Test 1**. If residual concentrations of any previously used dyes are high, the recommended tracer for **Test 1** would be changed.

A full array of dye receptors will be deployed, designed to accommodate both **Test 1** and **Test 2**. The receptor layout and monitoring plan is described after the description of **Test 2**.

### *Test 2 – Levee Wells to Codorus Creek*

After sufficient time has elapsed for **Test 1** (estimated to be 2 to 4 weeks), the groundwater extraction system in the WPL and Central Plant Area (CPA) will be shut down. This is part of the scope of hydrodynamic testing and monitoring described in Section 4.3.9 of the FSP. Water levels in numerous wells will be collected with continuous recorders and manually during the monitored shutdown. The wells in which water levels will be monitored and methods of monitoring are designated on **Table 2**. Dyes will be injected for **Test 2** after complete recovery of groundwater levels from pumping, to be determined by observation of continuous recorders. Complete recovery is expected in 3 weeks or less, depending on the amount of precipitation which occurs after shut down.

The objective of **Test 2** is to determine whether the shallow, intermediate and deep karstic groundwater flowing beneath the Site discharge to Codorus Creek. Three Levee wells, MW-147A, MW-99 D, MW-100 D, which are located west of the former plant and east of the Codorus Creek along the Levee access road, will be used as injection points. Different dyes will be injected into each of these wells on the same day, with minimal delay between injections. These wells intersect karst features between 211 and 216 feet deep (MW-147A), between 132 and 142 feet deep (MW-99D), and between 103 and 121 feet deep (MW-100D). The karst encountered in MW-147A represents a deep karstic pathway adjacent to Codorus Creek, and the karst encountered in MW-99D and MW-100D represents the shallow to intermediate pathways through this area.

Tracers to be injected:

- Rhodamine WT into MW-147A,
- Fluorescein into MW-99D, and
- Eosine into MW-100D.

Method and amount of injection are addressed later in this document.

# Monitoring Program and Deployment Schedule

Matrix interference and background testing, similar to the tests conducted in the creek, will be conducted in the 5 extraction wells, CW-8, CW-9, CW-13, CW-15A, and CW-17 to determine the background levels in these wells and potential for matrix interference. If high background levels of one or more dyes are found in these extraction wells, it may be necessary to rearrange the dyes specified for injection in the selected wells. At the same time, samples for background analyses of all monitoring stations will be collected.

Charcoal dye receptors provided by Crawford Hydrology Laboratory will be utilized in wells and surface water. The receptors consist of small packets constructed of vinyl-coated fiberglass screen mesh approximately four inches long and two inches wide. The mesh is filled with three to four grams of activated coconut charcoal. Each receptor is prepared in a dye-free environment and individually packaged in sealed polyethylene bags. The receptors will be placed into the known groundwater-fed springs in the bed and banks of Codorus Creek which have been previously located by GSC (Codorus Creek sampling stations COD-SW-17 and COD-SW-15). In addition, upstream and downstream locations in Codorus Creek, the tributaries to Codorus Creek, and the outfall of the York County Wastewater Treatment Plant will be monitored with dye receptors. Dye receptors will also be placed in the extraction wells CW-8, CW-9, CW-13, CW15A, and CW17.

Water samples will also be collected using grab sample vials. Grab sample vials are made of borosilicate glass suitable for fluorometric analysis. The caps used are PTFE lined to prevent contamination by fluorescent molecules that can leach out of standard rubber-lined caps. Grab samples will be collected each time a receptor is deployed or retrieved.

Appendix B contains procedural documents provided by Crawford Hydrology Laboratories, who will be providing the dyes and analytical services. Dye receptors will be deployed and retrieved in accordance with instructions specified in **Appendix B-1**, pages 5-7, and Dye Receptor Change-out Procedures, also in **Appendix B-1**. The Crawford Chain of Custody is provided in **Appendix B-2**. Shipping instructions are provided in **Appendix B-3**. MSDS sheets for the dyes are included in **Appendix B-4**.

**Figure 2** shows the locations of dye injection points and deployment locations of dye receptors. Dye receptors will be deployed one week prior to the injection of dye for **Test 1**, and will be changed out according to the frequency delineated on **Table 3**. In general, after the injection of tracer in CW-20 to initiate **Test 1**, the receptors will be retrieved and replaced every one to three days during the first two weeks depending on location, then dropping to weekly. After injection of tracers for **Test 2**, the receptors will be retrieved and replaced every one to three days during the first two weeks depending on location, then dropping to weekly. In addition, grab samples will be collected from COD-SW-15 and COD-SW-17 every one to four hours for the first 2 days after injection.

**Test 1** will continue for 2 to 4 weeks. **Test 2** will be initiated at the completion of **Test 1** and will continue for a minimum of one month, and could be extended to two or three months. A decision to end the dye receptor monitoring and to reactivate the groundwater extraction system will be based on an evaluation of the results of the testing. Conditions that may extend the test are weather, precipitation and stream flow that delay data collection or complicate data interpretation, or dye tracer not appearing as predicted.

### **Tracer Injection**

The dye tracers will be injected into karstic channel flow which has been intersected by boreholes at four different locations, as described above. The dye will become entrained in the channel flow which will transport the dye through the karstic aquifer. The dye tracer is expected to discharge to Codorus Creek at two substantial groundwater-fed springs, which were located by GSC in 2013 (see Background discussion in the beginning of this document), and potentially through diffuse pathways to the streambed of the creek. Because the karst aquifer boundary in the downstream direction is a few hundred feet downstream from the Site at the fault contact

with the Harpers Phyllite, it is expected that discharges to the creek through the carbonate aquifer will be south of the fault (see **Figure 2**).

Polyethylene coil pipe will be placed down the well bore to the depth of the target karst feature noted above. Prior to injection of dye, potable water will be injected into the well through the coil pipe to determine the rate at which liquid can be injected into the well.

Pre-mixed liquid dyes will be poured into the pipe. Fifty gallons of potable water will be used to flush the dye into the aquifer. Care will be taken to avoid spilling and cross contamination, using methods described in **Appendix B-1**.

### **Determination of Tracer Injection Mass**

The goal of a dye tracer study is to use sufficient tracer to be assured of detection in receptors along the path of the tracer without causing undue disturbance to surface water where groundwater discharges. Telephone conversations with two experts in designing dye studies resulted in the warning not to use too little dye, because the worst technical result of a tracer test is no recovery. Only in extra sensitive areas should injection masses be cautiously calculated. Another general rule shared was that tracer injection into wells should be 2 to 5 times higher than tracer injection into swallets or sink holes. Concentrations of dyes on the order of 100  $\mu$ g/l can be seen in a laboratory sample, with slightly lower concentrations being visible in larger bodies of water.

The following information was considered in selecting the mass of tracer to be used:

• Nicholas Crawford of Crawford and Associates designed and conducted a dye trace investigation at fYNOP in the summer of 2000. Four dyes were injected into wells in the carbonate aquifer within the CPA and the WPL. Twenty-five pounds of dye were injected in each of the injection points. All four dyes were detected in the groundwater extraction system wells. The dyes ran through the treatment system, and then were detected in Johnsons Run below the groundwater treatment plant discharge, and in Codorus Creek only downstream of where Johnsons Run discharges to Codorus Creek. There were no reports of discoloration of effluent. Detections of dyes in the creek as a

result of discharging extracted groundwater never exceeded 10  $\mu$ g/l on charcoal receptors. At this level, there would have been no visibly detectable effects on Codorus Creek.

Even more specifically to the design of the current tests, Sulphorhodamine B dye was injected into MW-75S in 2000. This injection point is adjacent to the currently planned injection point of CW-20 for **Test 1**, with the only difference that CW-20 connects with a deeper karst feature at a depth of 213 feet, while MW-75S connects with a karst feature at a depth of approximately 170 feet below ground surface. In the previous test conducted in 2000 Sulphorhodamine B showed a maximum concentration in Codorus Creek eluted from charcoal receptors of slightly higher than 9  $\mu$ g/l that occurred one month after injection. This would have been a result of groundwater from MW-75S being captured by the extraction system wells and discharged through the groundwater treatment plant to Johnsons Run, which then discharged to Codorus Creek. Since CW-20 is deeper in the aquifer than MW-75S, and since the alternate location for discharge is COD-SW-17, the submerged spring in Codorus Creek, the results of the previous dye study suggest that considerably more than 25 pounds of dye could be used for **Test 1** without a concern that objectionable concentrations of dye would be reached in a reasonably attenuated sample from Codorus Creek.

• The conclusion of the Crawford tracer study was that all groundwater from the CPA/WPL area where dyes were injected was being captured by the groundwater extraction system. This conclusion was a result of all four dyes being detected in the capture wells and groundwater treatment plant effluent and that no detections of these dyes occurred in Codorus Creek upstream of the Johnsons Run discharge or in any other suspected discharge areas where dye receptors were deployed. Below the Johnsons Run discharge to Codorus Creek, all injected dyes were detected as a result of the groundwater treatment plant discharging to Johnsons Run. By the end of the two months of investigation, concentrations of dyes were dropping, suggesting a fairly direct and efficient connection between injection points and the extraction wells. Since this scenario caused concentrations that would have been at least an order of magnitude less than visible concentrations in the creek after being run through the treatment plant, it is probable that injection of similar amounts of dye in levee wells (for **Test 2**) would also

not result in objectionable concentrations of dye discharging to the creek due to the large dilution caused by the creek flow.

• A formula published by Worthington and Smart (2003) has been used to calculate the mass of dye for "sink to spring" tests in karst. The number calculates the mass of the tracer, given the discharge or flow rate (in this case the flow in Codorus Creek), the distance from injection to measuring point, and the maximum expected concentration. Using the visible concentration of dye (100 µg/l), the distance from the well injection point to the suspected submerged spring in Codorus Creek, and the average flow in the creek for the month of December (215 cubic feet per second [cfs])Worthington and Smart's formula yields 5 pounds of dye for Test 1 (distance from CW-20 to COD-SW-17). For Test 2, the distance from MW-147A to COD-SW-15 yields 4 pounds and the distance from MW-99D to the northern extent of the carbonate aquifer (the fault to the north) yields 5 pounds. If the average discharge in the creek for the month of November were used (154 cfs), the results would range from 3 to 3.6 pounds. Current flows are well over 500 cfs, due to the massive rainfall which occurred on October 10, but falling rapidly. The calculation and the stream statistics are included in **Appendix C**.

Lee Anne Bledsoe of Crawford Hydrology Laboratories commented that injection mass should be 2 to 5 times higher if using a well as an injection point, as opposed to a sink. The Worthington formula was developed for sink to spring, thus it would be appropriate to increase the injection mass to accommodate the conditions of this test. In addition, Ms. Bledsoe recommended that the mass of Eosine dye, when used in the same test as Fluorescein, should be two to three times higher than Fluorescein because of interference between the dyes.

Based on the above considerations, and assuming the creek discharge is approximately 200 cfs, the following dyes and amounts will be used:

• For **Test 1**, 25 pounds of Sulphorhodamine B will be injected into well CW-20. This amount was used in the test in 2000 in almost the same setting. The Worthington and Smart calculation for this test used the distance from CW-20 to COD-SW-17 and the flow of Codorus Creek, since that is the likely location of the tracer to discharge if it were not captured by extraction well CW-9.

• For **Test 2**, 15 pounds of Rhodamine WT will be injected into MW-147A, 15 pounds of Fluorescein will be injected into MW-99D, and 30 pounds of Eosine will be injected into MW-100D. This is three times the mass calculated by the Worthington formula, since this is a tracer injection using wells, and two times more Eosine to account for the interference between Eosine and Fluorescein.

### Codorus Creek Flow Monitoring and Sampling

The flow in Codorus Creek upstream and downstream of the Site and the discharges to Codorus Creek will be measured after recovery of the aquifer from pumping, conditions permitting. The measurements will be taken during a time of base flow in the creek. In addition, samples will be taken at these locations for VOCs, common ions and alkalinity. The surface water samples will be collected at the end of **Test 2**, just prior to turning on the groundwater treatment system. These results will be compared to similar measurements taken while the extraction system was pumping.

# References

Crawford and Associates, Inc., 2000. Dye Tracer Investigation of the Harley-Davidson Site, York, Pennsylvania. Internal report submitted to Langan Engineering, November 30, 2000.

GSC, 2011. <u>Supplemental Remedial Investigation Groundwater Report (Part 1) Former York</u> <u>Naval Ordnance Plant</u>, September.

GSC, 2012. <u>Field Sampling Plan (FSP) for Part 2 of the Supplemental Groundwater Remedial</u> <u>Investigation</u>, April.

GSC, 2012. <u>Quality Assurance Project Plan – Former York Naval Ordnance Plant, June</u>.

Worthington, S. and Smart, C., 2003. <u>Empirical Determination of Tracer Mass for Sink to</u> <u>Spring Tests in Karst</u>, Ed. B.F. Beck, Geotechnical Special Publication No. 122, American Society of Civil Engineers, pp. 287-295. Tables

#### Table 1 Codorus Creek Sampling Event - August 22, 2013 Former York Naval Ordnance Plant - York, PA

	ocation/ID	MSC	MSC	Federal	EPA RSL	COD-SW-6	COD 614 6		COD-SW-7	COD 614/ 8	COD-SW-8		COD-SW-9	COD 5W 10	COD-SW-11	COD 5W 13	COD-SW-13	COD 5W/ 15	COD-SW-16	COD 5W/ 17	COD-SW-18
	Depth (ft.)	IVISC	IVISC	rederal	EPA KSL	COD-3W-0	COD-3W-0	COD-3W-7	COD-3W-7	COD-3W-8	COD-3W-8	COD-3W-9	COD-3W-9	COD-SW-10	COD-SW-11	COD-3W-12	COD-5W-15	COD-SW-15	COD-3W-16	COD-SW-17	COD-3W-18
	mple Type					SWTR	SWTR	SWTR	SWTR	SWTR	SWTR	SWTR	SWTR	SWTR	SWTR	SWTR	SWTR	SWTR	SWTR	SWTR	SWTR
	mple Date					8/22/2013	8/22/2013	8/22/2013	8/22/2013	8/22/2013	8/22/2013	8/22/2013	8/22/2013	8/22/2013	8/22/2013	8/22/2013	8/22/2013	8/22/2013	8/22/2013	8/22/2013	8/22/2013
	mple Time	Used Aquifer R	Used Aquifer NR	MCL	Tap Water	8:40	16:10	8:45	16:15	9:25	15:20	9:30	15:25	10:50	11:45	12:05	10:20	12:25	15:15	13:20	14:25
Parameter	inpie inne	(ug/L)	(ug/L)	(ug/L)	(ug/L)	0.40	10.10	0.45	10.15	5.25	15.20	5.50	15.25	10.50	11.45	12.05	10.20	12.25	15.15	13.20	14.25
Alkalinity		(46/1)	(46/1)	(46/ 1/	(ug/L)																I
ALKALINITY, BICARBONATE						110000 B	95000 B	110000 B	100000 B	110000 B	104000	120000 B	120000 B	200000 B	200000 B	170000 B	130000 B	220000 B	100000 B	244000	120000 B
ALKALINITY, CARBONATE						7800	8900	5000 U	820 J	5000 U	3140 J	5000 U	660 J	8600	8700	5000 U	5000 U	5000 U	1300 J	5000 U	5000 U
ALKALINITY, TOTAL						120000 B	100000 B	110000 B	100000 B	110000 B	107000	120000 B	120000 B	210000 B	210000 B	170000 B	130000 B	220000 B	110000 B	244000	120000 B
METAL						120000 5	1000000	110000 5	1000000	11000000	10,000	120000 5	120000 0	210000 5	210000 0	1,0000 5	100000 0	220000 5	110000 5	211000	120000 0
Antimony		6	6	6	6	0.18 J	0.23 J	0.16 J	0.14 J	0.23 J	0.22 J	0.18 J	0.22 J	0.079 J	0.05 J	0.41 J	0.14 J	0.17 J	0.19 J	0.13 J	0.17 J
Arsenic		10	10	10	0.045	10	0.48 J	0.45 J	1 U	0.43 J	10	10	0.46 J	1 U	1 U	10	0.66 J	10	10	10	0.4 J
Barium		2000	2000	2000	2900	42 B	35 B	40 B	36 B	40 B	36 B	39 B	33 B	60 B	31 B	19 B	49 B	39 B	37 B	47 B	40 B
Beryllium		4	4	4	16	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	0.044 J	1 U	1 U	1 U	1 U
Cadmium		5	5	5	6.9	10	0.15 J	0.18 J	10	10	10	10	10	0.15 J	1 U	10	0.47 J	10	10	0.12 J	0.12 J
Chromium		100	100	100		0.68 J	0.94 J	0.85 J	0.8 J	1.3 J	1 J	1.1 J	1 J	8.1	2.9	0.95 J	3.7	6.6	0.8 J	3.9	0.98 J
Copper		1000	1000	1300	620	3.8	4.7	4.3	3.8	3.6	3.4	3.2	3	1.9 J	3.2	3.2	7.9	2	2.6	3.6	5
Lead		5	5	15		0.56 J B	1.1 B	0.97 J B	0.71 J B	0.91 J B	0.55 J B	0.68 J B	0.45 J B	0.11 J B	0.3 J B	0.78 J B	4.4 B	0.23 J B	0.38 J B	1.9 B	4 B
Mercury		2	2	2	0.63	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U				
Nickel		100	100		300	1	0.92 J	1.2	0.81 J	0.97 J	0.89 J	1.2	1.2	1.5	0.78 J	2.3	1.9	1.1	0.98 J	1.6	1
Selenium		50	50	50	78	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U
Silver		100	100		71	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
Thallium		2	2	2	0.16	1 U	0.15 J B	0.086 J B	0.046 J B	0.22 J B	0.088 J B	0.089 J B	0.049 J B	0.047 J B	0.027 J B	0.024 J B	0.02 J B	0.19 J B	0.094 J B	0.082 J B	0.043 J B
Vanadium		260	720		63	1.5	1.7	1.7	1.9	1.3	1.7	1.5	2	0.19 J	0.63 J	0.8 J	1.2	1 U	1.9	0.39 J	1.4
Zinc		2000	2000		4700	9.5	8.1	8.7	13	7.4	8.6	12	13	8.6	9.1	29	56	5.7	4.9 J	11	20
METAL (Dissolved)																					
Antimony		6	6	6	6	0.12 J B	0.13 J B	0.23 J B	0.14 J B	0.14 J B	0.18 J B	0.17 J B	0.19 J B	0.054 J B	0.055 J B	0.61 J B	0.19 J B	0.11 J B	0.12 J B	0.1 J B	0.16 J B
Arsenic		10	10	10	0.045	0.42 J	1 U	1 U	1 U	1 U	1 U	0.43 J	1 U	1 U	1 U	0.58 J	1 U	1 U	1 U	0.36 J	0.38 J
Barium		2000	2000	2000	2900	40	37	39	36	39	36	38	32	60	31	20	43	39	36	47	39
Beryllium		4	4	4	16	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
Cadmium		5	5	5	6.9	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
Chromium		100	100	100		0.7 J	0.67 J	1.1 J	1.1 J	1.1 J	1.1 J	1.1 J	1.2 J	8	3.1	0.97 J	2.3	6.4	0.86 J	3.1	0.97 J
Copper		1000	1000	1300	620	2.3	2.6	2.4	2.9	2.1	2.3	2.2	2.8	1.4 J	1.9 J	2.6	3.3	1.8 J	2.2	1.6 J	3.1
Lead		5	5	15		0.12 J B	0.12 J B	0.16 J B	0.11 J B	0.067 J B	0.071 J B	0.13 J B	0.19 J B	0.022 J B	1 U	0.95 J B	0.32 J B	0.079 J B	0.067 J B	1 U	0.15 J B
Mercury		2	2	2	0.63	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U	0.2 U				
Nickel		100	100		300	0.89 J	0.86 J	0.83 J	1.1	0.86 J	0.83 J	1	1.1	1.2	0.74 J	2.1	0.86 J	1.1	0.89 J	1.1	0.82 J
Selenium		50	50	50	78	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	1 J	5 U
Silver		100	100		71	1 U	1 U	1 U	1 U	1 U	10	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
Thallium		2	2	2	0.16	0.023 J	0.02 J	0.22 J	0.16 J	0.083 J	0.083 J	0.046 J	0.052 J	0.035 J	0.03 J	0.019 J	0.019 J	0.017 J	10	0.017 J	1 U
Vanadium		260	720		63	1.4	1.7	1.5	1.5	1.4	1.9	1	1.7	0.38 J	0.7 J	0.21 J	0.21 J	10	1.3	10	1
Zinc		2000	2000		4700	8.9 B	7.5 B	7 B	9.8 B	8.4 B	9.5 B	8.1 B	14 B	5.9 B	7.9 B	33 B	17 B	9.2 B	6.4 B	6.6 B	12 B
SO4, CL, NO3			250000			40000	46000	44000	42000	16000	46006	52000	64.000	4 400000	20000	110000	62000	00000	44000	74000	50000
Chloride		10000	250000	10000	25000	49000	46000	44000	42000	46000	46000	53000	61000	140000	39000	110000	63000	82000	44000	74000	50000
Nitrate As N		10000	10000	10000	25000	2400 H	2500	2500 H	2500	2500 H	2500	2600 H	2800	3200 H	3900	2900	2500 H	3600	2500	3300	2400
Sulfate						31000	42000	47000	47000	46000	45000	48000	47000	27000	19000	44000	38000	37000	45000	34000	38000

#### Table 1 Codorus Creek Sampling Event - August 22, 2013 Former York Naval Ordnance Plant - York, PA

	Location/ID	MSC	MSC	Federal	EPA RSL	COD-SW-6	COD-SW-6	COD-SW-7	COD-SW-7	COD-SW-8	COD-SW-8	COD-SW-9	COD-SW-9	COD-SW-10	COD-SW-11	COD-SW-12	COD-SW-13	COD-SW-15	COD-SW-16	COD-SW-17	COD-SW-18
s	Depth (ft.) Sample Type Sample Date					SWTR 8/22/2013															
S	Sample Time	Used Aquifer R	Used Aquifer NR	MCL	Tap Water	8:40	16:10	8:45	16:15	9:25	15:20	9:30	15:25	10:50	11:45	12:05	10:20	12:25	15:15	13:20	14:25
Parameter	-	(ug/L)	(ug/L)	(ug/L)	(ug/L)																
ΤΟΤΑΙ VOC																•	•			•	I
						0.5	1.48	0.96	0.67	0.68	0.73	0.73	3.27	0.45	0	0.22	4.44	9.5	4.25	76.88	4.22
Volatile Organic Compound																					
1,1,1,2-Tetrachloroethane		70	70		0.5	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
1,1,1-Trichloroethane		200	200	200	7500	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	2.5	1 U
1,1,2,2-Tetrachloroethane		0.84	4.3		0.066	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
1,1,2-Trichloroethane		5	5	5	0.24	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
1,1-Dichloroethane		31	160		2.4	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	0.59 J	1 U
1,1-Dichloroethene		7	7	7	260	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	0.6 J	1 U
1,2-Dibromoethane		0.05	0.05	0.05	0.0065	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
1,2-Dichloroethane		5	5	5	0.15	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
1,2-Dichloropropane		5	5	5	0.38	1 U	1 U	1 U	1 U	1 U	1 U	0.14 J	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
1,4-Dioxane		6.4	32		0.67	200 U															
2-Butanone		4000	4000		4900	5 U	0.63 J	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U
2-Hexanone		11	44		34	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U
4-Methyl-2-Pentanone		2900	8200		1000	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U
Acetone		33000	92000		12000	5 U	5 U	5 U	5 U	5 U	5 U	5 U	2.7 J	5 U	5 U	5 U	2.5 J	5 U	3.4 J	5 U	2.8 J
Acrylonitrile		0.72	3.7		0.045	20 U															
Benzene		5	5	5	0.39	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
Bromochloromethane		90	90		83	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
Bromodichloromethane		80	80		0.12	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
Bromoform		80	80		7.9	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
Bromomethane		10	10		7	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
Carbon Disulfide		1500	6200		720	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
Carbon Tetrachloride		5	5	5	0.39	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
Chlorobenzene		100	100	100	72	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
Chlorodibromomethane		80	80		0.15	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
Chloroethane		230	900		21000	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
Chloroform		80	80		0.19	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	0.21 J B	1 U	0.29 J B	1 U
Chloromethane					190	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
cis-1,2-Dichloroethene		70	70	70	28	1 U	0.28 J	0.42 J	0.36 J	0.3 J	0.32 J	0.25 J	0.3 J	0.45 J	1 U	1 U	0.59 J	2.1	0.36 J	7.9	0.4 J
cis-1,3-Dichloropropene		6.6	26		0.41	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
Ethylbenzene		700	700	700	1.3	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
Methyl tert-butyl ether		20	20		12	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
Methylene chloride		5	5		9.9	0.29 J B	0.27 J B	0.18 J B	1 U	1 U	1 U	1 U	1 U	1 U	1 U	0.22 J B	0.23 J B	0.29 J B	0.21 J B	1 U	0.26 J B
Styrene		100	100	100	1100	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
Tetrachloroethene		5	5	5	9.7	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	0.3 J	3.2	1 U	45	0.3 J
Toluene		1000	1000	1000	860	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
trans-1,2-Dichloroethene		100	100	100	86	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
trans-1,3-Dichloropropene		6.6	26		0.41	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
Trichloroethene		5	5	5	0.44	0.21 J	0.3 J	0.36 J	0.31 J	0.38 J	0.41 J	0.34 J	0.27 J	1 U	1 U	1 U	0.82 J	3.7	0.28 J	20	0.46 J
Vinyl Chloride		2	2	2	0.015	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
Xylenes (Total)		10000	10000	10000	190	3 U	3 U	3 U	3 U	3 U	3 U	3 U	3 U	3 U	3 U	3 U	3 U	3 U	3 U	3 U	3 U

### Table 2

Wells Designated for Recorder Installation During Dye Tracer and Monitored Shutdown Testing Multiparameter recorders will be installed in the following wells

CW-20 MW-96D MW-97 MW-99S MW-99D MW-100D MW-145A MW-147A MW-113

Water Level/Temperature recorders will be installed in the following wells

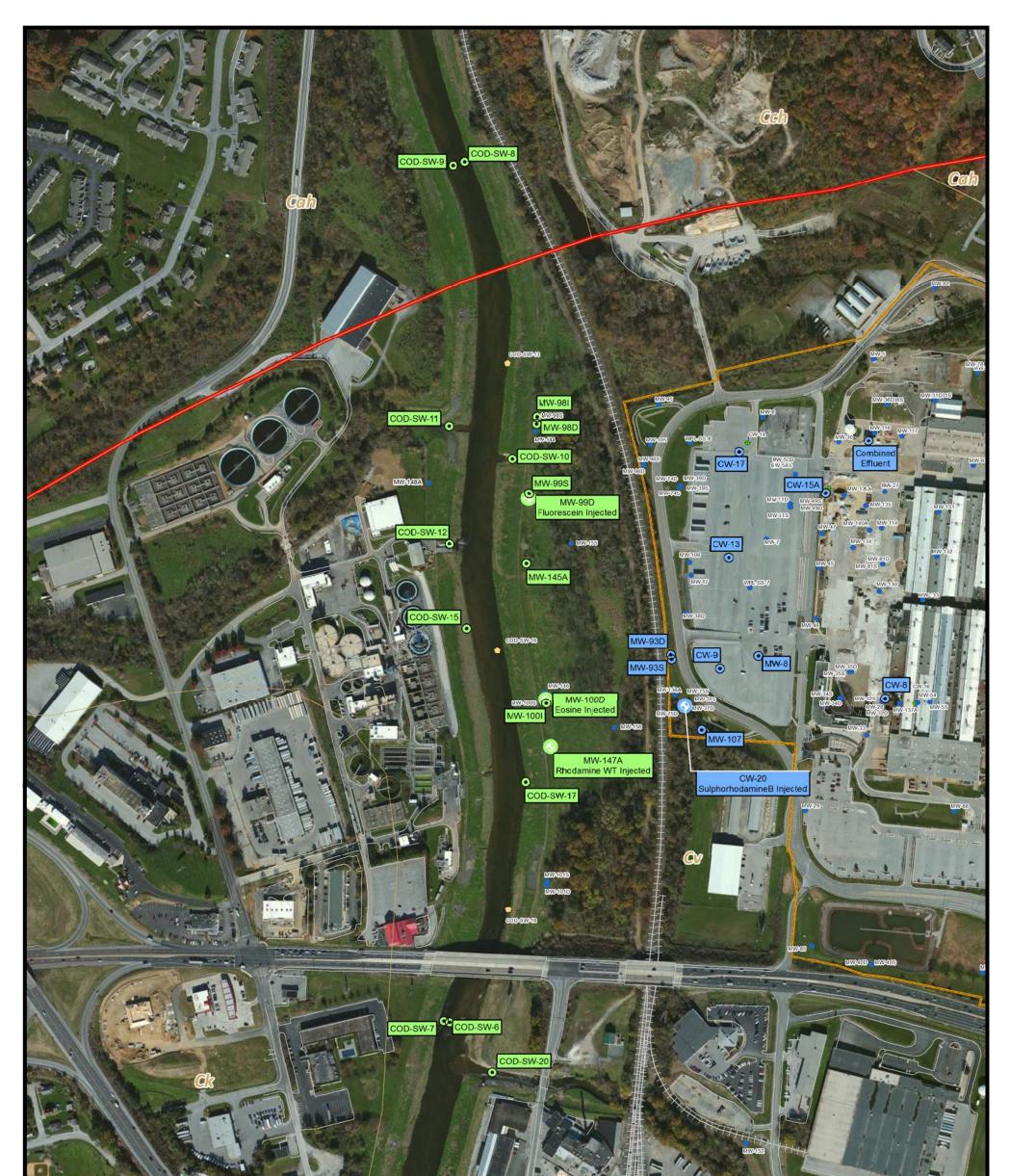
Table 3Dye Tracer Testing and Monitored Shutdown Schedule

D	ays from Star	rt	
Test 1	Shut Down	Test 2	Task Description
			Sample extraction wells (CW-8, CW-8, CW-13, CW-15A, and CW-17) for Background
	ASAP		and Matrix Interference testing.
			Deploy dye receptors and collect grab samples at all stations. Deploy all water level
-7			recorders.
			Retrieve and deploy dye receptors and collect grab samples at all stations. Inject
0			tracer in CW-20.
			Retrieve and deploy dye receptors and collect grab samples at Test 1 Receptor
1 thru 6			Locations.
7			Retrieve and deploy dye receptors and collect grab samples at all stations.
			Retrieve and deploy dye receptors and collect grab samples at Test 1 Receptor
9, 11			Locations.
			Complete full Site-wide round of water levels, including off-site locations. Measure
			Codorus Creek and tributary flows; sample surface water stations for VOCs and
			common ions. Retrieve and deploy dye receptors and collect grab samples at all
14*			stations.
			Retrieve and deploy dye receptors and collect grab samples at all stations.
15	0		Shutdown groundwater extraction wells.
			Retrieve and deploy dye receptors and collect grab samples at all stations;
21	7		Download water level recorders.
			Retrieve and deploy dye receptors and collect grab samples at all stations;
28	14		Download water level recorders.
			Retrieve and deploy dye receptors and collect grab samples at all stations;
35	21		Download water level recorders.
36	22	0	Inject tracers in MW-147A, MW-99D, and MW-100D
			Retrieve and deploy dye receptors and collect grab samples in all Test 2 locations.
			Collect grab samples at COD-SW-15 and COD-SW-17 at a frequency of 1 to 4 hours
42	28	1 thru 6	for the first 2 days.
45, 47	31, 33	9, 11	Retrieve and deploy dye receptors and collect grab samples in all Test 2 locations.
50	36	14	Retrieve and deploy dye receptors and collect grab samples in all Test 2 locations.
53, 55	39, 41	17, 19	Retrieve and deploy dye receptors and collect grab samples in all Test 2 locations.
			Retrieve and deploy dye receptors and collect grab samples in all Test 2 locations.
57	43	21	Download recorders.
	.5		Retrieve and deploy dye receptors and collect grab samples in all Test 2 sample
			locations. Complete full Site-wide round of water levels, including off-site locations.
			Measure Codorus Creek and tributary flows; sample surface water stations for VOCs
64	50	28**	and common ions.
65	50	29	Restart extraction wells
		-	ling upon results, delaying this activity and the start of subsequent tasks.
			epending upon results, which would delay this activity.

Figures





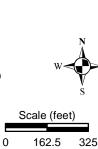


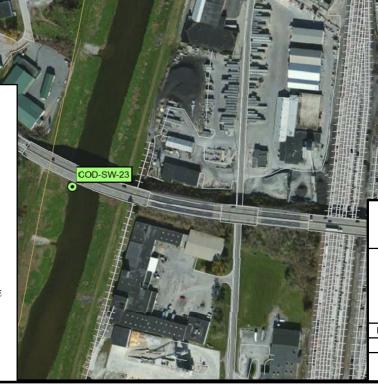
### Legend

### Dye Injection Well, Test 1

• Dye Receptor Sample Location, Test 1

- Oye Injection Well, Test 2
- Dye Receptor Sample Location, Test 2
- Collection Well
- Monitoring Well
- Stream Sample Locations
- Contact
- Block Fault
- FYNOP Property Boundary
- Railroad (2006)
- Roads and Curb Boundary (2006)
- Road Curb (2006)
- Unpaved Road (2006)
- Parking (2006)
- Walkway (2006)





# Figure 2

### Former York Naval Ordnance Plant 1425 Eden Road, York, PA 17402

Dye Tracer Injection and Monitoring Stations Test 1 and Test 2

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**GROUNDWATER SCIENCES CORPORATION** 

# Appendix A

Matrix Interference and Background Sampling and Report

# Memorandum



GROUNDWATER SCIENCES CORPORATION

To: file

From: Jennifer Reese

Date: July 1, 2013

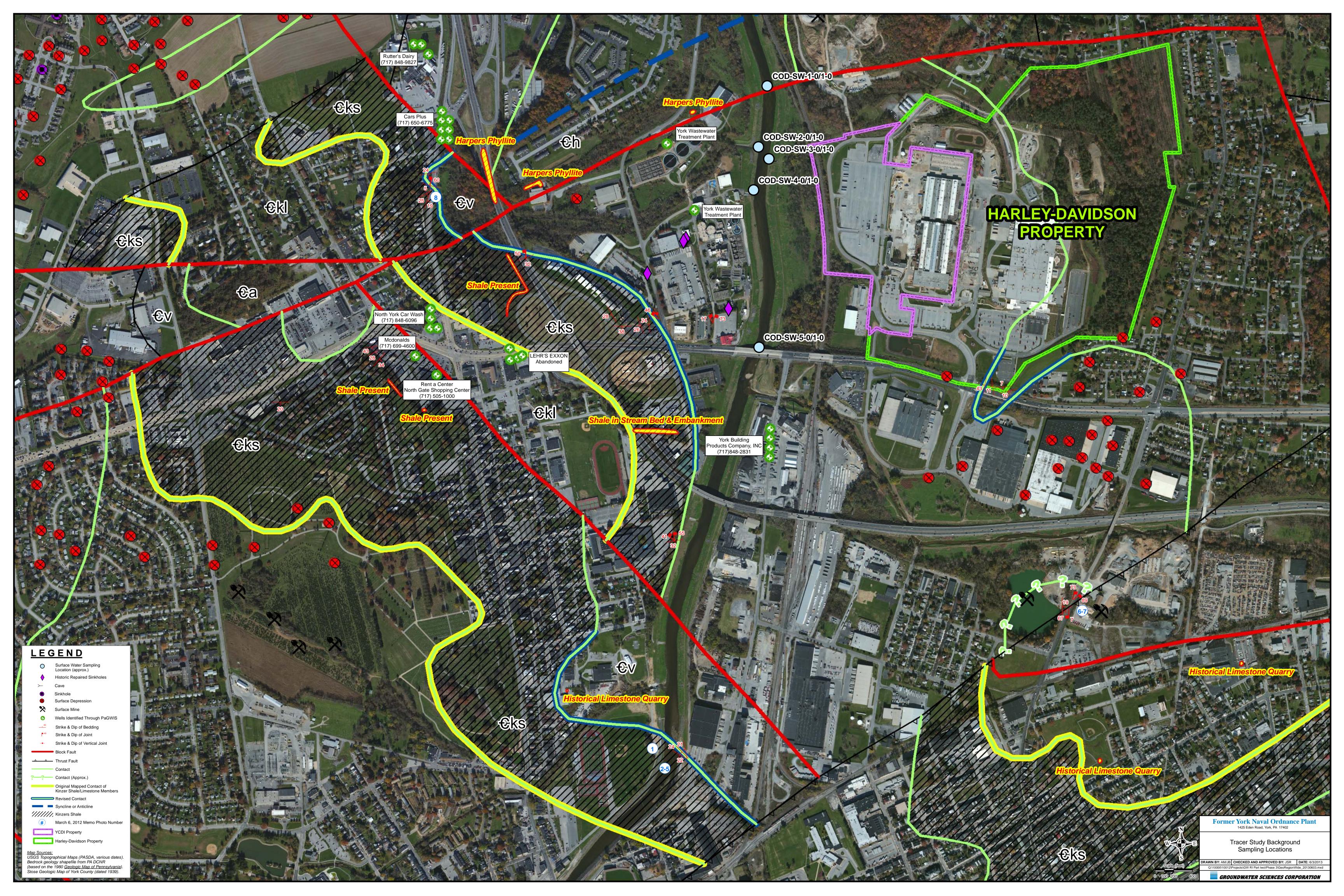
**Re:** fYNOP Background and Matrix Interference Sampling for Tracer Testing

On May 7, 2013, Nat Smith, Kait Fleming, and Jennifer Reese of GSC collected matrix interference samples and background samples to assess the feasibility of tracer testing at the Codorus Creek levee area. Samples were submitted to Crawford Hydrology Laboratory of Western Kentucky University for Matrix Interference analysis and for analysis of the 6 common dyes (Tinopal CBS-X, Fluoroscein, Eosine, D&C Red #28, Rhodamine WT, Sulphorhodamine B ) and to TestAmerica-Pittsburgh for analysis of bromide, chloride, and sodium ions.

Sampling locations from Codorus Creek are shown on the map. Samples were collected beginning with the downstream locations and working to the upstream locations to minimize disturbance of the creek bottom sediments. Samples from Codorus Creek downstream (SW-1) and upstream (SW-5) locations were obtained as composites of the creek. For SW-1 and SW-5, GSC personnel (Nat Smith) in waders traversed the width of the creek and collected eight samples approximately 15 feet apart using a 250 ml bottle. The samples were composited into a one-gallon plastic DI water jug and then transferred to laboratory-supplied containers. Sample SW-2 was collected as a grab sample in the Codorus Creek where the western tributary discharges into the Codorus Creek; sample SW-3 was collected as a grab sample in the Codorus Creek where the creek; and SW-4 was collected as a grab sample where the York City Wastewater Plant effluent discharges to the creek.

Well MW-147A, located within the active eagle nesting zone, was also sampled. The sample was collected with minimal time spent in the eagle nesting zone using a disposable bailer without purging the well, as dyes and ions are not volatile.

Summary tables of results are attached.



# **BACKGROUND DYE SAMPLING RESULTS**

Former York Naval Ordnance Plant 1425 Eden Road, York PA 17402 May 7, 2013 Sampling

			Dye Conce	ntration in ppb		
Sample ID	Tinopal CBS-X	Fluorescein	Eosine	D&C Red #28	Rhodamine WT	Sulphorhodamine B
HD-COD-SW-1-0/0-1	1.086	0.046	ND (0.01)	ND (0.01)	0.032	0.063
HD-COD-SW-2-0/0-1	1.218	0.089	ND (0.01)	ND (0.01)	0.079	0.163
HD-COD-SW-3-0/0-1	0.747	ND (0.01)	ND (0.01)	ND (0.01)	ND (0.01)	ND (0.01)
HD-COD-SW-4-0/0-1	3.129	0.333	ND (0.01)	ND (0.01)	0.160	0.364
HD-COD-SW-5-0/0-1	0.886	ND (0.01)	ND (0.01)	ND (0.01)	ND (0.01)	ND (0.01)
HD-COD-MW-147A-0/0-1	ND (0.1)	ND (0.01)	ND (0.01)	ND (0.01)	ND (0.01)	ND (0.01)

ND (0.10) - Not Detected (Detection Limit)

# **BACKGROUND TRACER SAMPLING RESULTS**

Former York Naval Ordnance Plant 1425 Eden Road, York PA 17402 May 7, 2013 Sampling

	Dye	e Concentration in m	ng/l
Sample ID	Bromide	Chloride	Sodium
HD-COD-SW-1-0/0-1	U (0.50)	64	53
HD-COD-SW-2-0/0-1	U (0.50)	76	47
HD-COD-SW-3-0/0-1	U (0.50)	51	47
HD-COD-SW-4-0/0-1	1.0	110	73
HD-COD-SW-5-0/0-1	U (0.50)	52	53
HD-COD-MW-147A-0/0-1	U (0.50)	75	39

U (0.50) - Not Detected (Reporting Limit)

# **Groundwater Sciences Corporation- Harley Davidson Matrix Interference and Background Analysis Report**

May 30, 2013 Crawford Hydrology Laboratory Western Kentucky University

## **Results of water sample analysis:**

All dyes were detected in their expected wavelengths in the HD-COW-SW-1 matrix sample. Concentrations of all dyes were within 10% of the de-ionized water control at Time (T) = 0 hours and all but Fluorescein at T = 168 hours. Fluorescein concentration in the spiked matrix sample at T=168 hours was just below 15% of the de-ionized water control. No significant effect in the decrease of dye concentration or peak shifts related to time exposed to the matrix was noted, as concentrations between T = 0 and T = 168 hours are very similar.

### **Results of eluted charcoal sample analysis:**

All dyes were detected in their expected wavelengths in the dye receptors exposed to spiked samples of the HD-COW-SW-1 matrix. The dye receptor placed in the HD-COW-SW-1 matrix blank exhibited some fluorescence in the range of Tinopal and Sulphorhodamine B but at low levels.

### **Summary and Recommendations:**

No degradation or peak shifts over time (one week) were seen for CHL dyes in the HD-COW-SW-1 matrix water sample. Dye receptors were able to adsorb all dyes from the spike HD-COW-SW-1 matrix, and dyes were eluted and quantified, with similar concentrations of those dye receptors soaked in the de-ionized water matrix. From these results, we expect no problems using dye receptors to adsorb any of the six CHL dyes tested for the Harley Davidson dye trace project. Lower concentrations of Tinopal in charcoal receptors is expected compared to the other dyes and therefore requires increased dosing if using charcoal receptors for recovery of this dye.

Due to background concentrations of Tinopal, it is recommended that the use of this dye be avoided for this particular dye trace or the amount of dye injected be significantly increased. If Fluorescein or Sulphorhodamine B are used, increased dosing is recommended as the initial background levels of fluorescence in the range of these dyes is greater than ten times the lowest detection limits in some of the background samples submitted.

# CRAWFORD HYDROLOGY LAB \* CENTER FOR CAVE AND KARST STUDIES

P. Hydrogeologists, Edwinonmental Scientists * Karst Groundwater Investigations * Fluorescent Dye Analysis LABORATORY REPORT SHEET FLUORIMETRIC ANALYSIS RESULTS Harley Davidson Analysis requested by: Jennifer Reese - GSC TNOPAL CBS X FLUOREMETRIC Response Dete Police FLUOREMETRIC Response Police Collected Feature Name Police Police Fultorescent Dye Analysis Harley Davidson Analysis requested by: Jennifer Reese - GSC FLUOREMETRIC Response Police Response Spectrolence/State State Police Response Spectrolence/State State Police Response Pol	Comments
LABORATORY REPORT SHEET       TNOPAL CBS X       FLORESCEN       SCIENCE       Date       Date Report       Colonations         FLUORIMETRIC ANALYSIS RESULTS       Flores Register       Colonations       Col	
LABORA TORY REPORT SHEET FLUORIMETRIC ANALYSIS RESULTS         TNDPAL CBS         FLUORESCEN         DESNE         DAC RED 23         RHOMAINEW         SULPHORHOMENEE           FLUORIMETRIC ANALYSIS RESULTS         Fairie Briefering         Color Index:         Colo	
FLUORIMETRIC ANALYSIS RESULTS       Parker Strutts	
Agen 35       Agid Yellow 73       Adid Ref 7       Adid Ref 7 </td <td></td>	
Name       Dys Receptor:       Dys Recepto	
Analysis requested by:       Activated Charcoal       Activated Charcoal       Activated Charcoal       Activated Charcoal       Activated Charcoal       Analysis by:       Analysis by: <td></td>	
Analysis requested by:       Analysis p:       Analys	
Jennifer Reses - GSC       Spectrolluorophotometri       Spectrolluorophotometri	
MATRIX SAMPLES         PQL in Eluent: 0.00 ppb       PQL in Eluent: 0.005 ppb       PQL in Water: 0.010 ppb       PQL in Eluent: 0.005 ppb       PQL in Water: 0.010 ppb       PQL in W	
Lab       Bate       Date       Fature Name       Mater: 510 on       ND       A in Eluent: 516. on       A in Elue	
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	
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Lab $\frac{1}{2}$ Date       Feature Name $\frac{1}{2}$ <	
Lab       i       Date       Date <th< td=""><td></td></th<>	
WATER-1         QA-WATER         ND	
WATER-1         QA-WATER         ND	
WL-OB-1         QA-TINOPAL CBS-X         +         0.101         ND         ND         ND         ND         ND         ND         ND         1ppb           WL-OB-1a         QA-TINOPAL CBS-X         +         1.006         ND         ND         ND         ND         ND         ND         ND         ND         1ppb	r
WL-FL-1 QA-FLUQRESCEIN ND + 0.009 ND ND ND ND 0.1 ppb	
WL-FL-1a         QA-FLUORESCEIN         ND         +         0.091         ND         ND         ND         ND         ND         1 ppb	
WL-EO-1         QA-EOSINE         ND         ND         +         0.011         ND         ND         ND         ND         .01ppb	
WL-EO-1a         QA-EOSINE         ND         ND         +         0.090         ND         ND         ND         ND         .1ppb	
WL-R3-1         QA-RED 3         ND         ND         ND         +         0.013         ND         ND         .1PPB	
WL-R3-1a         QA-RED 3         ND         ND         ND         +         0.103         ND         ND         1PPB           WL-R28-1         QA-D&C RED #28         ND         ND         ND         ND         +         0.103         ND         ND         101         101         101	
WL-R28-1         QA-D&C RED #28         ND         ND         ND         ND         +         0.011         ND         .01ppb           WL-R28-1a         QA-D&C RED #28         ND         ND         ND         ND         +         0.011         ND         .01ppb	
WE-N20-10         QA-SULPHORHODAMINE B         ND         ND <t< td=""><td></td></t<>	
Microsoft         Control Mathematics         No         No         No         No         Approximation           WLSRB-1a         QA-SULPHORHODAMINE B         ND         ND         ND         ND         ND         1000000000000000000000000000000000000	
WH-0B-1         QA-TINOPAL CBS-X         +         10.312         ND         ND         ND         ND         ND         10ppb	
WH-FL-1         QA-FLUORESCEIN         ND         +         10.220         ND         ND         ND         ND         ND         10ppb	
WH-EO-1         QA-EOSINE         ND         ND         +         9.419         ND	
WH-R3-1         QA-RED 3         ND         ND         ND         +         10.283         ND         ND         10ppb	
WH-R28-1         QA-D&C RED #28         ND         ND         ND         ND         +         10.156         ND         10ppb	
WH-SRB-1 QA-SULPHORHODAMINE B A ND	
WL-001-0         BG1         05/07/13         HDCODSW-1         1030         IB         1.086         393.6         IB         0.046         510.2         ND         ND         ND         ND         0.032         NPI         IB         0.063         579.0	
WL-002-0         BG1         05/07/13         HDCODSW-2         1110         IB         1.218         394.8         IB         0.089         510.2         ND         ND         ND         ND         0.079         NPI         IB         0.163         579.8	
WL-003-0         BG1         05/07/13         HDCODSW-3         1135         IB         0.747         392.8         ND         ND         ND         ND         ND         ND	
WH-004-0         BG1         05/07/13         HDCODSW-4         1150         IB         3.129         395.2         IB         0.333         510.2         ND         ND         ND         0.160         NPI         IB         0.364         580.0	
WL-005-0         BG1         05/07/13         HDCODSW-5         1300         IB         0.886         393.0         ND	
WATER-2     QA-WATER     ND     ND     ND     ND     ND     DI Wate	<u>r</u>
WL-OB-2         QA-TINOPAL CBS-X         +         0.089         ND         ND         ND         ND         ND         ND         .1ppb           WL-OB-2a         QA-TINOPAL CBS-X         +         1.089         ND         ND         ND         ND         ND         .1ppb	
WL-OB-2a         QA-TINOPAL CBS-X         +         1.080         ND         ND         ND         ND         ND         ND         1ppb           WL-FL-2         QA-FLUORESCEIN         ND         ND<	
WL-FL-2         QA-FLOORESCEIN         ND         +         0.009         ND         ND         ND         ND         ND         ND         .01 ppb           WL-FL-2a         QA-FLUORESCEIN         ND         +         0.093         ND         ND         ND         ND         ND         .01 ppb	
WL-EC-2         QA-EOSINE         ND         ND         +         0.012         ND         ND         ND         .11 ppb	
WE-EO-2a         QA-EOSINE         ND         ND         +         0.094         ND         ND         ND         .1ppb	
WE-R3-2         QA-RED 3         ND	
WL-R3-a         QA-RED 3         ND         ND         ND         + 0.105         ND         ND         1PPB	
WL-R28-2a         QA-D&C RED #28         ND         ND         ND         ND         +         0.007         ND         .01ppb	
WL-R28-2         QA-D&C RED #28         ND         ND         ND         ND         +         0.102         ND         .1ppb	

Western Kentucky University

					ſ																		1	
													Μ	IATRIX	SAM	PLES								
						TIN	NOPAL CB	S-X		FLUORESC	CEIN		EOSINE			D&C RED #	28		RHODAMIN	NE WT	SULPHORHODA	MINE B		
						PQL in	Eluent: 0.1	100 ppb	1	PQL in Eluent: (	0.005 ppb	Р	QL in Eluent: 0.0	05 ppb	1	PQL in Eluent: 0.	005 ppb	1	PQL in Eluent:	0.005 ppb	PQL in Eluent: 0.0	005 ppb		
						PQL in	Water: 0.1	100 ppb		PQL in Water: (	0.010 ppb	Р	QL in Water: 0.0	10 ppb	1	PQL in Water: 0.	010 ppb	1	PQL in Water:	0.010 ppb	PQL in Water: 0.0	10 ppb		
							luent: 396			λ in Eluent: 51			λ in Eluent: 540.			λ in Eluent: 564			λ in Eluent: 5		λ in Eluent: 577			
						λin V	Vater: 395.	.4 nm		λ in Water: 51	0.0 nm		λ in Water: 534.	9 nm		λ in Water: 556	.6 nm		λ in Water: 5	74.7 nm	λ in Water: 581			
Lab	/ent	Date		TIME	akfit			Peak Center			Peak Center			Peak Center			Peak Center			Peak Center		Peak Center		
ID	é	Collected	Feature Name	I	Pe	Results Co	nc in ppb	(nm)	Results	Conc in ppb	(nm)	Results	Conc in ppb	(nm)	Results	Conc in ppb	(nm)	Results	Conc in ppb	(nm)	Results Conc in ppb	( <b>nm</b> )		Comments
WL-SRB-2			QA-SULPHORHODAMINE B			ND			ND			ND			ND			ND			+ 0.008		.01ppb	
WL-SRB-2a			QA-SULPHORHODAMINE B			ND			ND			ND			ND			ND			+ 0.098		.1ppb	
WH-OB-2			QA-TINOPAL CBS-X			+ 1	0.518		ND			ND			ND			ND			ND		10ppb	
WH-FL-2			QA-FLUORESCEIN			ND			+	10.973		ND			ND			ND			ND		10ppb	
WH-EO-2			QA-EOSINE			ND			ND			+	9.472		ND			ND			ND		10ppb	
WH-R3-2			QA-RED 3			ND			ND			ND			+	10.290		ND			ND		10ppb	
WH-R28-2			QA-D&C RED #28			ND						ND			ND			+	10.244		ND		10ppb	
WH-SRB-2			QA-SULPHORHODAMINE B			ND			ND			ND			ND			ND			+ 10.961		10ppb	
	Anal	yzed by:	L.Bledsoe		on	0	)5/13/1	3																
	Eı	itered by:	L.Bledsoe		on	0	05/20/1	3																
	Co	mments:																						
	00																							
	<b>DUP</b> = Field Duplicate				NS = No Sample Recovered			ered	Q = Lab I	Duplic	ate		IB =	Initial Bac	kground									
	$\mathbf{B} = \mathbf{Background}$			GS = Grab Sample			~ ~ ~	<u> </u>	= Po			IB = Initial Background ?+ = Questionable Positive, needs two hits in a row to eq				to equal +								
	$\mathbf{B} = \mathbf{Background}$ $\mathbf{ND} = \mathbf{No} \text{ Detection}$						Peak Id		ed			it of Rang	p	• • -	Zucouona	10 1 05101	c, nec	us 170 m	.5 m a 10w	to equal 1				
		-	TAD - TAO DELECTION			141	1 - 110	I Cak IU	cnun	cu	10n - 10	an U	n or Kang	L I										

Page 2 of 4

Page 3 of 4

Page 4 of 4

# CRAWFORD HYDROLOGY LAB \*

* Karst Groundy	vater li	nvestigatio	nvironmental Scientists * ns * Fluorescent Dye Analys											Bowling ( (270) 745- E-mail: C	-9224			ku.edu		
LABORA	<b>TO</b>	RY R	EPORT SHEET	I		TINOPAL CBS-X	FLUORES	CEIN		EOSINE			D&C RED	#28		RHODAMIN	E WT	SULPHORHODAM	IINE B	
FLUORI	MET	RIC ANA	ALYSIS RESULTS			Fabric Brightening	Color Ind	ex:		Color Index			Color Ind	ex:		Color Ind	ex:	Color Index:		
			INDION			Agent 351	Acid Yellov	w 73		Acid Red 8			Acid Red					Acid Red 52		
	HAR	KLEY DA	VIDSON			Dye Receptor: Activated Charcoal	Dye Recep Activated Ch			Dye Recepto Activated Char			Dye Recep Activated Ch			Dye Recep Activated Ch		Dye Receptor Activated Charc		
	Anal	vsis reau	ested by:			Activated Charcoal Analysis by:	Activated Cn Analysis			Activated Char Analysis by			Activated Cn Analysis			Activated Cr Analysis		Activated Charc Analysis by:		
		1				Spectrofluorophotometer	Spectrofluoroph		s	pectrofluorophot			Spectrofluoroph			Spectrofluoroph		Spectrofluorophoto		
(	<del>GWS-</del>	JENNIFI	ER REESE																	1
										N	ATRIX	SAM	IPLES							
						TINOPAL CBS-X	FLUORES	CEIN		EOSINE			D&C RED	#28		RHODAMIN	E WT	SULPHORHODAN	IINE B	
						QL in Eluent: 0.100 ppb	PQL in Eluent:			QL in Eluent: 0.0			PQL in Eluent:			PQL in Eluent:		PQL in Eluent: 0.0		
						QL in Water: 0.100 ppb	PQL in Water:			QL in Water: 0.	**	ļ	PQL in Water:		ļ	PQL in Water:		PQL in Water: 0.0		4
						λ in Eluent: 396.0 nm λ in Water: 395.4 nm	λ in Eluent: 5 λ in Water: 5			in Eluent: 540			λ in Eluent: 5			λ in Eluent: 5		λ in Eluent: 577. λ in Water: 581.		4
Lab	Ħ	Date		E		Peak Center	A III Water. 5	Peak Center		A III Water. 554	Peak Center		A III Water. 5	Peak Center		A III Water. 5	Peak Center	A III Water. 561.	Peak	-
ID	Event	Collected	Feature Name	TIME	Results	(nm)	Results Conc in ppb	reak Center (nm)	Poculte	Conc in ppb	(nm)	Doenite	Conc in ppb	reak Center (nm)	Doculte	Conc in ppb	reak Center (nm)	Results Conc in ppb	Center (nm)	Comments
WATER-1		concercu	QA-WATER		ND	Conc in ppb	ND		ND	Conc in ppo		ND	Conc in ppo		ND	cone in ppo		ND	(1111)	DI Water
WH-OB-1			QA-TINOPAL CBS-X		+	10.312	ND		ND			ND			ND			ND		10ppb
WH-FL-1			QA-FLUORESCEIN		ND		+ 10.220		ND			ND			ND			ND		10ppb
WH-EO-1			QA-EOSINE		ND		ND		+	9.419		ND			ND			ND		10ppb
WH-R28-1			QA-D&C RED #28		ND				ND			+	10.283		ND			ND		10ppb
WH-RWT-1			QA-RHODAMINE WT		ND		ND		ND			ND			+	10.156		ND		10ppb
WH-SRB-1			QA-SULPHORHODAMINE B		ND		ND		ND			ND			ND			+ 10.888		10ppb
WL-000-0	M1		DI Water Control	0 HRS	ND		ND		ND			ND			ND			ND		
WH-100-0	M1		HDCODSW1-01-0	0 HRS	IB	0.900 393.0	IB 0.049	509.2	ND			ND			ND	0.030	NPI	IB 0.065	579.2	
WH-00A-0	M1		DI Water Control	0 HRS	+	104.002 395.2						+	11.874	556.6		1. 1.				
WH-10A-0	M1		HDCODSW1-01-0	0 HRS	+	101.780 395.4	1					+	10.854	556.6						
WH-00B-D	M1		DI Water Control	0 HRS	100		+ 17.502	510.0	1.1			1	100	22.22	+	6.364	574.6			
WH-10B-0	M1		HDCODSW1-01-0	0 HRS			+ 16.872	510.0		· · · ·	· · ·			·: ·:	+	5.846	574.6			
WH-00C-0	M1		DI Water Control	0 HRS	2.2				+	11.474	534.4	1. 1.	1. 1. 1. 1.	1.1.1.1	1.1	1. 1. 1. 1.	1.1.1	+ 10.840	582.0	
WH-10C-0	M1		HDCODSW1-01-0	0 HRS	2.12				+	10.805	534.4					1.1.1.1.1.1		+ 10.657	582.0	
WATER-2			QA-WATER		ND		ND		ND			ND			ND			ND		DI Water
WH-OB-2			QA-TINOPAL CBS-X		+	10.518	ND		ND			ND			ND			ND		10ppb
WH-FL-2			QA-FLUORESCEIN		ND		+ 10.973		ND			ND			ND			ND		10ppb
WH-EO-2			QA-EOSINE		ND		ND		+	9.472		ND			ND			ND		10ppb
WH-R28-2			QA-D&C RED #28		ND		ND		ND			+	10.290		ND			ND		10ppb
WH-RWT-2			QA-RHODAMINE WT		ND		ND		ND	-		ND			+	10.244		ND		10ppb
WH-SRB-2			QA-SULPHORHODAMINE B		ND		ND		ND			ND			ND			+ 10.961		10ppb
		yzed by:	L.Bledsoe		on	05/13/13														
	En	ntered by:	L.Bledsoe	-	on	05/20/13														
	Сог	mments:	MATRIX TIME=0 H	OURS																

DUP = Field Duplicate	NS = No Sample Recovered	Q = Lab Duplicate	
B = Background	GS = Grab Sample	+ = Positive	
ND = No Detection	NPI = No Peak Identified	POR = Peak Out of Range	

# CRAWFORD HYDROLOGY LAB \*

, , ,	,	•	nvironmental Scientists * ns * Fluorescent Dye Analys.	is									(270	0) 745-9	reen, KY 42 9224 rawford.Hyc		/ku.ed	lu			
LABORA	ТО	RY R	EPORT SHEET			TINOPAL CBS-X		FLUORES	CEIN	EOSIN	2	D&	C RED #28		RHODAM	TINE WT	SU	LPHORHODAMI	NE B		
FLUORIN	METI	RIC ANA	LYSIS RESULTS			Fabric Brightening		Color Ind	ex:	Color Inde	ex:	Co	or Index:		Color 1	ndex:		Color Index:			
			INDGON			Agent 351		Acid Yello	w 73	Acid Red	87	Ad	id Red 92					Acid Red 52			
	HAR	LEY DA	VIDSON			Dye Receptor:		Dye Recep		Dye Recep			Receptor:		Dye Re			Dye Receptor:			
,	Anal	vsis reau	ested by:			Activated Charcoal Analysis by:		Activated Ch Analysis		Activated Ch Analysis I			ted Charcoal alysis by:		Activated Analys			Activated Charcoal Analysis by:	4		
		~~~~				Spectrofluorophotometer		Spectrofluoroph		Spectrofluoroph			uorophotomete	er	Spectrofluor		S	pectrofluorophotome	eter		
G	<del>WS-</del>	<mark>JENNIFI</mark>	ER REESE																	Ì	
										]	MATRIX	SAMPLE	5								
						TINOPAL CBS-X		FLUORES	CEIN	EOSIN	2	D&	C RED #28		RHODAN	IINE WT	SU	LPHORHODAMIN	NE B		
						QL in Eluent: 0.100 ppb		PQL in Eluent:		PQL in Eluent:		-	uent: 0.005 pj	-	PQL in Eluer			L in Eluent: 0.005			
						QL in Water: 0.100 ppb λ in Eluent: 396.0 nm	1	PQL in Water: λ in Eluent: 5		PQL in Water: 0 λ in Eluent: 54		-	/ater: 0.010 pj ent: 564.2 nm		PQL in Wate λ in Eluent			2L in Water: 0.010			
						λ in Water: 395.4 nm		λ in Eluent: 5		λ in Ellent: 54 λ in Water: 53			ent: 564.2 nm ter: 556.6 nm		λ in Eluent			in Eluent: 577.1 r			
Lab	Ħ	Date		Ξ		Peak Center			Peak Center		Peak Center			k Center		Peak Center	-		Peak		
ID	Eve	Collected	Feature Name	TIME	Peakfit Beautis	Conc in ppb (nm)	Results	Conc in ppb	(nm)	Results Conc in ppb	(nm)	Results Conc ir	(	()	Results Conc in pp	(	Results	Conc in ppb	Center (nm)	Com	ments
WATER-1			QA-WATER		ND		ND			ND		ND			ND		ND			DI Water	
WH-OB-1			QA-TINOPAL CBS-X		+	10.178	ND			ND		ND			ND		ND			10ppb	-
WH-FL-1			QA-FLUORESCEIN		ND		+	10.608		ND		ND			ND		ND			10ppb	
WH-EO-1			QA-EOSINE		ND		ND			+ 9.385		ND			ND		ND			10ppb	
WH-R28-1			QA-D&C RED #28		ND					ND		+ 10.1	59		ND		ND			10ppb	
WH-RWT-1			QA-RHODAMINE WT		ND		ND			ND		ND			+ 9.586		ND			10ppb	
WH-SRB-1			QA-SULPHORHODAMINE B		ND		ND			ND		ND			ND		+	10.115		10ppb	
WL-000-0	M2		DI Water Control	168HR	ND		ND			ND		ND			ND		ND				
WH-100-0	M2		HDCODSW1-01-0	168HR	IB	1.036	IB	0.048	510.8	ND		ND			ND 0.033	NPI	IB	0.059	578.2		
WH-00A-0	M2		DI Water Control	168HR	+	103.353 395.6						+ 11.7	13 5	56.6							
WH-10A-0	M2		HDCODSW1-01-0	168HR	+	99.430 395.4						+ 10.7	79 5	56.6							
WH-00B-D	M2		DI Water Control	168HR			+	17.276	510.2						+ 6.039	574.4	1				
WH-10B-0	M2		HDCODSW1-01-0	168HR			+	14.587	510.2		1. 1.	1			+ 5.455	574.6					
WH-00C-0	M2		DI Water Control	168HR	2.12	S. 1999 S. 199	1.1	1.5	1.1.1.1	+ 11.452	534.4	1.8	1.1	12.2	1. 1. 1.	1.5	÷ +	10.097	582.0		
WH-10C-0	M2		HDCODSW1-01-0	168HR	10.00					+ 10.788	534.6				1. N. N. N.		+	10.023	582.0		
WATER-2			QA-WATER		ND		ND			ND		ND			ND		ND			DI Water	
WH-OB-2			QA-TINOPAL CBS-X		+	10.475	ND			ND		ND			ND		ND			10ppb	
WH-FL-2			QA-FLUORESCEIN		ND		+	0.101		ND		ND			ND		ND			0.1PPB	
WH-EO-2			QA-EOSINE		ND		ND			+ 9.212		ND			ND		ND			10ppb	
WH-R28-2			QA-D&C RED #28		ND		ND			ND		+ 10.1	77		ND		ND			10ppb	
WH-RWT-2			QA-RHODAMINE WT		ND		ND			ND	-	ND			+ 10.278		ND			10ppb	
WH-SRB-2	ļ		QA-SULPHORHODAMINE B		ND	0.5/00/1/2	ND			ND		ND			ND		+	10.895		10ppb	
	•	zed by:	L.Bledsoe	-	on	05/20/13															
		tered by:	L.Bledsoe		on	05/21/13															
	Cor	nments:	MATRIX TIME=168		K)													-			

DUP = Field Duplicate	NS = No Sample Recovered	Q = Lab Duplicate	
B = Background	GS = Grab Sample	+ = Positive	
ND = No Detection	NPI = No Peak Identified	<b>POR</b> = Peak Out of Range	

### CRAWFORD HYDROLOGY LAB \* CENTER FOR CAVE AND KARST STUDIES

RAWF	ORI	d Hyi	DROLOGY L	AB *	CENTER FOR CAV	'E AND	KARST STUD	IES				Western I	Kentu	cky Univ	versity				
			nvironmental Scientists ns * Fluorescent Dye Ar		Geophysical Subsurface Inves	stigations						Bowling (270) 745		, KY 4210	01				
	nuter n	rresuguad		larysis								E-mail: C		ord.Hvdro	oloav@	wku.e	du		
BORAT	ΓOR	Y RE	PORT SHEE	2	TINOPAL CBS-X		FLUORESCEIN	EOS	INE		FD&C RF			D&C RED #			SULPHORHO	DAMINE B	
LUORIM	ETRI	C ANAI	YSIS RESULTS		Fabric Brightening		Color Index:	Color	ndex:		Color Inc	lex:		Color Index	c		Color In	dex:	
		0.11.012			Agent 351		Acid Yellow 73	Acid I	ed 87		Food Red	114		Acid Red 92	2		Acid Re	1 52	
		Natrium			Dye Receptor:		Dye Receptor:	Dye Re			Dye Rece			Dye Recepto			Dye Rece		
	•	is reques	•		Activated Charcoal		Activated Charcoal	Activated	Charcoal		Activated Cl	harcoal		Activated Char	coal		Activated C	harcoal	
RAWF	'ORI	D HYI	DROLOGY L	AB *	CENTER FOR CAV	E AND	KARST STUD	IES				Western	Kentu	cky Univ	rsity				
Hydrogeologists, Geologists, Environmental Scientists * Karst Geop			Geophysical Subsurface Inves	stigations						Bowling (		, KY 4210	01						
arst Ground	water In	ivestigation	ns * Fluorescent Dye Ar	nalysis								(270) 745		مرام المرام					
RORAT	LUB	VRF	PORT SHEE	•	TINOPAL CBS-X		FLUORESCEIN	EOS	INF		D&C REI	E-mail: C	rawic				<b>'UU</b> SULPHORHOI	AMINE B	
-	-			4															
JUUKIMI	ETRI	C ANAL	YSIS RESULTS		Fabric Brightening Agent 351		Color Index: Acid Yellow 73	Color Acid I			Color Inc Acid Rec			Color Index	c		Color In Acid Re		
Н	IARL	EY DAV	IDSON		Dye Receptor:		Dye Receptor:	Dye Re			Dye Rece			Dye Recepto	or:		Dye Rece		
					Activated Charcoal		Activated Charcoal	Activated	Charcoal		Activated Cl	harcoal		Activated Char	reoal		Activated C	harcoal	
Al	natysi	is reques	ieu Dy:		Analysis by: Spectrofluorophotometer		Analysis by: Spectrofluorophotometer	Analy Spectrofluor			Analysis Spectrofluoropi		s	Analysis by pectrofluorophot			Analysis Spectrofluorop		
GW	VS-JE	<b>NNIFE</b>	R REESE														1		
									MATRI	X SAN	<b>IPLES</b>								
					TINOPAL CBS-X		FLUORESCEIN	EOS	ÍNE		D&C REI	D #28		RHODAMINE	WT	1	SULPHORHO	DAMINE B	
					PQL in Eluent: 0.100 ppb		PQL in Eluent: 0.005 ppb	PQL in Elue			PQL in Eluent:			QL in Eluent: 0.0			PQL in Eluent		
					PQL in Water: 0.100 ppb	1	PQL in Water: 0.010 ppb	PQL in Wat			PQL in Water:			QL in Water: 0.0			PQL in Water:		
					λ in Eluent: 396.0 nm λ in Water: 395.4 nm	_	λ in Eluent: 516.1 nm λ in Water: 510.0 nm	λ in Eluent λ in Water			λ in Eluent: 5 λ in Water: 5			in Eluent: 567			λ in Eluent: 8		
Lab	ent	Date		TIME	Peak Cent Results Conc in ppb (nm)	er	Peak Center		Peak Center	r					Peak Center			Peak Center (nm)	
ID	Eve	Collected	Feature Name	Ê		Results	Conc in ppb (nm)	Results Conc in	opb (nm)	r	Conc in ppb	Peak Center (nm	Results	Conc in ppb	(nm)	Results	Conc in ppb	Peak Center (nm)	Comments
ELUENT-1			QA-ELUENT		ND	ND		ND		ND			ND			ND			ELUENT
EL-OB-1 EL-OB-1a			QA-TINOPAL QA-TINOPAL		+ 0.118 + 1.055	ND ND		ND ND		ND ND			ND ND			ND ND			.1ppb 1ppb
EL-OB-1a EL-FL-1			QA-FLUORESCEIN		+ 1.055 ND	ND +	0.005	ND		ND			ND			ND		-	.005ppb
EL-FL-1a			QA-FLUORESCEIN		ND	+	0.105	ND	-	ND			ND			ND			.1ppb
EL-EO-1			QA-EOSINE		ND	ND		+ 0.00	1	ND			ND			ND			.005ppb
EL-EO-1a			QA-EOSINE		ND	ND		+ 0.10	i	ND			ND			ND			.1ppb
EL-R28-1			QA-D&C RED #28		ND ND	ND		ND ND		+			ND ND			ND ND			.005 PPB
EL-R28-1a EL-RWT-1			QA-D&C RED #28 QA-RHODAMINE WT		ND	ND ND		ND		+ ND			ND	0.003		ND			1 PPB .005ppb
L-RWT-1A			QA-RHODAMINE WT		ND	ND		ND		ND			+	0.090		ND			.1ppb
EL-SRB-1			QA-SRB		ND	ND		ND		ND						+	0.006		.005 PPB
EL-SRB-1a			QA-SRB		ND	ND		ND		ND			$\square$			+	0.094		.1 PPB
EH-OB-1			QA-TINOPAL		+ 10.055	ND	0.740	ND		ND			ND			ND			10 PPB
EH-FL-1 EH-EO-1			QA-FLUORESCEIN QA-EOSINE		ND ND	+ ND	9.719	ND + 10.08	8	ND ND			ND ND			ND ND			1 PPB 1 PPB
EH-R28-1			QA-D&C RED #28		ND	ND		ND 10.00		+	10.581		ND			ND			1 PPB
EH-RWT-1			QA-RHODAMINE WT		ND	ND		ND		ND			+	9.058		ND			1 PPB
EH-SRB-1			QA-SRB		ND	ND		ND		ND	-		ND			+	9.846		1 PPB
EL-000-0	M3		DI Water Control		ND	ND		ND		в	0.022	564.8	В	0.028	569.6	ND			
EL-100-0	M3		HDCODSW1-01-0		B 0.420 403.0,PC	DR B	0.044 510.8,POR	ND		ND			ND			IB	0.077	572.0	
EH-00A-0	M3		DI Water Control		+ 5.532 396.0					+	18.747	564.4							
EH-10A-0	M3		HDCODSW1-01-0		+ 3.650 398.2			· · · · ·		+	30.388	564.4		· · · ·					
EH-00B-D	M3		DI Water Control			+	7.732 515.8	1.1.1.1.1	1. 1. 1. 1.		1.1		+	7.892	568.4				
			HDCODSW1-01-0			S 🖌 🛓	13.154 516.0		20 B 20 B	1.1	1.1.1.1.1.1.1	1. 1. 1. 1.	1 .	13.529	568.4		1.1.1.1.1.1		
EH-10B-0	M3		HDCODSWI-01-0				10.104 010.0		_					10.025	00011				

					[							I	MATRIX	SAN	<b>IPLES</b>								
							TINOPAL CI	BS-X	1	FLUORESCEIN		EOSINE			D&C REI	D #28	[	RHODAMINE	WT	<u> </u>	SULPHORHOI	DAMINE B	
						1	PQL in Eluent: 0	.100 ppb	1	PQL in Eluent: 0.005 ppb	Р	QL in Eluent: 0.0	005 ppb		PQL in Eluent:	: 0.005 ppb	Р	QL in Eluent: 0.	005 ppb		PQL in Eluent:	0.005 ppb	
							PQL in Water: 0.	.100 ppb	1	PQL in Water: 0.010 ppb	Р	QL in Water: 0.0	010 ppb		PQL in Water:	0.010 ppb	Р	QL in Water: 0.	010 ppb		PQL in Water:	0.010 ppb	
					ľ		λ in Eluent: 39	6.0 nm		λ in Eluent: 516.1 nm	j	in Eluent: 540	0.2 nm		λ in Eluent: 5	564.2 nm		λ in Eluent: 567	.5 nm		λ in Eluent: 5	577.1 nm	
					+		λ in Water: 39	5.4 nm		λ in Water: 510.0 nm		\ in Water: 534	.9 nm		λ in Water: 5	i56.6 nm		λ in Water: 574	.7 nm		λ in Water: 5	81.9 nm	
Lab	ent	Date		TIME	akfit			Peak Center		Peak Center			Peak Center			Peak Center (nm)			Peak Center			Peak Center (nm)	
ID	Ę	Collected	Feature Name	F		Results	Conc in ppb	(nm)	Results	Conc in ppb (nm)	Results	Conc in ppb	(nm)	Results	Conc in ppb		Results	Conc in ppb	(nm)	Results	Conc in ppb		Comments
EH-10C-0	M3		HDCODSW1-01-0			•			•	N . N . N . N	+	10.011	540.2		1. 1. 1.			1. 1.		+	15.180	578.0	
EL-2			QA-ELUENT			ND			ND		ND			ND			ND			ND			ELUENT
EL-OB-2			QA-TINOPAL			+	0.112		ND		ND			ND			ND			ND			.1ppb
EL-OB-2a			QA-TINOPAL			+	1.094		ND		ND			ND			ND			+			1PPB
EL-FL-2			QA-FLUORESCEIN			ND			+	0.005	ND			ND			ND			ND			.005 PPB
EL-FL-2a			QA-FLUORESCEIN			ND			+	0.104	ND			ND			ND			ND			.1 PPB
EL-EO-2			QA-EOSINE			ND			ND		+	0.003		ND			ND			ND			.005 PPB
EL-EO-2a			QA-EOSINE			ND			ND		+	0.103		ND			ND			ND			.1 PPB
EL-R28-2			QA-D&C RED #28			ND			ND		ND			+			ND			ND			.005 PPB
EL-R28-2a			QA-D&C RED #28			ND			+		ND			+			ND			ND			1 PPB
EL-RWT-2			QA-RHODAMINE WT			ND			ND		ND			ND			+	0.008		ND			.005 PPB
EL-RWT-2A			QA-RHODAMINE WT			ND			ND		ND			ND			+	0.094		ND			.1 PPB
EL-SRB-2			QA-SRB			ND			ND		ND			ND			ND			+	0.005		0.005
EL-SRB-2a			QA-SRB			ND			ND		ND			ND			ND			+	0.102		.1ppb
EH-OB-2			QA-TINOPAL			+	10.607		ND		ND			ND			ND			ND			10 ppb
EH-FL-2			QA-FLUORESCEIN			ND			+	9.557	ND			ND			ND			ND			1ppb
EH-EO-2			QA-EOSINE			ND	-		ND		+	10.036		ND			ND			ND	-		1ppb
EH-R28-2			QA-D&C RED #28			ND			ND		ND			+	10.541		ND			ND			1 PPB
EH-RWT-2			QA-RHODAMINE WT			ND			ND		ND			ND			+	9.203		ND			1 PPB
EH-SRB-2			QA-SRB			ND			ND		ND			ND			ND			+	9.924		1 PPB
	Analy	zed by:	L.Bledsoe	on		05/2	28/13																
	En	tered by:	L.Bledsoe	on		05/2	29/13																
	Con	nments:	MATRIX TIME=	-48 H	OU	RS (1	receptors	s left in s	pike	d solution 48 hrs)	)												

<b>DUP</b> = Field Duplicate	NS = No Sample Recovered	Q = Lab Duplicate	IB = Initial Background
B = Background	GS = Grab Sample	+ = Positive	?+ = Questionable Positive, needs two hits in a row to equal +
ND = No Detection	NPI = No Peak Identified	POR = Peak Out of Range	

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# CRAWFORD HYDROLOGY LAB \*

		nvironmental Scientists * ns * Fluorescent Dye Analysi	s										(270) 745	Green, KY 421 -9224 Crawford.Hydr		ku.ed	u			
LABORA	LABORATORY REPORT SHEET			TINOPAI	CBS-X	FLUORESCEIN			EOSINE		D&C RED #28		RHODAMINE WT		SULPHORHODAMINE B					
FLUORI	METRIC ANA	ALYSIS RESULTS		Fabric Bri	htening	Color Index:			Color Index:			Color Ind	lex:	Color Ind	lex:	Color Index:				
				Agent	351	Acid Yello	ow 73		Acid Red 8	7		Acid Red	92				Acid Red 52			
	HARLEY DA	VIDSON		Dye Rec	•	Dye Recep	•		Dye Recepto			Dye Recep		Dye Recep			Dye Receptor:			
	Analysis requ	ested by:		Activated Analys		Activated Ch Analysis			Activated Char Analysis by			Activated Ch Analysis		Activated Ch Analysis			Activated Charce Analysis by:	bal		
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(	<mark>GWS-JENNIF</mark> I	ER REESE																	1	
									N	MATRIX	SAM	PLES								
				TINOPAI		FLUORES			EOSINE			D&C RED		RHODAMIN			PHORHODAM			
				PQL in Eluen		PQL in Eluent:			QL in Eluent: 0.			PQL in Eluent:		PQL in Eluent:			L in Eluent: 0.00			
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				λ in Water:		λ in Water: 5			λ in Eluent: 540			λ in Eluent: 5		λ in Water: 5			in Water: 581.9			
Lab	🗧 Date		TIME		Peak Cente	r	Peak Center			Peak Center			Peak Center		Peak Center			Peak		
ID	Sector	Feature Name	TIME	Results Conc in p	(	Results Conc in ppb	( <b>nm</b> )	Results	Conc in ppb	( <b>nm</b> )	Results	Conc in ppb	(nm)	Results Conc in ppb	( <b>nm</b> )	Results	Conc in ppb	Center (nm)		Comments
WATER-1		QA-WATER		ND		ND		ND			ND			ND		ND			DI Water	
WH-OB-1		QA-TINOPAL CBS-X		+ 10.17	i	ND		ND			ND			ND		ND			10ppb	
WH-FL-1		QA-FLUORESCEIN		ND		+ 10.608		ND			ND			ND		ND			10ppb	
WH-EO-1		QA-EOSINE		ND	_	ND		+	9.385		ND			ND		ND			10ppb	
WH-R28-1		QA-D&C RED #28		ND				ND			+	10.159		ND		ND			10ppb	
WH-RWT-1		QA-RHODAMINE WT		ND		ND ND		ND ND			ND			+ 9.586		ND	40.445		10ppb	
WH-SRB-1		QA-SULPHORHODAMINE B	_	ND							ND			ND		+	10.115		10ppb	
WL-000-0	M4	DI Water Control		ND		ND		ND			ND			ND		ND				
WL-100-0	M4	HDCODSW1-01-0		IB 0.035	392.8	ND		ND			ND			ND		ND	0.011	NPI		
WH-00A-0	M4	DI Water Control		+ 4.277	394.8		1.1.1.1				+	1.678	556.6					•		
WH-10A-0	M4	HDCODSW1-01-0		+ 5.319	395.4	1.2.1.2.2	1.1.1.1		1.1.1.1.1	1.1	+	2.097	556.4	1.2.1.2.2.2	1.1.1.1	1.1		•		
WH-00B-D	M4	DI Water Control				+ 1.763	510.0							+ 1.040	574.6					
WH-10B-0	M4	HDCODSW1-01-0				+ 3.470	510.0							+ 1.015	574.6					
WH-00C-0	M4	DI Water Control		1. 1. 1. 1. 1	1.2.1.2	1.1		+	2.174	534.8	1.1	1.1.1.1	1. 1. 1. 1.	1.2.2.2.2.2	1.1.1.1	+	2.589	582.0		
WH-10C-0	M4	HDCODSW1-01-0		1.1.1.1.1.1.1	(1,2,2,2)		1.1.1.1.1	+	0.394	535.4	1.1	1.11.11.1		1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.		+	0.532	582.0		
WATER-2		QA-WATER		ND		ND		ND			ND			ND		ND			DI Water	
WH-OB-2		QA-TINOPAL CBS-X		+ 10.47		ND		ND			ND			ND		ND			10ppb	
WH-FL-2		QA-FLUORESCEIN		ND		+ 0.101		ND			ND			ND		ND			0.1PPB	
WH-EO-2		QA-EOSINE		ND	_	ND		+	9.212		ND			ND		ND			10ppb	
WH-R28-2		QA-D&C RED #28		ND		ND		ND			+	10.177		ND		ND			10ppb	
WH-RWT-2		QA-RHODAMINE WT		ND ND	_	ND ND		ND ND			ND ND			+ 10.278 ND		ND	40.005		10ppb	
WH-SRB-2	Analyzed by:	QA-SULPHORHODAMINE B L.Bledsoe		n 05/20	/13	טא	I	NU		I	NU			טא		+	10.895		10ppb	
	Entered by:	L.Bledsoe	_	05/20		-														
		Water after charcoal																		
	Comments.		nas De	en removeu																

DUP = Field Duplicate	NS = No Sample Recovered	Q = Lab Duplicate	
B = Background	GS = Grab Sample	+ = Positive	
ND = No Detection	NPI = No Peak Identified	<b>POR</b> = Peak Out of Range	

# Appendix B

Tracer Procedures from Crawford Hydrology Laboratory

- Appendix B-1 Karst Groundwater Investigation Research Procedures and Dye Trace Instructions
- Appendix B-2 Chain of Custody Form
- Appendix B-3 Shipping Instructions
- Appendix B-4 MSDS Sheets for Dye Tracers



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# KARST GROUNDWATER INVESTIGATION RESEARCH PROCEDURES

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# KARST GROUNDWATER INVESTIGATION RESEARCH PROCEDURES

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APPENDIX I: Approximate Emission Wavelengths for Fluorescent Dyes

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## Introduction

Since 1970, the following research procedures have been utilized and developed by Crawford Hydrology Laboratory (CHL) to investigate the flow of groundwater in karst aquifers. This document describes the current standard procedures and criteria used by CHL in both the field and laboratory.

CHL can provide services for a full field investigation, consultation and project design, quality supplies, and laboratory analysis or any combination of these for your dye trace. A typical scope of work consists of a literature review, field survey for the karst hydrogeologic inventory, dye receptor deployment and retrieval, a background fluorescence study, dye injection, subsequent monitoring and fluorescent dye analysis. The scope of work may include all or portions of these components, outlined below, according to the needs of the particular investigation.

# **Delineation of Study Area**

To ensure dye resurgence locations will not be missed during the investigation, the study area must extend in all directions away from the site until one of the following conditions is met:

- 1. The water table has been established by measurement to be higher than at the proposed dye injection location on site.
- 2. A definite discharge boundary has been reached, such as a large perennial stream.

## **Review of Literature**

Prior to the initial the field survey, a desktop study is conducted to identify and review, as available, the following types of resources that pertain to karst features in the study area.

- Aerial photographs
- Topographic maps

• Geologic maps

• Soil surveys

• Flood maps

• Storm water reports

• Cave maps

- Previous reports about the site
- Maps showing locations of water and sewer pipes

References are sought from state and federal agencies, and local caving organizations. Pertinent information from these resources is transferred to a working base map to plan the subsequent field survey.

## Karst Hydrogeologic Inventory

The field survey for the Karst Hydrogeologic Inventory (KHI) is conducted under conditions that range from moderate to high flow during a wet period so the dominant resurgence points are active. The survey is conducted by walking or floating all streams and associated impoundments (lakes, ponds) in the study area to visually identify karst features that include but are not limited to:

- Springs
   Soil springs
   Seeps
- Sinkholes Swallets Karst windows
- Sinking streams Caves

Each feature is plotted on topographic map, given a name, and a unique inventory number. General information and physical characteristics of the feature are recorded on the Karst Feature Inventory Form. The physical characteristics of each monitoring location include a measurement or estimate of the discharge volume, measurement of the discharge temperature, specific conductance, and pH. The feature is photographed and coordinates recorded from a hand-held Global Positioning System (GPS) receiver to complete the inventory record.

The equipment needed for the field survey includes the following:

- 1. Base maps and air photos for plotting features (7.5 minute topographic quadrangles)
- 2. Inventory forms
- 3. Meters for the measurement of temperature, pH, and specific conductivity.
- 4. Hand-held GPS Unit
- 5. Camera to capture two photos of each spring and surface stream location (one from about 10-15 feet and one from about 100 feet)
- 6. Flagging to mark features for surveying and/or monitoring
- 7. Steam gage equipment

## **Background Fluorescence Investigation**

The background fluorescence investigation involves the monitoring of resurgence points and streams in the study area for possible background fluorescence from previous dye traces, man-made substances, and/or natural interference. The results from the monitoring locations are used to determine the appropriate dyes and dye concentrations to be used.

Dye receptors are typically deployed during of the Karst Hydrogeologic Inventory and for the same duration as proposed for post-injection receptor exchanges. Because of background fluctuation, particularly in urban and/or industrial areas, it may be necessary to measure the background weekly

over a two or three week period. All monitoring activities are conducted in accordance with Dye Receptor Deployment and Retrieval Procedures described later in this document.

The receptors consist of small packets constructed of fiberglass screen mesh filled with approximately three grams of activated coconut charcoal. Each receptor is secured in the main flow of the stream or resurgence point with the use of a system of floats and weights, as needed, with black nylon twine (for low visibility) or non-fluorescent monofilament line. In small springs or streams, the channel may be altered by moving rocks or by other minor means in order to maximize flow past the receptor. In shallow water, the receptors may be shielded to minimize photochemical decay of dyes in the sunlight. Receptors are secured so that they can be retrieved under high water conditions.

Upon retrieval, each dye receptor is washed off in the source water, placed in a clearly labeled, sealed plastic bag, and stored in a dark environment, such as a cooler to reduce exposure to sunlight. Each receptor is prepared in accordance with CHL procedures and analyzed for the presence of dyes that may be used during the investigation. The dyes used by Crawford Hydrology Laboratory include:

- Fluorescein
- Sulphorhodamine B
- Rhodamine WT
- D&C Red 28

- Eosine
- Tinopal CBS-X
- FD&C Red #3
- D & C Green #8

If the dye trace does not begin within two weeks of the collection of the background dye receptors, a second Background Fluorescence Investigation is recommended. Since background fluorescence can change, it is important to know the background fluorescence the week previous to dye injection.

## **Matrix Interference Investigation**

A matrix interference investigation may be needed previous to selection of the dye or dyes to be used. This involves a bench-top investigation to measure the potential impact of chemicals in the groundwater on the dye concentration, dye peak wavelengths, the adsorption of the dye by the charcoal, or the release of dye from the charcoal during elution. The procedures used to conduct this investigation are outlined below:

## MATRIX INTERFERENCE INVESTIGATION RESEARCH PROCEDURES

## 1. SAMPLE COLLECTION

A water sample is collected from each monitoring location and dye injection point for which a matrix interference test is desired. The selection of these locations is based on:

- 1. pH and conductivity results
- 2. Abnormal water color or odor
- 3. Results of previous analytical tests
- 4. The size and location of the hydrologic feature
- 5. The anticipated dye injection location(s) or dye recovery locations

A water sample volume of at least 500 ml is collected in a clean, labeled container. The label includes the name and inventory number of the hydrologic feature, the project name, date and time of sample collection, and initials of persons that collected the sample.

Along with water samples from selected monitoring locations, a 500 ml volume of deionized (provided by CHL) will be used as a control mechanism. This control sample is processed using the same procedures as the matrix interference samples. The control sample is used to quantify any effects the contaminants may have on the dyes that are tested.

### 2. SPIKED WATER SAMPLES AND BACKGROUND DYE LEVELS

Standard concentrations of dye are used to spike the water samples to achieve a target spike concentration of 10 ppb. 100 microliters of 10 ppm standard for each dye is added to 100 ml of sample water. For Tinopal CBS-X (optical brightener), 100 microliters of 100 ppm standard is used; the result is a concentration of 100 ppb in the sample jar. For fluorescein, 50 microliters of 10 ppm standard is used; the result is a concentration of 5 ppb in the sample jar. Two dyes are tested in each individual flask. The de-ionized water control, and a control sample of the water from each test sample, is also analyzed. This provides a background dye analysis for each sample submitted.

The sample flasks are agitated to ensure the dye is thoroughly mixed. Approximately three milliliter aliquots are removed from the sample jars and placed in labeled, borosilicate glass test tubes. The water samples are tested for the selected dyes by analysis in accordance with CHL Procedures.

Sample jars are stored in a dark place (not refrigerated) and analysis is repeated after at least 48 hours. Changes in dye concentration since the initial analysis demonstrate degradation of the dyes by sample constituents.

## 3. SPIKED CHARCOAL SAMPLES

Charcoal packets that contain equal amounts of activated coconut charcoal are placed in each spiked solution. The charcoal packets remain within the flasks for a minimum of 12 hours before they are individually removed, processed, and analyzed.

## 4. RESIDUAL DYE

An aliquot of water is removed from each of the spiked solutions and placed into labeled test tubes. These are analyzed to obtain the concentration of dyes that remain in the spiked solution after removal of the charcoal.

## 5. MATRIX INTERFERENCE REPORT

The results from each of the four analysis events are recorded and plotted. Results are analyzed to assess the impact of contaminants upon tested dyes. A short report is generated that addresses the impact of matrix interference on each of the dyes tested. Dye type and quantity may be determined, in part, by the information included in the report.

## Dye Trace Notification or Permit Application

In Tennessee and Kentucky, the injection of a dye into subsurface waters requires that the Tennessee Division of Water Supply or the Kentucky Division of Water, respectively, be notified prior to injection. Therefore, the appropriate application will be made, and an acceptance notification received from that agency prior to the initiation of any injection of dye at a site in Tennessee or Kentucky. In other states, the State Division of Water will be contacted and permission obtained from the appropriate state agency previous to dye injection.

## **Dye Injection**

After the analysis of the background dye receptors, and the placement of dye receptors in all monitoring locations that may include: springs, karst windows, cave streams, lakes, surface streams, monitoring wells, and selected water wells, dye is injected directly into a sinking stream, sinkhole, well, or excavated soil pit.

If a sinking stream or sinkhole can be located in the appropriate place for dye injection, it is utilized. However, it is sometimes necessary to either dig a dye injection pit with a backhoe or drill an injection well. If it is more than roughly 17 feet to bedrock, then an injection well is the only choice. It may not be necessary to drill a new well, however. Capacity tests can be performed on all existing monitoring wells, and if they will take water at a sufficient rate for dye injection and flushing, then it may be possible to use one or more of them for dye injection. If not, then it is necessary to drill an injection well (which can also serve as a monitoring well). The well or wells will be drilled at sites where there is a good chance of intersecting a karst conduit. Such sites are where lineaments intersect, or where geophysical techniques (microgravity or natural potential) have indicated significant conduits or fractures. Potable water is used to flush the dye past the soil into a bedrock crevice that leads to a cave stream. Usually approximately 500 gallons of priming water are injected into the hole or well to make sure that it drains sufficiently and to wet the soil so that less dye will be absorbed. The dye is then injected and flushed with approximately 2,000 gallons of water. Usually three or four dye traces can be performed simultaneously using different dyes.

## Dye Receptor Deployment and Retrieval

Activated coconut charcoal dye receptors are typically collected and replaced on a weekly interval depending on study objectives, weather and other factors but longer deployment intervals may be appropriate. If time-of-travel data is necessary, samples may be exchanged more frequently during the first one to two weeks. Usually, dye receptors are exchanged weekly for at least two months after the first detection of dye at a spring. This is necessary to allow sufficient time for the dye to reach other receptor locations. If the karst aquifer has turbulent flow through well-developed bedrock conduits, the dye will usually resurge from a spring or springs rather quickly. However, if the dye must travel through a laminar flow, porous-media aquifer, even for a short distance, it could be several weeks to months before the first arrival of dye at a resurgence location. It is also recommended and CHL standard procedure to collect a water sample at the time of receptor collection. Water samples for quantitative dye tracing are processed and analyzed in accordance with CHL Procedures described later in this document. The field procedures below describe CHL protocol and are otherwise provided as guidance.

## DYE RECEPTOR DEPLOYMENT AND RETRIEVAL PROCEDURES

## 1. RECEPTOR CONSTRUCTION

The receptors consist of small packets constructed of vinyl-coated fiberglass screen mesh approximately four inches long and two inches wide. The mesh is filled with three to four grams of activated coconut charcoal. Each receptor is prepared in a dye-free environment and individually packaged in sealed polyethylene bags.

## 2. GRAB SAMPLE VIALS

Grab sample vials are made of borosilicate glass suitable for fluorometric analysis. The caps used are PTFE lined to prevent contamination by fluorescent molecules that can leech out of standard rubber-lined caps. CHL tests 10% of all vials upon receipt from the supplier to ensure that they are dye-free. Each charcoal receptor provided by CHL is accompanied by a grab sample vial.

## 3. RECEPTOR PLACEMENT

Each receptor (along with a grab sample vial) is sealed in a polyethylene bag and transported in a cooler or other container under chain of custody procedures to the site. The receptors are inspected for signs of damage prior to deployment. Disposable nitrile gloves are worn when handling the receptors in order to avoid the transfer of dyes from clothing and other items. New gloves are used for the placement of each receptor.

Each receptor is deployed in the water flow of the monitoring location. The receptor is secured using a system of weights, floats, and tethers as necessary to secure the receptor in a location where flow past the receptor is maximized and exposure to sunlight is minimized. In areas accessible to the public, it may be necessary to make the receptor anchoring system inconspicuous in order to avoid tampering. In small springs or streams, the channel may be altered by rearranging rocks, or by other minor means, in order to maximize flow past the receptor. Each receptor is secured so that they can be retrieved under high water conditions.

Two dye receptors may be deployed at separate nearby locations at key resurgence and stream points and at any site accessible to the public. This provides a backup in the event that the primary receptor is lost or stolen.

## 4. RECEPTOR AND GRAB SAMPLE RETRIEVAL

During receptor retrieval, the condition of the stream or resurgence point is examined for the presence of dye or evidence of tampering or other disturbance. The receptor is retrieved from the monitoring location by means of its tether. Where wading is necessary, the receptor is approached from downstream. Disposable nitrile gloves are worn for each receptor when handled. The receptor is rinsed in the water from which it was removed to clean it of accumulated sediment. The receptor is placed in a labeled, sealed, polyethylene bag. A water grab sample is taken from the location the dye receptor occupies at the time of the receptor collection. The vial is then placed in the same bag as the dye receptor and stored in a closed container to shield it from sunlight. The receptor bag is labeled (with a black permanent ink marker) with the Project name, sample identification number, name of monitoring location, date and time of retrieval, and initials of staff who collected the receptor.

## 5. SAMPLE TRANSPORT

Dye adsorbed onto charcoal receptors is extremely stable at ambient temperatures. Retrieved receptors are transported under chain of custody procedures at ambient temperatures in a dark container, such as a sample cooler. If holding time of the receptors is more than 24 hours, they are refrigerated to prevent possible microbial growth.

Charcoal receptors and water samples collected for submission to CHL should be shipped promptly or stored under refrigeration until shipment. CHL recommends shipping samples in a cooler with or without a frozen ice pack. We do not recommend shipping samples with wet ice as this can create potential for cross contamination. Please ship samples using UPS or Fed Ex Services. The U.S. Postal Service does not deliver to the lab directly. CHL can only accept shipments Monday through Friday from 8:00 a.m. to 4:30 p.m.

# **Laboratory Procedures**

## Sample Custody and Storage

Water samples and charcoal dye receptors may be received by Crawford Hydrology Laboratory via courier or mail delivery. Chain-of-custody forms should accompany all samples submitted. Upon receipt the forms are verified, signed and filed in the appropriate project folder. The chain-of-custody form is added to the laboratory custody records and samples are stored in the lab refrigerator.

## **Sample Processing**

Each dye receptor and grab sample vials are kept in the original, labeled, sealed, polyethylene, ziplock bag until it is removed from the refrigerator. The bags are opened one at a time and the receptor removed. It is washed in a high-speed jet of tap water to remove excess sediment. The receptors can be washed in de-ionized upon request by the client. A typed laboratory identification tag containing the project name, lab identification number (lab ID) and collection date are stapled to the receptor. It is then placed on a tray in a drying oven and dried at  $49^{\circ}$  C for a minimum of 12 hours.

The exterior of the accompanying water sample grab vial is bleached, rinsed, and dried. A label with the project name, lab ID, and collection date is attached to each vial. The vials are then placed in a vial tray in the refrigerator to await analysis. If samples are collected in containers other than those provided by CHL water sample aliquots are taken from each bottle with a disposable pipette, placed in borosilicate glass vials and given labels with the project name, date, and lab ID. They are placed in the refrigerator until analyzed. All pipettes, vials, and sample containers are discarded after one use.

## **Charcoal Preparation**

- 1. Charcoal dye receptors are washed under a high-speed jet of tap water to remove as much sediment as possible.
- 2. A typed label containing the site location name, sample number, and date of collection is stapled to each receptor.
- 3. The receptors are placed in an oven and dried for 12 hours at  $49^{\circ}$  C.
- 4. 1.0 grams of charcoal is weighed and placed into a disposable plastic container that is labeled with the sample identification number.
- 5. The remainder of the charcoal is returned to its original zip-lock bag and stored for six months past project completion (not refrigerated).
- 6. 5.0 ml of Smart solution (an eluent consisting of 1-propanol 100% assay, de-ionized water, and ammonium hydroxide 28-30% assay mixed at a ratio of 5:3:2) is added to the charcoal and the disposable sample container is capped.
- 7. After 30 minutes, the eluent is transferred into a borosilicate glass test tube that is then sealed with a polypropylene cap. The eluted charcoal is then discarded. Precautions are taken to avoid any charcoal from entering the sample vials during transfer but if this occurs removal is not attempted.
- 8. Unless analyzed immediately, eluted samples are placed in the refrigerator
- 9. Samples are placed in a constant temperature bath, covered to prevent photochemical decay and allowed to equilibrate to 30° C just before analysis.

## Water Sample Preparation

- 1. Water samples in CHL provided sample vials are bleached, rinsed and labeled upon receipt.
- 2. If a water sample is received in a non-CHL provided container, an aliquot is drawn from the bottle using a disposable polyethylene pipette and placed into a borosilicate glass test tube which is then sealed with a polypropylene cap.
- 3. Unless analyzed immediately, water samples are placed in the refrigerator

- Water samples (amount remaining in the original containers received by Crawford Hydrology Laboratory) are stored for six months past project completion unrefrigerated.
- Samples are placed in a constant temperature bath, covered to prevent photochemical decay and allowed to equilibrate to 30° C just before analysis.

## Analysis

Eluent and water samples are analyzed for dye by synchronous scanning on a Shimadzu Model RF 5301PC scanning spectrofluorophotometer. Our instrument was installed on-site by the manufacturer and has been operated and maintained under their guidelines. We carry a Shimadzu maintenance and insurance policy on our instrument which includes annual maintenance visits, and if needed repair, by a Shimadzu-authorized technician.

Analysis on a scanning spectrofluorophotometer provides low detection limits and reliable dye analysis. For a typical analysis, a synchronous scan is performed where the excitation and emission monochromators are kept at a fixed wavelength separation during the scan, 15 nanometers for eluted charcoal samples and 18nm for water samples. CHL uses an excitation scan of 350-625 nm that allows for the detection of all eight dyes that we commonly use. The scanning technique for water is similar to the analysis for eluted charcoal samples with the scanning parameters adjusted to compensate for shifts in the excitation and emission maximum wavelengths as well as differences in the Stoke's shift caused by the differences in pH and polarity of water as compared to eluent.

Typical Synchronous Scan Parameters for Charcoal Samples

Scan Speed: Fast Sensitivity: High Excitation Slit Width: 3.0 Emission Slit Width 5.0

Only the emission fluorescence from the synchronous scan is displayed on the monitor and plotted on a graph. The resulting printout has the sample identifier, scanning parameters, and calibration parameters at the bottom of the page. The proprietary software uses spectrum integration and calibration curves stored in the computer to determine the concentration of the dye in question. If the scan indicates positive results for fluorescent dye, a second printout is made to identify peak centers, again using proprietary software. Refer to Appendix I for emission peak centers of the fluorescent dyes used at CHL.

For samples with dye concentrations that meet or exceed the maximum threshold in the high sensitivity scan (fluorescent peak intensity and dye concentration cannot be accurately measured above a peak intensity of 1000), the samples are next analyzed using a low sensitivity scan. Serial dilutions are made with the appropriate matrix until peak intensity is within the measurable range. Typical dilutions are 100 fold (1:100) or 1000 (1:1000) fold. This involves combining one part of the test sample to 99 parts water or eluent or 999 parts for each dilution, respectively. All volume measurements for samples are made with an Acura Micropipette. All water and eluent measurements are made with a 5 or 10 mL Barnstead Thermolyne pump dispenser which will pump with 1.5% of the set value.

If the emission spectra from two or more dyes overlap, the spectra for each dye is separated by use of a non-linear curve-fitting computer program specifically designed for spectral separation. Spectrum integration and calibration curves stored in the computer are then used to determine the concentration of each individual dye present in the sample. All samples and standards analyzed on the Shimadzu RF 5301 are stored electronically with sample information. Sample processing and analysis is recorded in a laboratory logbook.

# **Dye Quantification**

Dye concentrations are expressed in parts per billion (ppb) and are calculated by separating fluorescence peaks based on known emission ranges for each dye then calculating the fluorescence peak area. The area of the sample is proportional to the dye standard solution peak area. Dye standards are analyzed before and after each sample set. The dye standards run are according to the analysis needs of a specific project. For example, if a sample set needs to be analyzed for Fluorescein and Sulphorhodamine B the following standards would be run before and after the samples:

For Eluent:	0.005 ppb Fluorescein and Sulphorhodamine B
	0.100 ppb Fluorescein and Sulphorhodamine B
	10.00 ppb Fluorescein and Sulphorhodamine B
For Water:	0.010 ppb Fluorescein and Sulphorhodamine B
	0.100 ppb Fluorescein and Sulphorhodamine B
	10.00 ppb Fluorescein and Sulphorhodamine B

Also the lowest concentration standards for both dyes are run every 20 samples. If 20 or more samples must be analyzed in our low sensitivity scan then the highest concentration is run every 20<sup>th</sup> sample as well.

Although the dye concentration in water samples expressed in ppb is an accurate quantitative measurement of the amount of dye in the stream at the time the sample was collected, the same is not

true for the eluted charcoal samples. It is only semi-quantitative compared with the actual quantity of dye in the water passing over the receptor. The quantity of dye adsorbed by the charcoal is a function of the dye concentration in the water and the quantity, velocity, temperature and duration of exposure. Turbidity and the quantity and species of molecules competing with the dye for the charcoal adsorption sites can reduce the quantity of dye absorbed onto the charcoal. Also, the quantity of dye eluted from the charcoal is dependent on the amount of charcoal, the type of eluent, whether the charcoal was wet or dry before elution, and the length of time the charcoal is eluted before analysis. The laboratory procedures are standardized but the variables the receptor is exposed to in the stream cannot be standardized.

Dye concentrations for eluted samples are measured and recorded in ppb, however these values will virtually always be much higher than the dye concentrations reached in the stream. Also, because of several water exposure variables, the concentration of dye adsorbed by the charcoal does not necessarily represent the quantity of dye that flowed in the stream past the dye receptor. Analysis of two dye receptors placed in the same general area of the same stream for the same time period of time can result in differences in dye concentrations when expressed in ppb. Therefore, the following abbreviations are used to express the dye concentration in more general terms rather than ppb:

ND	Non-Detect
+	Positive
++	Very Positive
+++	Extremely Positive
В	Background
IB	Initial Background

**Non-Detect Results (ND)** - No dye detected at or above the determined quantitation limit.

**Initial Background (IB)** - Designation given to samples collected before dye injection. Initial background samples are the standard against which all post-injection samples from an individual site are compared in order to determine true positives (+).

**Background Results (B)** - Any sample which has a concentration greater than or equal to the quantitation limit, but less than 10 times the concentration of the highest initial background dye receptor analyzed shall be reported as Background (B) on the report sheet. Also included is any sample that does not meet the qualification for a positive result designation.

Positive Results (+, ++ or +++) - Any sample that is determined to be positive

Although dye concentrations obtained from charcoal dye receptors do not precisely reflect the concentration in the source water, detection of dye at a sufficient concentration above background levels does constitute a positive trace. If a quantitative dye trace is necessary, it must be based on dye analysis of water samples, not charcoal. The Crawford Hydrology Laboratory frequently performs quantitative traces by collecting water samples with an ISCO automatic water sampler. This method provides a dye breakthrough curve, which is an accurate measurement of the dye concentration in the stream as the dye cloud passes the monitoring site.

# **Preparation of Standards**

The standards for analysis of water samples are prepared in de-ionized water. Standards for eluted charcoal sample analysis are prepared in Smart solution. Research by Crawford Hydrology Laboratory indicates that Smart solution elutes more dye from the charcoal than other eluents tested. The dye concentration in the dye sample used for standard preparation is based upon the dye assay figures provided by the dye manufacturer. The Crawford Hydrology Laboratory contacts the dye manufacturer and obtains the certificates of analysis on dyes used to make standards. Dye standards are made as follows:

- 1. A sample of the dye is weighed into a dye-free amber bottle. The sample is then diluted to make a 1% dye solution stock by weight. The 1% stock solutions must set overnight to make sure all the dye is dissolved. A stock solution is prepared for each dye separately and is considered our long term standard.
- 2. A set of serial dilutions are then made using de-ionized water for water standards and Smart solution for eluent standards. We most commonly prepare 100 mL or 50 mL of each dilution. Standard dilutions used for calibration and analysis range from 0.005 ppb to 100 ppb for eluent and 0.010ppb to 100 ppb for water. These are considered short term standards and are made as needed.
- 3. All water standards are stored in amber bottles and placed in refrigeration. Eluent standards are made and stored in amber bottles at room temperature in a secure, dark lab cabinet.

# **Quality Control/ Quality Assurance**

**Field Duplicates** - Duplicate dye receptors are placed at 10 percent or more of the sites to be monitored. The second receptor serves as a back-up in the event that the primary receptor is lost or stolen and/or can be analyzed as QA/QC duplicate.

**Eluent Blank (for eluted samples only)** - Each batch of Smart solution is analyzed for each dye before it is used to elute charcoal samples. Additionally, an eluent blank is analyzed at the beginning, end, and every  $20^{th}$  sample throughout the analysis.

**De-ionized Water Blank (for water samples only)** - Each batch of de-ionized water is analyzed for each dye before it is used. Additionally, a de-ionized water blank is analyzed at the beginning, end, and every 20<sup>th</sup> sample throughout analysis.

**Charcoal Blank**- A sample from each new sealed container of activated charcoal is eluted and analyzed for each dye before the remainder of the charcoal in the container is used. Charcoal receptors are also randomly tested on a monthly basis after construction so that all components used in manufacturing (charcoal, mesh bags, staples, paper clips, cable ties, gloves and polyethylene bags) are tested and confirmed dye-free.

**Raman Scattering Sample**- A Raman scattering pattern and signal-to-noise ratio check is performed on a de-ionized water blank at the beginning and end of each sample set analysis. This is the method recommended by the manufacturer for insuring that the instrument is working within specified parameters and for calibrating the instrument.

**Laboratory Control Standards-** Two low concentration standards and one high concentration standard for each of the dyes to be analyzed, is analyzed before and after each set of samples. A subset of these standards is also analyzed after each set of 20 samples. This demonstrates that the Shimadzu is capable of detection at the minimum detection limit and provides data that can be used to determine the accuracy and precision of the analysis.

## **Criteria for Interpreting Results of Synchronous Scanning**

Interpretation of dye tracing data is not the same as interpreting the results of chemical analyses. Background levels of dye are often present above the quantitation limits of the fluorescent dyes used for tracing. One of the reasons for these background levels is due to the commercial use of the various dyes used for tracing. There are only a few non-toxic fluorescent dyes. For this reason, the dyes used for tracing can often be found in products ranging from food coloring to toilet bowl cleaners. Another reason for these background levels is the extremely low detection limits of fluorescent dyes. Virtually any tracer will have background levels if one can measure at very low concentrations. Background levels often fluctuate more in karst aquifers and to this end, Crawford Hydrology Laboratory developed a standard protocol to determine what constitutes background levels, what is positive, and what is negative (non-detect). This protocol is based upon the results of numerous dye traces that Dr. Crawford and the Crawford Hydrology Laboratory have performed since the 1970s. The protocol has been used for dye trace studies at numerous industrial sites, for federal and state projects and at EPA superfund sites.

## **Background Samples**

In order for background fluorescence to be recorded, it must meet the following conditions:\

- The determined concentration for each dye must be greater than or equal to the lowest detection limit for that dye.
- The recorded peak of the emission curve must be + / 5 nm for Fluorescein, Eosine, FD&C Red 3, D&C Red 28, Rhodamine WT, Tinopal CBS-X, and Sulphorhodamine B, and + or - 10 nm for D&C Green 8. The only times exceptions may be made are:
  - A water sample collected at the same location verifies the presence of the dye in question.
  - The emission spectrum from one dye overlaps the excitation spectra of another dye, causing a shift in peak position.
- The shape of the curve from the synchronous scanning must be the characteristic symmetrical shape of each particular dye as determined from its laboratory standard.

## **Post- Dye Injection Samples**

Post-Dye Injection Samples must meet the following criteria for the determination of a positive trace:

- The determined concentration for each dye must be ten times greater than initial background concentrations or the lowest detection limit for that dye. This means that for a dye with a quantitation limit of 0.01 parts per billion (ppb), no sample can be designated Positive (+) unless its concentration is greater than or equal to 0.100 parts per billion.
- The recorded peak of the emission curve must be + / 5 nm for Fluorescein, Eosine, FD&C Red 3, D&C Red 28, Rhodamine WT, Tinopal CBS-X (optical brightener), and Sulphorhodamine B, and + or - 10 nm for D&C Green 8. The only times exceptions may be made are:
  - A water sample collected at the same location verifies the presence of the dye in question.
  - The emission spectrum from one dye overlaps the excitation spectra of another dye, causing a shift in peak position.

- The shape of the curve from the synchronous scanning must be the characteristic symmetrical shape of each particular dye as determined from its laboratory standard.
- Two consecutive samples that meet the above criteria. The concentration of the dye eluted from the charcoal should display a rise and fall, similar to a dye breakthrough, over a period of time. Consequently, no location shall be called positive if there is only one occasion when the dye concentration met the above criteria. A minimum of two consecutive positives is needed in order to say that a particular location had a positive trace. If only one sample qualifies for a positive designation, then the location will either be designated as a potential positive, or the trace will be repeated.
- The presence of dye at a particular location must not be attributable to any source other than the dye injected for the purpose of conducting the dye trace.

# **APPENDIX I**

# Approximate Emission Wavelengths For Fluorescent Dyes

# ELUTED CHARCOAL SAMPLES

Tinopal CBS-X	391.7 nm
D&C Green #8	494.5 nm
Fluorescein	516.1 nm
Eosine	540.2 nm
FD&C Red #3	549.8 nm
D&C Red #28	564.2 nm
Rhodamine WT	567.5 nm
Sulphorhodamine B	577.1 nm

## WATER SAMPLES

Tinopal CBS-X	. 395.4 nm
D&C Green #8	. 491.3 nm
Fluorescein	. 510.0 nm
Eosine	. 534.9 nm
FD&C Red #3	. 546.0 nm
D&C Red #28	. 556.6 nm
Rhodamine WT	. 574.7 nm
Sulphorhodamine B	. 581.9 nm

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# CONTAMINATION: PRECAUTIONS FOR THE USE OF FLUORESCENT DYES AS TRACERS

Contamination is the most detrimental factor to a successful dye trace. Fluorescent dyes used in leak detection and groundwater tracing are prepared from high-purity powders. Highly concentrated aqueous solutions of dye are then injected into the flow path to be studied. After injection, key points are monitored using activated charcoal receptors inspected for fluorescence using a delicate and precise instrument, the scanning spectrofluorophotometer, that can detect dyes at part per trillion levels.

Due to the concentration of dye used for injection and the sensitivity of methods used for analysis, contamination of materials, personnel, and equipment is of great concern.

When concentrated dyes are injected into the flow path, personnel wear at the very minimum latex gloves and rubber booties to prevent dye from coming into contact with the hands and feet. These are the most vulnerable to splashes and the easiest means of contaminating other materials, etc. with dye. The immediate area around the dye injection point is routinely covered with plastic sheeting, 2-4 mil, and absorbent padding to confine and control unwanted spills. Care is used when handling injection equipment (pumps, tubing, etc.) and injection is usually performed by *one person* who will not have any contact with other materials or perform any other procedures until they have had a shower and change of clothes.

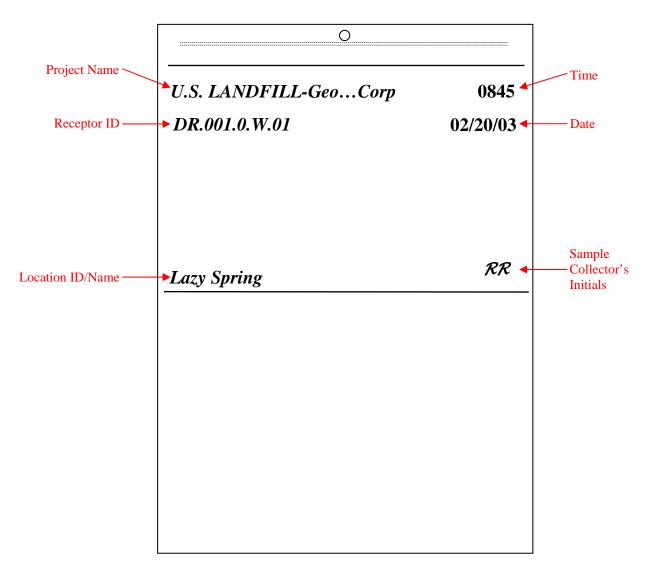
For the purpose of decontaminating materials and equipment a 50/50 solution of bleach and water should be used. Pumps should be adequately flushed and all potentially contaminated surfaces sanitized. Containers used to hold concentrated dye and/or disposable tubing used for injection should be disposed of *off-site* to minimize potential for unintended introduction of dye to any water pathways. Contamination is the primary cause of skewed data and may compromise the results of the dye trace.

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# **DYE RECEPTOR CHANGE-OUT PROCEDURES**

(must be followed in order)

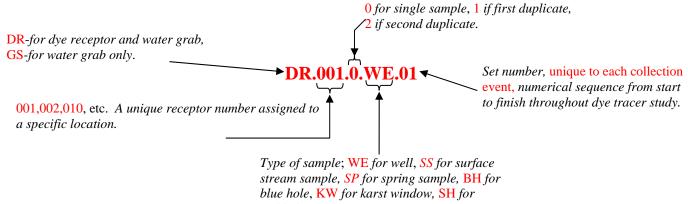
- 1. Enter receptor location from a downstream direction.
- 2. Put on a new pair of disposable latex gloves.
- 3. Check for any tampering of receptor itself, and in the surrounding area. (Note any evidence of tampering on chain-of-custody.)
- 4. Write all pertinent information (project name, receptor ID number, name of monitored point, date and time of retrieval, and initials of collectors) on bag with permanent BLACK ink.
- 5. Remove new dye receptor and grab sample vials from polyethylene bag and set aside.
- 6. Adjust polyethylene bag so that the old dye receptor can be easily placed inside with touching the bag.
- 7. Detach old receptor from string and wash off excess dirt and debris directly in the stream; be sure to remove paper clip or extra cable ties from receptor to prevent puncture of bag.
- 8. Place old receptor into new polyethylene bag.
- 9. Place new receptor into the original receptor location, making sure to position receptor to receive optimal water flow.
- 10. Take a water grab sample from the water source directly feeding the receptor.
- 11. Place grab vial into polyethylene bag with old receptor.
- 12. Remove latex gloves and place in trash bag.
- 13. Seal polyethylene bag.
- 14. Place sealed bag into sealable cooler when leaving the field.



# LABELLING A SAMPLE BAG

**Project Name--** Usually the site name followed or preceded by project contractor name.

**Receptor ID--** A succinct identifier which follows a numeric sequence:



sinkhole.

**Location ID/Name--** Location name or identifier. This would be the name of the inventoried feature which corresponds uniquely to it's receptor ID number. For example MW-04 for a well name, or Bubbling Spring or Shelby Farm Karst Window for a feature, etc.

Location names are important for interpreting final data and finding features in the field. However, RECEPTOR ID NUMBERS ARE USED FOR TRACKING AND SORTING SAMPLES EFFICIENTLY THROUGH THE LABORATORY RECEIPT, ANALYSIS, AND DATA REPORTING PROCESS. It is important that receptor ID numbers follow the guidelines above for clarity and brevity.

**Time--** The time at which the sample was collected.

**Date--** The date on which the sample was collected.

Sample Collector's Initials-- The sample collector's initials.

# SUGGESTIONS FOR IMPROVING THE EFFICIENCY OF FIELD COLLECTION EVENTS:

- Label sample bags before going out to the field to collect receptors, with the exception of collection time or collector's initials (if more than one person is participating in sample collection). It may be convenient to pre-print adhesive bag labels using a computer and leaving blanks where information may be entered in the field such as date, time, and sample collector's initials.
- Pre-print the chain of custody so that the receptor ID follows a numeric sequence. This speeds checking sample receipt against the chain of custody at the lab and makes entering COC information in the field more efficient.
- Identify on the sample bag and on the COC any conditions relevent to the sample collection. For example: Receptor lost, Receptor out of water, Receptor frozen in ice. IF RECEPTOR IS MISSING FROM LOCATION, ALWAYS COLLECT A WATER SAMPLE IN A GRAB VIAL.
- DO NOT PUT PAPER CLIPS IN SAMPLE COLLECTION BAG. Remove the paper clip from the receptor and dispose of it with latex gloves. A paper clip can puncture a sample bag and cause contamination problems.
- ALWAYS USE A FRESH PAIR OF LATEX GLOVES WHEN COLLECTING EACH INDIVIDUAL SAMPLE. ADDITIONALLY USE LATEX GLOVES WHEN HANDLING SAMPLES FOR PACKAGING AND SHIPPING. Not only can samples cross-contaminate each other, but the collector can contaminate samples or sample collection bags inadvertantly by handling the samples all the way up to the time of shipping.
- If collecting samples on the same day that a dye injection is performed, separate personnel should fulfill each duty. No personnel who will be performing a sample collection should come into contact with dye, dye containers, or materials used during dye injection.
- Samples suspected of having a high concentration of dye, or chemical product, or are covered in mud or animal waste can be wrapped in a latex glove prior to placing in sample collection bag. It is helpful if a charcoal receptor can be rinsed of mud or plant debris in the water source from which it is collected but this is not always practical.

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# STREAM RECEPTOR INSTALLATION

- 1. Determine where the receptor is to be placed.
- 2. Put on a new pair of latex gloves.
- 3. Attach black nylon twine to a gumdrop (deep water) or flat rock (shallow water).
- 4. Remove new receptor from bag and attach it to the weight with the paper clip on the stream receptor.
- 5. Place the weight and receptor into the water where it will receive the most optimal flow. (In extremely small bodies of water the channel may have to be manipulated to ensure proper flow over the receptor.)
- 6. Attach the other end of the twine, leaving some slack in the line, to a stable object (a tree or a post works great).
- 7. Mark the object that the receptor line is tied to with flagging tape so that it can found easier when the receptor is picked up. Put the receptor name and/or number on the ends of the tape.
- 8. Also attach a key tag to the object that the receptor is tied to. Put the receptor name and/or number on the key tag, this serves as a double check to the flagging tape in case the flagging tape falls off or is removed.
- 9. Mark the receptor location on a map of the area as accurately as possible. If no map is available draw a sketch map of the receptor area, so the receptor can be found when the receptor is retrieved.

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# STREAM RECEPTOR REMOVAL

- 1. Enter receptor location from a downstream direction.
- 2. Check for any tampering of receptor itself, and in the surrounding area. (Note any evidence of tampering on chain-of-custody.)
- 3. Fill out the necessary identification information (job name, receptor name, date, time, and person retrieving sample) on the sample bag with a **black permanent-ink marker** such as a "sharpie", otherwise the ink will smear and we will not be able to tell the samples apart. You may write directly on the white section of the bag. [Do Not Use Other Color Markers Only Black]
- 4. Put on a new pair of latex gloves and remove the new stream receptor and grab vial from the sample bag and set them on a clean surface out of the way.
- 5. With the sample vial in hand remove screw cap from grab vial and fill the grab vial. Replace the cap on grab vial and place it in the sample bag.
- 6. Using the nylon line pull in the stream receptor. Take the stream receptor in hand and remove the paper clip that connects the stream receptor to the weight. **Remove the paper clip from the stream receptor to prevent puncture of the sample bag**. Place the used receptor in the sample bag, seal it and set it aside.
- 7. Attach the new stream receptor to the weight, and reposition it in the water. Placing paper clip in palm first, remove latex gloves for disposal.
- 8. Place the sample bag into a cooler to be stored until shipping. Refrigerate samples if they are going to be shipped later than 24 hours after collecting.
- 9. Fill out all information on the chain of custody.

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# **GRAB SAMPLE COLLECTION PROCEDURE**

- 1. Put on a new pair of disposable latex gloves.
- 2. Write all pertinent information (project name, receptor ID number, name of monitored point, date and time of retrieval or collection, and initials of collectors) on bag with permanent ink. (BLACK INK ONLY)
- 3. Remove new grab sample vial(s) from polyethylene bag and set aside.
- 4. Adjust polyethylene bag so that the grab sample vial can be easily placed inside without touching the bag, if possible.
- 5. Take a water grab sample from the water source using a pipette or other similar transferring device and place in borosilicate glass vial and seal vial with provided cap.
- 6. Place grab vial into polyethylene bag.
- 7. Remove latex gloves and place in trash bag.
- 8. Seal polyethylene bag.
- 9. Transfer information on grab sample bag to the chain of custody.
- 10. Store samples out of direct contact with sunlight and under refrigeration until they are to be shipped.

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# **INSTUCTIONS FOR INSTALLING DYE RECEPTORS IN WELLS**

Dye receptors for use in monitoring wells are made with components that will not interfere with other types of tests being conducted from the well. Each receptor has two parts, the receptor that will be collected and returned to the laboratory and the marble packet, which will reattach to the new dye receptor during the collection process. DO NOT RETURN THE MARBLE PACKET TO THE LABORATORY. The marble packet is necessary to give the receptor enough weight to slide down the well.

## **Necessary Supplies**

- 1. 20 pound test monofilament fishing line (about 200 yards minimum)
- 2. Scissors (not a knife)
- 3. Latex gloves

## **Installation**

- 1. Measure the depth of the well.
- 2. Measure out enough monofilament fishing line so that the receptor will be approximately 3-4 feet above the bottom of the well.
- 3. If a log of the well is available, the receptor should be placed wherever the screened section of the well is located.
- 4. Tie a loop in one end of the monofilament fishing line and attach the dye receptor to the loop with the supplied cable tie. Make sure that the cable is not pulled tight as it will have to be cut in order to exchange receptors.
- 5. Lower the dye receptor down into the well; making sure that all of the measured monofilament line is used. (VERY IMPORTANT)
- 6. Be careful not cut the monofilament line when placing the cap back on the well.

## **Exchanging Receptors**

- 1. New gloves are to be worn at each location.
- 2. Remove new dye receptor from polyethylene bag.
- 3. Cut cable tie connecting dye receptor to fishing line.
- 4. Cut cable tie connecting dye receptor to the cable tie on the marble packet.
- 5. Place old dye receptor in bag that new dye receptor came in.
  - 6. Attach new dye receptor to marble packet with cable tie.
  - 7. Attach new dye receptor to fishing line.
  - 8. Lower dye receptor into the well, making sure that all of the fishing line is used. (VERY IMPORTANT)
  - 9. Label bag as indicated on Figure 1 using Sharpie permanent ink marker.
  - 10. Place bag in cooler.

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# WELL RECEPTOR INSTALLATION

- 1. Using a water level indicator or other comparable means measure the distance to the water level inside the well from the top of the casing.
- 2. Take that distance plus 15 feet (5 feet to tie the line off, and 10 extra feet to put receptor below water surface) to measure off the receptor line (20 to 25 lb. test non-fluorescent monofilament) to be used in that particular well.
- 3. Tie a loop in one end of the receptor line; this will be used to attach the well receptor to the line.
- 4. Attach the marble pack to the loop using the cable tie attached to the marble pack.
- 5. Attach the well receptor to the marble pack using the cable tie attached to the well receptor; leave some slack in the cable tie to make removal easier. (See sample receptor enclosed)
- 6. Using the extra five feet of receptor line wrap the free end of the line around the top of the well casing. (Make sure the line will not slip off the casing down into the well, if necessary tape the line to the casing with duct tape if there is no means of properly securing it to the casing)
- 7. With the top of the receptor line secured to the well lower the receptor and marble pack into the well.
- 8. Using another piece of line attach a key tag, with pertinent receptor and well information on it, to the outside of the well so it can be identified without removing the well cover.

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# WELL RECEPTOR INSTALLATION WITH SAMPLE VIAL

- 1. Using a water level indicator or other comparable means measure the distance to the water level inside the well from the top of the casing.
- 2. Put on a new pair of latex gloves.
- 3. Take that distance plus 15 feet (5 feet to tie the line off, and 10 extra feet to put receptor below water surface) to measure off the receptor line (20 to 25 lb. test non-fluorescent monofilament) to be used in that particular well.
- 4. Tie a loop in one end of the receptor line; this will be used to attach the well receptor to the line. Tie two more loops starting 5 inches above the first loop about 3 inches apart, the two loops will be used to secure the sample vial to the line.
- 5. Attach the marble pack to the bottom loop using the cable tie in the marble pack.
- 6. Attach the well receptor to the marble pack using the cable tie in the well receptor; leave some slack in the cable tie to make receptor removal easier. (See sample enclosed)
- 7. Secure the sample vial with 3 cable ties, 2 through the 2 remaining loops and the other around the middle of the sample vial, making sure the receptor line is secured with the middle cable tie.
- 8. Using the extra 5 feet of receptor line wrap it around the top of the well casing. Make sure the line will not slip off the casing into the well, if necessary tape the line to the casing with duct tape if there is no means of properly securing it to the casing.
- 9. With the top of the receptor line secured to the well lower the receptor and marble pack into the well.
- 10. Using another piece of line attach a key tag, with pertinent receptor and well information on it, to the outside of the well so it can be identified without removing the well cover.

Hydrogeologists, Geologists, Environmental Scientists Karst Groundwater Investigations • Fluorescent Dye Analysis

# WELL RECEPTOR REMOVAL

- 1) Fill out the necessary identification information (job name, receptor name, date, time, and person retrieving sample) on the sample bag.
- 2) Remove the well cover and set it aside. Put on a new pair of latex gloves and remove the new well receptor and grab vial from the sample bag and set the sample bag on a clean surface beside the well, out of the way.
- 3) Pull in receptor line slowly, wrapping the line around the palm of your hand. Do not allow the line to touch the ground or the outside of the well for it may have high levels of dye on it and cause possible contamination problems.
- 4) With the sample vial in hand remove screw cap from grab vial and fill the grab vial, if a water sample vial has been installed on the receptor line. Replace the cap on grab vial and place it in the sample bag.
- 5) Now take the well receptor and marble pack in hand and cut the cable tie that connects the well receptor to the marble pack. Remove the cut cable tie from the well receptor to prevent puncture of the sample bag. Place the used receptor in the sample bag, seal it and set it aside.
- 6) Attach the new well receptor to the marble pack, and lower into the well.
- 7) Then place the sample bag into a cooler to be stored until shipping. Refrigerate samples if they are going to be shipped later than 24 hours after collecting.
- 8) Fill out all information on the chain of custody.

# **CENTER FOR CAVE AND KARST STUDIES** \* WESTERN KENTUCKY UNIVERSITY

* Hydrogeologists, Geologists, Environmental Scientists CCKS/Crawford								¥ 270-745-9224			
* Karst Groundwater Investigations *Fluorescent Dye Analysis			1906 College Heights Blvd #61066 Bow ling Green, KY 42101-1066						<pre># 270-745-3252 # 270-745-3961</pre>		
* Karst Geophysical Subsurface Investigations			Relinquished b			Date	Received by (Signature)	Date			
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Lab # 270-745-9224

# CRAWFORD HYDROLOGY LABORATORY\* WESTERN KENTUCKY UNIVERSITY

\* Hydrogeologists, Geologists, Environmental Scientists

\* Karst Groundwater Investigations \*Fluorescent Dye Analysis

# CHAIN OF CUSTODY RECORD

**Project:** 

## Analysis requested by:

DR: dye receptor GS: water grab sample

Date		
Date	Received by (Signature)	Date
Time	Representing:	Time
Date	Received by (Signature)	Date
Time	Representing:	Time
	Date	Date Received by (Signature)

Crawford Hydrology Lab

1906 College Heights Blvd. #319

√ DR	√ GS	LAB ID	Event	Feature Name	Station ID	Date	Time	Initials	Preservation Method	Comments Please list dyes to analyze for, or write ''6-dye background'' for full spectrum.

Hydrogeologists, Geologists, Environmental Scientists Karst Groundwater Investigations • Fluorescent Dye Analysis

Dye Receptor and Grab Sample Shipping Recommendations

- Make sure each sample bag is labeled properly and closed securely.
- Fill out and enclose a Chain of Custody for all samples in the shipment.
- Place all samples in a larger bag or liner inside the shipping box or cooler.
- If shipping in a cooler, ice packs are recommended. If using ice, take extra care in packaging samples to avoid ice melt from entering sample bags. Also enclose Chain of Custody in a sealed bag and tape to top of cooler.
- Bubble wrap or some type of insulating material is suggested when grab sample vials are included to prevent breakage.
- Ship all samples to:

Crawford Hydrology Laboratory 319 1906 College Heights Blvd. #31066 Bowling Green, KY 42101-1066

• Shipping charges will apply for cooler return to client.

# Material Safety Data Sheet (FLUORESCEIN) 15174 URANINE C

CHEMCENTRAL/Dyes & Pigments 13395 Huron River Drive Romulus, MI 48174 PEL

#### **SECTION I - IDENTIFICATION**

#### SECTION II - HAZARDOUS INGREDIENTS

CAS NUMBER

PERCENT

HAZARDOUS INGREDIENT NONE as per 29CFR part 1910.1200 or Sara Title III

HMIS HAZARD RATINGS (if applicable):

 HEALTH:
 1

 FIRE
 0

 REACTIVITY
 0

### SECTION III - PHYSICAL DATA

SECTION IV - FIRE AND EXPLOSION DATA

# Material Safety Data Sheet (FLUORESCEIN) 15174 URANINE C

### SECTION V - REACTIVITY DATA

#### SECTION VI - HEALTH DATA

THRESHOLD LIMIT VALUE:.. Not Established

**OVER EXPOSURE EFFECTS:** Contact with eyes may result in severe irritation. Contact with skin may result in irritation. Ingestion may result in gastric disturbances. Inhalation of dust may irritate respiratory tract.

### SECTION VII FIRST AID

**FIRST AID PROCEDURES:** Flush eyes with flowing water at least 15 minutes. If irritation develops, consult a physician. Wash affected skin areas thoroughly with soap and water. If irritation develops, consult a physician. Remove and launder contaminated clothing before reuse.

If swallowed, dilute with water and induce vomiting. Get immediate medical attention. If inhaled, move to fresh air. Aid in breathing, if necessary, and get medical attention.

\*\*NEVER GIVE FLUIDS OR INDUCE VOMITING IF PATIENT IS UNCONSCIOUS OR HAS CONVULSIONS.\*\*

#### SECTION VIII EMPLOYEE PROTECTION

**RESPIRATORY PROTECTION:** NIOSH/OSHA approved dust respirator as necessary.

PROTECTIVE GLOVES: ..... To prevent skin contact.

EYE PROTECTION: ..... Goggles.

ADDITIONAL MEASURES: ...... Eye wash fountains should be easily accessible.

HANDLING AND STORAGE:... Keep away from excessive heat and moisture. Keep containers closed. VENTILATION:...... Local exhaust to control dusts.

#### SECTION IX - SPILL AND DISPOSAL DATA

# Material Safety Data Sheet (FLUORESCEIN)

## 15174 URANINE C

#### SECTION X - TRANSPORTATION DATA

#### SECTION XI - ADDTIONAL INFORMATION

**FOOT NOTES:** This information is furnished without warranty, representation, or license of any kind, except that it is accurate to the best of CHEMCENTRAL Corporation's knowledge or obtained from sources believed by CHEMCENTRAL Corporation to be accurate.

The CHEMCENTRAL Corporation does not assume any legal responsibility for use or reliance upon same. Customers are encouraged to conduct their own tests. Before using any product, read its label.

# **KEYSTONE**

# SAFETY DATA SHEET

## **Keystone Aniline Corporation**

www.dyes.com

Corporate Headquarters 2501 West Fulton Street Chicago, IL 60612 Tel 312-666-2015 Fax 312-666-8530 Manufacturing Facility 2165 Highway 292 Inman, SC 29349 Tel 864-473-1601 Fax 864-473-2377 24 Hour Emergency Phones In U.S. Call CHEMTEL 1-800-255-3924 Outside U.S. call CHEMTEL <u>Collect at;</u> 1-813-248-0585

HMIS RATINGS: HEALTH: 2 FIRE: 0 REACTIVITY: 0 PERSONAL PROTECTION: H

#### **SECTION 1: PRODUCT IDENTIFICATION**

Product I.D.: Product Name: Product Description: Chemical Family: Effective Date:

70301027 KEYACID<sup>™</sup> RHODAMINE WT LIQUID Aqueous Acid Red Colorant Solution Confidential xanthene dye August 4, 2010

### SECTION 2: HAZARD IDENTIFICATION AND EMERGENCY OVERVIEW

#### Emergency Overview:

Unprotected contact may cause eye irritation and slight skin irritation in sensitive individuals. Slight possibility of allergic reactions from repeated contactin some individuals.

#### Eye Contact:

Depending on duration and personal sensitivity, unprotected contact may cause mild irritation, discomfort, redness, watering, itching or other effects. Heavy contact or for prolonged period may increase effects. Follow ALL supervisor and Personal Protection instructions in Section 8 of this SDS.

#### Skin Contact:

Depending on amount of direct unprotected contact, possibility of irritation and allergic reactions in some individuals with redness, itching or other effects. Other delayed effects are possible, including rash. Prolonged or repeated contact may cause inflammation in some individuals. Follow section 8 protection precautions.

#### Inhalation:

Unprotected inhalation of product vapors, mists, aerosols or dusts may cause irritation of the nose, throat, lungs and mucous membranes. Effects may include shortness of breath, cough, nausea, dizziness, headache or other effects. Prolonged or heavy exposure, or heating of liquid material may increase severity of symptoms.

#### Ingestion:

May cause mouth, throat and digestive tract irritation. May be harmful if swallowed.

#### Medical Conditions Aggravated by Exposure:

Improper protection allowing contact with vapors, mists, aerosols, splashes or dusts of product by inhalation, eye contact, skin contact or swallowing may aggravate one or more of the following pre-existing medical conditions: Respiratory problems (asthma, allergies, etc.), skin conditions, eye conditions. Ingestion or inhalation may have potential to aggravate kidney or liver disorders. Heavy or long-term contact may increase effects. Avoid contact/exposure. Individuals with above-noted conditions should avoid working with product.

#### **Skin Sensitization:**

Not known to cause skin sensitization. With careful handling and when good chemical hygiene procedures are followed, harmful effects are not expected. As a precaution against unforeseen or unexpected sensitivity or possible allergic reactions, follow ALL Personal Protection instructions in Section 8 of this SDS.

#### **Respiratory Sensitization:**

In liquid form, under normal and safe operating conditions, components of this product are not expected to cause respiratory sensitization or allergic reactions. As an extra precaution, careful handling and good chemical hygiene procedures should be followed. See section 8 of this Safety Data Sheet.

#### Special Warnings:

None for this material

#### **Unusual Health Hazards:**

None for this material

#### Supplemental Hazard Information:

No additional information is currently available

#### Notes to Physician:

Treat Symptomatically based on Section 2 Hazard Warnings and Section 3 ingredients unless indicated otherwise

#### **Cancer Information:**

#### \*\*\* Not known to contain carcinogens \*\*\*

## **SECTION 3: OSHA HAZARDOUS INGREDIENTS**

Component	CAS Number	Wt %	OSHA - PEL	ACGIH - TLV	Recommended PEL
Confidential Rhodamine dye liquid (2)	Undisclosed	1 - 10%	Not established	Not established	Lowest possible exposure or zero with best PPE.
Diethylene Glycol (Ethanol, 2,2'-oxybis)	111-46-6	.1 - 1%	Not established	Not established	See Airborne Exposure Limits, Section 8
Confidential Rhodamine dye liquid (1)	Undisclosed	1 - 10%	Not established	Not established	Lowest possible exposure or zero with best PPE.
Trimellitic acid	528-44-9	1 - 10%	Not established	Not established	Lowest possible exposure or zero with best PPE.

### Important Notice:

Unprotected contact with ingredients listed in Section 3 may be hazardous based on OSHA 29 CFR 1910.1200 & related appendices. Components not listed are trade secrets, non-hazardous, or not reportable. This SDS is not intended to offer full disclosure, but all component information is available to medical or emergency personnel. All hazards are based on contact exposure. Effects may be unpredictable and may vary from person to person due to individual reactions. Reducing or eliminating contact can reduce or eliminate risk. Use protective equipment and clothing in Section 8 to minimize or eliminate contact. Users are responsible for hazard determination and communication. Unless indicated otherwise, non-carcinogenic components are indicated within a 1-10% range, and investigated or potential carcinogens within a 0.1-1% range. HMIS ratings are based on data interpretation, and vary from company to company. They are intended only for quick, general identification of the degree of potential hazards. Hazards range from 0 (Minimal) up to 4 (Severe). Consult the National Paint & Coatings Association HMIS Manual for detailed information on ratings. To handle material safely, consider all information in this SDS.

## **SECTION 4: FIRST AID INSTRUCTIONS**

#### Eye Contact:

Immediately rinse with flowing water for at least 15 minutes while holding eyelids open. Get immediate medical attention, as a precaution. Have a copy of this Safety Data Sheet available.

#### Skin Contact:

Immediately remove contaminated clothing. Wash affected area with soap and rinse with plenty of water. Get medical attention, as a precaution. Have a copy of this Safety Data Sheet available.

## Inhalation:

Immediately move person to fresh air. If breathing is difficult give oxygen, call 911 immediately. If person is experiencing a tight chest, lung spasms, or other breathing-related symptoms, or chest pain call 911 immediately. Calm and comfort the individual. If not breathing, immediately call 911, continue to give artificial respiration (CPR) until medical help arrives. Have this Safety Data Sheet printed out and available on hand.

### Ingestion:

Do not induce vomiting unless directed to do so by a doctor or by other emergency medical personnel. Forced vomiting of certain chemicals may cause aspiration and lung damage. Have this Safety Data Sheet available.

## **SECTION 5: FIRE FIGHTING INSTRUCTIONS**

## Auto-ignition Temperature:

Not applicable

#### LEL:

Not applicable

## UEL:

Not applicable

Unusual hazards:

None expected

## Other Hazards:

None known

## Types of Extinguishers:

CO2, dry chemical, foam, water fog or spray depending on type of fire

## Fire Fighting Directions:

NA

# SECTION 6: ACCIDENTAL SPILL OR RELEASE INSTRUCTIONS

## **Special Precautions:**

None known. Follow general precautions shown below.

#### **Reporting:**

Check the applicable RQs in Section 15

#### Static Discharges:

IMPORTANT - FOR DYES CONTAINING FLAMMABLE SOLVENTS (Check section 3 for ingredients, section 5 or 9 for flash point, section 14 for transport classification). IF FLAMMABLE, GUARD AGAINST FIRE AND EXPLOSION: Take precautionary measures against static discharges when cleaning up leaks or spills of combustibles, flammables and powders. Containers should be properly grounded with metal straps, cables or other appropriate means to relieve static electricity build-up or generation. IMPORTANT: When using, mixing, filling, or otherwise dispensing any types of solvents, do not allow buildup of flammable or combustible vapors or vapor-air mixtures in confined spaces, storage tanks, or any other areas or enclosures. Totes, drums, pails, and all other containers should be completely sealed when not in use. Flammable vapors can travel a distance to ignition sources and cause fire or explosion. Take every precaution and monitor all safety factors and systems, including maintaining more-than-adequate air-exchange ventilation.

## **Environmental Protection:**

Immediately dike liquid spills with inert absorbent material (sand, "Oil Dry" or other commercially available spill absorbent) to contain and soak up liquid. Prevent material from entering floor drains, sewers, or any bodies of water. For powder spills, use sweeping compound, sawdust, or other appropriate material to contain dust. If possible, recover any uncontaminated materials to re-use.

#### Protective equipment and clothing:

Wear all proper personal protective equipment and clothing to care for spill situation. See section 8 of this Safety Data Sheet.

## Clean up:

## **SAFETY DATA SHEET (continued)**

#### 70301027 KEYACID™ RHODAMINE WT LIQUID

After containing liquid spill by diking and soaking up with inert absorbent material, place in labeled container to be sealed for proper and regulated disposal. Only the slightest residue should remain. Try to save uncontaminated material for reuse whenever possible. For powders, use sweeping compound to minimize dust and pick up as much product as possible. Do not allow liquids to seep into drains, sewers, lakes, rivers, etc. Check Sections 1 and 2 for dye description or type. Solvent dye residue may be cleaned by scrubbing with detergent, depending on type. Do not add water to water-soluble dyes. Dye is concentrated. This will increase amount of color to remove. All cleaning or scrubbing liquids used should be absorbed and placed in labeled containers for correct disposal. Absorbent material containing solvents may release combustible or flammable vapors and should be handled accordingly, properly labeled and disposed. Check Sections 2, 5, 13 & 15 for applicable instructions and regulations.

# SECTION 7: HANDLING AND STORAGE

## Warnings and Precautions:

No special precautions anticipated. Wear all PPE in section 8 as a precaution, and avoid physical contact with material.

## Personal Protection:

Wear ALL proper personal protective equipment as outlined in section 8 of this SDS.

## Handling, Storage & Temperature Conditions:

Keep containers tightly sealed in cool & dry area, out of direct sunlight. IMPORTANT: FOR PRODUCTS LISTING FLAMMABLE/COMBUSTIBLE SOLVENTS or LOW FLASH POINTS - GUARD AGAINST FIRE AND EXPLOSION: Store away from fire hazards and ignition sources, high heat, open flames, welding, hot plates, steam pipes, radiators, etc. Maintain good ventilation. Guard against static discharges. Ground all containers before mixing or filling. Use non-sparking tools to open, close or otherwise work with containers. Limit indoor storage to approved areas with automatic sprinklers. Vapors expected to be released when material is heated during process operations.

STATIC CHARGES: Take precautionary measures against static discharges when mixing, cleaning, filling or otherwise dispensing combustible or flammable liquids. Containers should be properly grounded with metal straps, cables or other appropriate means to relieve static electricity build-up or generation.

VAPORS: IMPORTANT: DO NOT ALLOW buildup of flammable or combustible vapors or vapor-air mixtures in confined spaces, storage tanks, or any other areas or enclosures. Totes, drums and all other containers should be completely sealed when not in use. Vapors can travel a distance to ignition sources and cause fire or explosion. Take every precaution and monitor all safety factors and systems, including maintaining more-than-adequate air-exchange ventilation.

POWDERS: General precautions: Although unlikely in most instances, GUARD AGAINST DUST EXPLOSION HAZARD. Eliminate or keep dust to a minimum. Under the right conditions, high dust concentrations of certain particle sizes mixed with air in a critical ratio in the presence of an ignition source can theoretically cause a dust explosion. Be sure to PROPERLY ground containers when filling, mixing or otherwise dispensing powders. KEEP WORK AREA CLEAN AND DUST-FREE. Follow all Section 8 recommendations for Exposure Controls and Personal Protection.

## WATER-BASED PRODUCTS: DO NOT ALLOW TO FREEZE.

## SECTION 8: EXPOSURE CONTROLS AND PERSONAL PROTECTION

#### Note: Selecting protective equipment & clothing:

When choosing personal protective equipment and clothing, consider each worker's environment, all chemicals being handled, temperature, ventilation, and all other conditions. Determination of the level of protection needed for the eyes, skin and respiratory system under working conditions is the responsibility of the product end-user or shift supervisor. Safety Data Sheet Sections 2, 3, 8 and 11 should be consulted.

## Eye protection:

As a precaution, wear indirectly vented, splash-proof chemical safety goggles. When handling liquids, wear splash-proof goggles under a clear face-shield. Face shield is not to be used without these goggles. The type or extent of protection needed should be determined by the product end-user or shift supervisor.

## **Skin Protection:**

Always wear impervious, chemical-resistant synthetic or rubber gloves. Check with manufacturer for best glove for the material being handled. Wear good quality long sleeved work shirt, coveralls, and a rubber or plastic apron. Wash hands after handling and before eating, drinking or using restroom. Shower after each shift. Clean contaminated but reusable protective equipment and clothing before reusing and wearing again. Discard contaminated disposable gloves and clothing. The type or extent of protection needed should be determined by the product end-user or shift supervisor.

### **Respiratory Protection:**

Depending on type of material handled and processing conditions, the appropriate NIOSH approved air-purifying organic vapor/mist respirator or dust respirator (with proper pre-filters if required) should be worn as a precaution when any inhalation contact with product is possible. A properly selected, disposable NIOSH approved air-purifying mask may be acceptable (Check with the mask manufacturer). After each shift or when equipment becomes contaminated, clean the respirator and replace filters in compliance with 29 CFR 1910.134. Discard disposables as often as required. The type or extent of protection needed should be determined by the product end-user, shift supervisor or other appropriate on-site manager.

## Eye Washes and Other Protection:

Eye wash stations and drench showers should be located within 100 feet or 10-second walk of the work area per ANSI standard Z358.1-1990.

## Ventilation:

Local exhaust or other appropriate ventilation should be used to maintain exposure limits below specified amounts recommended by OSHA, NIOSH, or ACGIH and to draw spray, aerosol, vapors, or dusts away from workers and prevent routine inhalation. At least 10 air changes per hour are recommended for good room ventilation. IMPORTANT - GUARD AGAINST FIRE AND EXPLOSION: When using, mixing, filling, or otherwise dispensing any types of solvents, do not allow buildup of flammable or combustible vapors or vapor-air mixtures in confined spaces, storage tanks, or any other areas or enclosures. Totes, drums and all other containers should be completely sealed when not in use. Vapors can travel a distance to ignition sources and cause fire or explosion. Take every precaution and monitor all safety factors and systems, including maintaining more-than-adequate air-exchange ventilation.

## Airborne Exposure Limits:

Chemical Name	CAS #	WT %	NIOSH - REL	NIOSH - IDLH	0
Diethylene Glycol (Ethanol, 2,2'-oxybis)	111-46-6	.1 - 1%	Not established	Not established	ہ Vap PP

#### OTHER OEL'S

AIHA WEEL Vapor/Aerosol 50 PPM Aerosol 10 mg/m3

# **SECTION 9: PHYSICAL AND CHEMICAL PROPERTIES**

Flash Point:	Not applicable
pH:	Not established
% Water:	Not established
% Total Solids:	0
% Total VOC:	0.08
% Solvents:	0
Boiling Point:	~ 212 ºF (100 ºC)
Appearance:	Reddish liquid
Odor:	Slight or none
Freezing Point:	~ 32 °F (0 °C)
Lbs. per gallon (Liquid):	Not established
Specific Gravity (Liquid):	Not established
Vapor Pressure:	Not established
Viscosity:	Not established
Solubility:	Miscible in water
Other Properties:	No further data

All Data shown above are typical values, not specifications.

## SECTION 10: STABILITY AND REACTIVITY

## 70301027

## KEYACID™ RHODAMINE WT LIQUID

## Stability:

Product is expected to be stable under normal, ambient (controlled) conditions concerning heat, moisture, pressure, fire and ignition hazards, and ventilation. Contact with incompatible or reactive materials may cause hazardous reactions in some products if indicated. Check information below.

### Hazardous Polymerization:

Product will not undergo polymerization.

## Conditions to Avoid:

None known

**Incompatible Materials:** 

None known

#### Hazardous Decomposition Products:

In fire: Oxides of carbon and nitrogen.

## Possible Hazard Reactions:

None known

## SECTION 11: TOXICOLOGICAL INFORMATION

Component	Eye Effect	Skin Effect	Skin Sens	Resp Sens	Oral LD50	Inh LC50	Mutagen	Other Tox Data	Other Info
Confidential Rhodamine dye liquid (2)	May irritate	No Data	No Data	No Data	No Data	No Data	No Data	May be harmful if swallowed	Possibility of allergic reaction in individuals
Diethylene Glycol (Ethanol, 2,2'-oxybis)	Mild irritant	Mild irritant	No Data	No Data	12565 mg/kg (Rat)	No Data	No Data	Oral LD50: 23700 mg/kg (Mouse) Dermal LD50: 11890 mg/kg (Rabbit)	No Data
Confidential Rhodamine dye liquid (1)	May irritate	No Data	No Data	No Data	No Data	No Data	No Data	May be harmful if swallowed	Possiblity of allergic reaction in individuals
Trimellitic acid	May cause chemical inflammation	Irritant	No Data	No Data	No Data	No Data	No Data	No Data	May cause delayed pulmonary edema

# **SECTION 12: ECOLOGICAL DATA**

Component	ΑΟΧ	Aquatic Tox	BOD	Biodeg.	COD	Ecotoxicity	Sewage	Other Test Data	Other Info

\*\*\* No Data \*\*\*

## SECTION 13: DISPOSAL AND ENVIRONMENTAL CONSIDERATION

#### **Reuse of materials:**

Reclaim all uncontaminated material to reuse, recycle or otherwise rework whenever possible.

## Contain - Do not release:

Do not release into sewers, water systems, ground systems or ecosystems without proper authorization.

#### **Disposal Methods:**

Incinerate, treat, or bury (landfill), after sampling and testing, at facility approved by applicable federal, state, and local authorities.

## **Empty Containers:**

Empty containers may contain residue and/or vapors and should not be reused unless professionally cleaned and reconditioned. Crush if not cleaned, to prevent reuse.

Applicable Regulations:See Section 15 if regulatedSpecial Instructions:See Section 15 if regulated

# SECTION 14: SHIPPING AND TRANSPORTATION INFORMATION

## **DOT Regulations (Ground):**

Notes/Special Precautions:	Not regulated. Protect from freezing. Attach PROTECT FROM FREEZING label.
IATA Regulations (Air):	
Notes/Special Precautions:	Not regulated. Protect from freezing. Attach PROTECT FROM FREEZING label.
IMDG / IMO Regulations (Water):	
Notes/Special Precautions:	Not regulated. Protect from freezing. Attach PROTECT FROM FREEZING label.

# **SECTION 15: REGULATORY INFORMATION**

## FEDERAL AND STATE LISTS

Component	CAS Number	Weight %	Regulatory List
Confidential Rhodamine dye liquid (2)	Undisclosed	1 - 10%	No listings known to be applicable.
Diethylene Glycol (Ethanol, 2,2'-oxybis)	111-46-6	.1 - 1%	SOCMI Chemical, State Lists: MN, PA
Confidential Rhodamine dye liquid (1)	Undisclosed	1 - 10%	No listings known to be applicable.
Trimellitic acid	528-44-9	1 - 10%	No listings known to be applicable.

## SARA 311/312 Hazard Categories:

Immediate / Acute Health Hazard:	YES
Chronic / Delayed Hazard:	YES
Fire Hazard:	NO
Sudden Release of Pressure Hazard:	NO
Reactivity Hazard:	NO

## **GLOBAL CHEMICAL REGISTRATION LISTINGS:**

AICS (Australia):	Not all components listed
DSL (Canada):	All components listed except Trimellitic acid (NDSL listed)
ECL (Korea):	Not all components listed
EINECS (Europe):	Components listed
ENCS (Japan):	Not all components listed
IECSC (China):	Not all components listed
NZIoC (New Zealand):	Not all components listed
PICCS (Phillippines):	Not all components listed
TSCA (US):	Components listed

Keystone has taken all relative steps to ensure REACH-Compliance. Please contact us with any REACH-Related questions.

## **OTHER LISTINGS:**

Trimellitic acid NDS Llisted

## Additional Info:

For additional international, federal or state regulatory compliance information not shown: Call 312-666-2015.

# **SECTION 16: OTHER INFORMATION**

Reason for Revision: Reviewed: Adjustment to ingredient reporting and global listings. 080410

## **Disclaimer:**

The information and recommendations contained herein are based upon data believed to be correct. However, no guarantee or warranty of any kind, expressed or implied, is made with respect to the information contained herein. This Safety Data Sheet was prepared to comply with the OSHA Hazard Communication Standard 29 CFR 1910.1200, and supersedes any previous information. Previously dated sheets are invalid and inapplicable.

## END OF SDS

### MATERIAL SAFETY DATA SHEET

15189 Eosine OJ FOSINE SECTION I - IDENTIFICATION MANUFACTURER/DISTRIBUTOR, CHEMCENTRAL/Dyes & Pigments Division 13395 Huron River Drive Romulus, Michigan 48174 EMERGENCY PHONE NUMBER... (313) 941-4800 EFFECTIVE DATE..... 10/25/1996 REVISED DATE ..... 10/25/1996 CHEMICAL NAME..... Acid Red 87 (Color Index name) TRADE NAME..... 15189 Eosine OJ CHEMICAL FAMILY..... Xanthene CHEMICAL FORMULA..... 45380 (Color Index formula) SECTION II - HAZARDOUS INGREDIENTS HAZARDOUS COMPONENTS HAZARDOUS % TLV (Units) PROD. CAS # None as per part 29 CFR 1910.1200. This product supplied is in compliance with TSCA Reporting Requirements. SARA Title III. Not Listed. SECTION III - PHYSICAL DATA BOILING Point(F)..... N/A FREEZING POINT (F)..... N/A VOLATILITY/VOL(%)..... N/A MELTING POINT ..... N/A VAPOR PRESSURE (mm Hg)... N/A VAPOR DENSITY (Air=1) .... N/A SOLUBILITY IN H20..... Moderate APPEARANCE/ODOR..... Red powder, no characteristic odor SPECIFIC GRAVITY (H20=1). Approximately 1 EVAPORATION RATE ..... N/A PH..... N/A SECTION IV FIRE & EXPLOSION HAZARD DATA FLASH POINT..... N/A LOWER FLAME LIMIT ..... N/A HIGHER FLAME LIMIT..... N/A EXTINGUISH MEDIA..... Water fog, CO2, or Dry chemical. FOR FIRE..... Fire fighters should be equipped with self contained breathing apparatus and turnout gear.

10/25/1996

## MATERIAL SAFETY DATA SHEET

15189 Eosine OJ

UNUSUAL FIRE HAZARD..... Adequate ventilation and clean up must be maintained to minimize dust accumulation. May form explosive dust/air mixture.

SECTION V - HEALTH HAZARD DATA THRESHOLD LIMIT VALUE.... Ingestion in rats, LD50=4,700 mg/kg OVER EXPOSURE EFFECTS.... Contact with eyes may result in severe irritation. Contact with skin may result in irritation. Ingestion may result in gastric disturbances. Inhalation of dust may irritate respiratory tract. FIRST AID PROCEDURES..... Flush eyes with flowing water at least 15 minutes. It irritation develops, consult a physician. Wash affected skin areas thoroughly with soap and water. If irritation develops, consult a physician. Remove and launder contaminated clothing before reuse. If swallowed, dilute with water and induce vomiting. Get immediate medical attention. If inhaled, move to fresh air. Aid in breathing, if necessary, and get medical attention. \*\*NEVER GIVE FLUIDS OR INDUCE VOMITING IF PATIENT IS UNCONSCIOUS OR HAS CONVULSIONS. \*\* SECTION VI - REACTIVITY DATA CHEMICAL STABILITY..... Stable CONDITIONS TO AVOID ..... N/A INCOMPATIBLE MATERIALS... Unknown DECOMPOSITION PRODUCTS... Carbon monoxide, Carbon dioxide, and oxides of Nitroger HAZARDOUS POLYMERIZATION. Does not occur POLYMERIZATION AVOID .... N/A SECTION VII - SPILL OR LEAK PROCEDURE containers. WASTE DISPOSAL METHOD .... Do not discharge into sewers or waterways. Dispose of in accordance with local regulations. SECTION VIII - SPECIAL PROTECTION RESPIRATORY PROTECTION... NIOSH/OSHA approved dust respirator as necessary. VENTILATION..... Local exhaust to control dusts. PROTECTIVE GLOVES..... To prevent skin contact. EYE PROTECTION..... Goggles. PROTECTIVE EQUIPMENT.... Eye wash fountains should be easily accessible.

## MATERIAL SAFETY DATA SHEET

15189 Eosine OJ

HANDLING AND STORAGE..... Keep away from excessive heat and moisture. Keep containers closed.

SECTION IX - SPECIAL PRECAUTIONS

HAZARD CLASS...... N/A DOT SHIPPING NAME..... Ink Material NMFC Item #101720 REPORTABLE QUANTITY (RQ). N/A UN NUMBER..... N/A NA #..... N/A DOT LABELS REQUIRED.... Mfg. Label Only SPECIAL SHIPPING INSTRUCTIONS: MANUFACTURER'S LABEL ONLY PACKAGING SIZE..... Various

FOOT NOTES

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N/A = Not applicable

REFERENCES

# Material Safety Data Sheet (SULPHORHODAMINE B)

17152 Acid Rhodamine DW

CHEMCENTRAL/Dyes & Pigments 13395 Huron River Drive Romulus, MI 48174

## SECTION I - IDENTIFICATION

## SECTION II - HAZARDOUS INGREDIENTS

CAS NUMBER

HAZARDOUS INGREDIENT PERCENT None as per part 29 CFR 1910.1200 HMIS HAZARD RATINGS (if applicable):

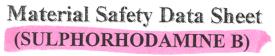
SECTION III - PHYSICAL DATA

SECTION IV - FIRE AND EXPLOSION DATA

## SECTION V - REACTIVITY DATA

STABILITY: ...... Stable CONDITIONS TO AVOID: ...... N/A

PEL



17152 Acid Rhodamine DW

## SECTION VI - HEALTH DATA

THRESHOLD LIMIT VALUE:.. Ingestion in rats, LD 50 > 5,000 mg/kg.

## SECTION VII FIRST AID

FIRST AID PROCEDURES:...... Flush eyes with flowing water at least 15 minutes. If irritation develops, consult a physician. Wash affected skin areas thoroughly with soap and water. If irritation develops, consult a physician. Remove and launder contaminated clothing before reuse.

If swallowed, dilute with water and induce vomiting. Get immediate medical attention. If inhaled, move to fresh air. Aid in breathing, if necessary, and get medical attention.

\*\*NEVER GIVE FLUIDS OR INDUCE VOMITING IF PATIENT IS UNCONSCIOUS OR HAS CONVULSIONS.\*\*

## SECTION VIII EMPLOYEE PROTECTION

**RESPIRATORY PROTECTION:** NIOSH/OSHA approved dust respirator as necessary.

PROTECTIVE GLOVES: ..... To prevent skin contact.

EYE PROTECTION: ..... Goggles.

ADDITIONAL MEASURES: ...... Eye wash fountains should be easily accessible.

HANDLING AND STORAGE: ... Keep away from excessive heat and moisture. Keep containers closed. VENTILATION:...... Local exhaust to control dusts.

## SECTION IX - SPILL AND DISPOSAL DATA

## SECTION X - TRANSPORTATION DATA

PROPER SHIPPING NAME: ..... Coal Tar Dyestuff HAZARD CLASS AND LABEL: N/A UN NUMBER: ...... N/A REPORTABLE QUANTITY: ..... N/A

# Material Safety Data Sheet (SULPHORHODAMINE B)

17152 Acid Rhodamine DW

# SECTION XI - ADDTIONAL INFORMATION

# Appendix C

Codorus Creek Stream Statistics Worthington and Smart Calculation of Tracer Mass

## **Tracer Input Mass Calculation**

fynop - 10/19/2013 JSR/SMS

Equation Used:  $M = 19 \times (LQC)^{0.95}$ 

Equation from Worthington and Smart, Empirical Determination of Tracer Mass for Sink to Spring Tests in Karst, Published in: Sinkholes and the engineering and environmental impacts on karst, Ed B.F. Beck, Geotechnical Special Publication No. 122, American Society of Civil Engineers, p. 287-295. The measuring point for Q is the location where the fault contact crosses Codorus Creek

#### where:

M = Tracer quantity, i.e. mass (g)

L = Distance from injection to measuring point = (m)

Q = Discharge or flow rate = 6.0888 (m<sup>3</sup>/sec) Average Discharge of Codorus Creek in December

C = Maximum expected concentration to be detected (ug/l)

	L (m)	Q (m <sup>3</sup> /sec)	C (g/m <sup>3</sup> )	M (g)	M (lbs)	Notes
						C of 100 ppb is 1,000X the MDL for dyes in water samples the
Test 1 - CW-20 to COD-SW-17	250	6.0888	0.10	2249.58	4.96	approximate visible concentration in water
						C of 100 ppb is 1,000X the MDL for dyes in water samples the
Test 2 - MW-147A to COD-SW-17	200	6.0888	0.10	1819.86	4.01	approximate visible concentration in water
						C of 100 ppb is 1,000X the MDL for dyes in water samples the
Test 2 - MW-99D to fault	250	6.0888	0.10	2249.58	4.96	approximate visible concentration in water

Notes:

From Crawford Hydrology Lab, MDL for dyes from charcoal detectors is 0.05 ppb From Crawford Hydrology Lab, MDL for dyes from water samples is 0.1 ppb **National Water Information System: Web Interface** 

**USGS Water Resources** 

Data Category:Geographic Area:Surface WaterVUnited States

News - updated April 18,2013 🔊



USGS Home Contact USGS Search USGS

USGS	<b>Surface-Water</b>	Monthly	Statistics for the
Natio	n		

The statistics generated from this site are based on approved daily-mean data and may not match those published by the USGS in official publications. The user is responsible for assessment and use of statistics from this site. For more details on why the statistics may not match, <u>click here</u>.

# USGS 01575500 Codorus Creek near York, PA

Available data for this site Time-series: Monthly statisti	cs 🗸 GO
York County, Pennsylvania	Output formats
Hydrologic Unit Code 02050306	HTML table of all data
Latitude 39°56'46", Longitude 76°45'20" NAD27 Drainage area 222 square miles	Tab-separated data
Gage datum 356.39 feet above NGVD29	Reselect output format

✓ GO

00060, Discharge, cubic feet per second,												
YEAR		Month	ly mear	ו in cfs	1940-08-01 -> 1996-09-30)							
IEAK	Jan	Feb	Mar	Apr	Мау	Jun	Jul	Aug	Sep	Oct	Nov	Dec
1940								126.3	294.0	153.5	334.9	309.0
1941	286.9	318.1	382.8	291.4	118.5	111.1	57.9	38.3	21.1	27.8	50.1	56.8
1942	50.5	143.3	169.4	255.6	300.5	361.6	188.6	378.6	197.4	417.6	272.5	404.1
1943	342.7	450.9	357.8	281.2	293.8	177.9	152.7	54.7	26.1	197.8	392.0	133.0
1944	422.1	146.1	553.2	400.9	320.3	134.3	50.4	28.0	52.1	59.3	70.0	210.9
1945	168.6	492.9	395.4	254.8	191.0	108.4	455.4	334.7	295.9	161.6	210.7	387.0
1946	335.3	235.0	311.9	161.9	237.4	444.7	134.8	134.0	59.4	81.8	63.4	75.0
1947	207.0	186.0	251.5	128.7	349.6	181.1	102.6	53.7	47.9	24.2	168.3	75.4
1948	228.5	343.1	352.6	337.5	490.2	324.0	181.5	147.8	55.3	80.5	124.1	337.9
1949	668.4	499.8	274.5	332.3	227.5	97.3	182.0	73.8	52.4	73.5	58.9	119.6
1950	100.8	359.8	415.9	223.2	345.2	203.3	85.6	44.4	119.2	83.0	259.6	534.6
1951	328.3	687.0	337.8	238.2	135.5	271.4	171.3	108.5	60.9	39.1	184.7	259.0
1952	578.6	403.6	616.8	961.4	637.9	221.5	116.2	66.4	182.8	62.4	332.8	374.1
1953	548.1	384.4	608.9	404.1	320.9	234.8	91.3	41.9	64.3	38.1	70.9	316.5
1954	134.8	105.5	276.5	147.8	203.5	52.8	26.8	38.8	23.2	37.9	68.6	111.3
1955	88.3	232.9	504.2	185.9	101.7	118.1	26.3	457.3	112.1	230.7	145.3	74.4
1956	124.2	473.9	539.5	367.9	162.0	92.5	137.0	89.7	62.5	86.0	183.3	241.9
1957	212.9	346.0	264.8	444.1	145.6	76.7	29.1	27.9	28.1	32.2	59.5	250.1
1958	458.5	385.5	722.2	638.9	558.4	185.2	87.6	114.6	75.3	38.8	86.4	56.9
1959	150.8	162.6	145.5	196.9	86.4	58.3	40.7	43.9	53.0	40.4	58.1	138.2
1960	162.2	249.5	303.6	463.6	339.2	235.3	157.4	212.7	299.2	114.6	100.3	74.9
1961	172.5	665.5	528.1	714.7	287.4	145.3	135.6	86.1	53.7	35.3	66.2	79.2
1962	219.5	453.1	626.1	375.1	131.3	67.4	39.0	39.9	23.4	75.5	196.6	113.5

USGS Surface Water data for USA: USGS Surface-Water Mon	thly Statistics
---------------------------------------------------------	-----------------

1963		156 1	710 0	153.2	02 1	66 1	22.2	25.9	27.2	19.2	64 1	71 6
	160.7	156.1	719.8		83.1	66.1	23.3					71.6
1964	377.2	193.2	571.3	463.4	267.4	77.1	53.9	26.5	22.7	25.7	28.0	80.4
1965	106.0	266.8	330.2	154.4	82.2	39.0	30.6	29.4	28.6	36.0	28.9	27.8
1966	38.4	308.0	209.5	136.0	149.5	31.5	18.1	17.9	28.0	31.3	47.2	72.2
1967	148.0	131.9	418.0	111.0	137.2	54.0	97.0	170.9	54.2	63.3	61.2	207.0
1968	193.9	146.9	286.0	142.4	191.3	180.3	76.6	62.2	134.2	60.2	169.3	111.8
1969	75.8	84.3	147.8	102.1	58.3	66.7	69.2	62.2	81.2	43.9	43.3	81.7
1970	113.9	442.3	294.0	757.0	233.2	211.1	603.9	145.6	70.4	84.0	192.9	238.6
1971	307.2	849.5	487.5	228.2	298.4	243.7	96.5	204.0	147.5	172.4	328.6	392.5
1972	276.0	430.5	495.5	443.1	346.7	2,047	461.8	143.4	89.9	79.2	220.9	584.4
1973	466.7	531.4	287.8	703.0	383.4	311.4	159.3	97.4	119.7	97.0	76.3	380.1
1974	400.6	206.7	226.0	603.9	200.3	137.8	86.1	82.5	128.2	70.6	76.6	269.8
1975	280.4	330.9	453.2	358.5	566.5	398.5	281.1	124.2	1,172	596.2	377.2	216.2
1976	658.8	421.7	252.2	291.5	159.2	142.2	115.5	112.7	114.2	321.2	137.6	128.5
1977	82.3	146.7	362.0	548.4	172.0	96.6	62.4	75.6	85.7	92.4	109.1	495.9
1978	693.1	331.9	883.6	339.8	346.9	154.9	142.8	111.7	80.8	80.8	82.9	144.8
1979	781.2	520.2	626.8	296.2	187.0	189.4	150.1	153.8	398.1	837.2	280.6	192.7
1980	151.7	116.5	286.0	421.1	442.8	230.9	124.3	118.5	74.3	85.9	98.3	60.3
1981	41.5	326.8	143.4	220.8	118.7	136.7	104.8	71.1	48.2	56.8	54.6	73.2
1982	111.3	426.0	186.1	243.8	120.4	334.2	120.5	67.3	67.7	64.9	86.9	85.4
1983	89.4	182.3	338.3	863.6	440.8	252.0	124.1	98.5	55.7	89.6	168.5	546.7
1984	225.7	636.5	527.6	815.5	417.2	236.1	282.9	206.8	118.9	116.8	197.9	232.0
1985	150.4	449.4	168.0	142.0	219.2	112.1	147.7	93.7	92.1	92.8	223.4	248.3
1986	141.5	415.6	336.9	324.7	157.5	97.1	77.4	75.8	52.2	56.6	133.1	254.3
1987	270.7	204.1	291.1	257.4	178.3	105.0	90.1	55.7	136.0	90.2	180.4	165.1
1988	199.2	349.3	207.1	158.5	468.4	139.7	98.2	75.6	72.3	70.1	106.8	81.8
·i	·	i		11	1		ii		1			

	125.4	128.4	236.8	176.5	643.5	201.4	163.4	113.5	89.3	179.5	175.2	116.1
1990	299.1	277.1	190.2	293.5	336.8	204.8	97.7	177.4	109.1	237.5	202.8	313.4
1991	469.9	238.0	285.1	236.1	149.8	72.0	57.5	73.7	117.1	82.9	99.7	220.2
1992	137.5	127.1	298.3	201.7	139.5	133.5	78.7	71.0	89.3	68.9	203.7	255.6
1993	226.8	177.1	997.7	1,006	303.1	149.7	91.5	111.3	137.0	105.0	273.1	554.3
1994	335.6	568.4	1,506	573.4	253.2	111.6	132.4	165.7	111.2	86.8	165.1	215.3
1995	437.8	179.7	248.4	136.6	150.2	156.2	292.0	101.0	74.1	158.5	357.6	181.2
1996	950.8	470.9	464.2	527.0	385.2	271.2	230.6	238.0	305.9			
Mean of monthly Discharge	277	330	405	361	264	202	134	111	119	117	154	215
** No Incomplete data have been used for statistical calculation												

\*\* No Incomplete data have been used for statistical calculation

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