From: "Hinrichs, Gary H" <ghinric@entergy.com>
To: "Timothy Rice" <tbrice@gw.dec.state.ny.us>, "John White" <JRW1@nrc.gov>, "James Noggle" <JDN@nrc.gov>
Date: 12/21/2006 12:53:25 PM
Subject: FW: Tracer test plan

Sorry, I though I sent this out a wile ago.

From: David Winslow [mailto:dwinslow@gza.com]
Sent: Friday, August 25, 2006 5:12 PM
To: Hinrichs, Gary H; Adler, Joseph J.; Mayer, Donald M
Cc: mbarvenik@gza.com; mpowers@gza.com
Subject: Tracer test plan

Attached please find a draft of the Tracer Test Plan for Units 1 and 2.

Note, this is a very comprehensive plan and the scope of the test is significantly greater then originally contemplated. Following consultation with our Tracer Test subconsultant, it was determined that the amounts of dye we plan to inject should be measurable in most of the downgradient wells along the river (if groundwater from the injection points migrates to these wells). Therefore, in order to assess the complete flow path from the injection points, we recommend that most of the on-site wells be monitored during the dye injection. By doing this we may be able to identify the majority of flow paths from the areas to be tested and assess the ultimate fate of contaminants emanating from these points. Originally, we only planned to assess whether groundwater flowed from MW-30 towards the transformer yard, and assess how groundwater may have escaped the curtain drain system at Unit 1. Since we only get one shot at this and it is an expensive test we have decided to provide a comprehensive tracer test plan. This is one of the reasons we recommended waiting for completion of all the wells prior to performing the tests. In addition, we are using some of the stormwater catch basins as monitoring points.

David M. Winslow, Ph.D., P.G.

Senior Project Manager

GZA GeoEnvironmental of New York

440 Ninth Avenue

B155

New York, NY 10001

212-594-8140 (tel)

212-279-8180 (fax)

347-242-7107 (cel)

<http://www.gza.com/images/GZA-Disclaimer.gif>

DRAFT

WORKPLAN FOR A GROUNDWATER TRACING STUDY AT INDIAN POINT NUCLEAR POWER PLANT BUCHANAN, NEW YORK.

AUGUST 2006

Thomas Aley, PHG and PG

President and Senior Hydrogeologist
Ozark Underground Laboratory, Inc.
And
GZA GeoEnvironmental Inc.
FOR

Indian Point Energy Center
295 Broadway
Buchanan, New York

INTRODUCTION

This groundwater tracing plan was prepared by Ozark Underground Laboratory, Inc (OUL) with the assistance of GZA GeoEnvironmental of New York, Inc. (GZA). It was prepared to develop an improved understanding of groundwater flow patterns in the vicinity of Reactors #1 and #2 at the Indian Point Nuclear Power Plant, Buchanan, New York.

The plan has been developed based a site visit on June 14, 2006 by Thomas Aley, PHG & PG, President of Ozark Underground Laboratory, Inc. (OUL), in consultation with Dr. David Winslow, GZA.

The purpose of this study is to use groundwater tracing techniques employing fluorescent tracer dyes to better characterize groundwater flow directions and travel in areas identified as being affected by water contaminated with strontium and tritium. The selected tracer dyes are routinely used in groundwater studies and are safe when used for these purposes. This is demonstrated by the attached papers by Smart (1984) and Field et al. (1995). Use of these tracer dyes can be highly effective in defining contaminant flow in complex geologic terrains, (Stone et al., 1995). Further documentation on the proposed tracer dyes is available in the form of MSDS data sheets for each dye mentioned in the workplan. These MSDS sheets are available in the form of Adobe Acrobat® compatible PDF files. A copy of each has been provided to GZA by OUL.

The OUL is a consulting firm that specializes in groundwater tracing investigations using fluorescent tracer dyes. The OUL provides, or assists in, tracer test design, dye introductions, sample analysis, data reduction and analysis, and preparation of reports on the results of groundwater tracing investigations. The OUL portions of this project will be under the direction of Thomas Aley.

Sampling for tracer dyes will be conducted by GZA. OUL will assist GZA with dye introduction and will train GZA personnel in sampling approaches specific to sampling for tracer dyes.

OVERVIEW OF THE GROUNDWATER TRACING INVESTIGATION

The purpose of this overview is to enhance understanding of the detailed plan that follows.

In order to understand to the site-specific conditions and issues Thomas Aley visited the site on June 14, 2006. Mr. Aley was given a tour of the facility and areas of current interest. Mr. Aley also met with relevant personnel at the site and was able to gain their input on the study requirements. In addition, Mr. Aley received direct input from GZA personnel familiar with the site and with existing data.

This workplan defines the timetable and methods to be employed in this study, includes review comments and input from GZA personnel, and provides a document to guide the investigation.

Background Sampling

Background samples will be collected and analyzed prior to any tracer dye introduction. The objective of this background sampling is to identify and quantify the presence of tracer dyes or compounds with fluorescence characteristics similar to tracer dyes at sampling stations to be used in this study. This will aid in final determination of which dyes will be used at which locations and what quantities of dyes will be required. The plan assumes three rounds of background sampling at all sampling locations, although it may not be possible for every one of them to be sampled during the background sampling period.

The results of the first two rounds of background samples will be evaluated for fluorescence conditions indicating that the initially planned dye types, quantities, and identified locations need to be re-evaluated. If background fluorescence conditions warrant, the OUL may, in consultation with GZA, alter the type of dye to be used at each introduction site and the quantities of dyes to be used.

Dye Introductions

The workplan calls for two initial dye introductions. These are through:

- Dye Introduction Point (DIP) TI-U1-2. Ten pounds of fluorescein dye mixture will be introduced at this location along with flush water. This dye introduction location is beneath a failed fuel pool for Reactor 1.
- DIP TI-U2-1. Fifteen pounds of eosine dye mixture will be introduced at this location along with flush water. This dye introduction location is adjacent to Reactor 2.

If fluorescein from DIP TI-U1-2 is not detected at Monitoring Well 42 within five to seven days after dye introduction then a third dye introduction will be considered. The third dye introduction is being delayed to ensure that the dye from TI-U1-2 does not quickly reach MW 42, thereby negating the need for a third tracer dye. If the third dye introduction is needed it will be made through DIP TI-U1-1. Thirty pounds of rhodamine WT dye mixture will be used for this dye introduction. If this dye introduction is needed it will be introduced about 8 to 10 days after the initial two dye introductions.

Monitoring for Tracer Dyes

The primary means of sampling for tracer dyes will be with activated carbon samplers. Grab samples of water will be collected from locations where it is not feasible to use activated carbon samplers. Activated carbon samplers are preferred as they are continuous and accumulating samplers.

Monitoring points will be established in relevant stormwater sewers and in monitoring wells. Many of the monitoring wells sample water at different elevations. Where this is the case we will sample all of the levels in the relevant monitoring wells. Control stations will be established upgradient of the study area to detect fluorescent compounds from other sources that might unexpectedly enter the study area.

Sample Analyses

All samples will be shipped to the OUL for laboratory analysis. The analysis procedures and criteria for positive dye detections are included in the OUL's "Procedures and Criteria" document attached to this work plan. The analysis will be done on a Shimadzu Model 5301 Spectrofluorophotometer operated under a synchronous scan protocol. There are no EPA or ASTM formalized methods for tracer dye analysis, but the methods that will be employed by the OUL in this investigation are the same or similar to those employed in most professionally directed groundwater tracing studies. The methods the OUL will use for this project have previously been used in contract studies for numerous state and federal agencies including the U.S. Department of Energy at the Idaho National Engineering and Environmental Laboratory; U.S. Army; U.S. Navy; and U.S. Environmental Protection Agency.

Anticipated Results

The product of this investigation will be improved understanding of groundwater flow directions and travel rates from the dye introduction locations. In addition, this study will investigate the possibility of hydrologic connections between these subsurface waters and the stormwater sewer system.

Reporting

The OUL will prepare the following reports:

- Weekly preliminary laboratory results spread sheets.
- Rapid email notification of apparent new dye detection sites.
- Draft and Final reports on the investigation and findings.

Final Disposal of Sampling Materials

Samples will be returned to the site through GZA for proper disposal when they are no longer required for analytical purposes.

DETAILED WORK PLAN

Sampling, Handing, and Analysis

The OUL will provide two styles of activated carbon samplers. Both styles of activated carbon samplers are packets of fiberglass screening partially filled with approximately 4.25 grams of activated coconut charcoal. The charcoal used by the Ozark Underground Laboratory is Barnebey and Sutcliffe coconut shell carbon, 6 to 12 mesh, catalog type AC. The OUL's normal sampler style measures about 7cm by 12cm by 0.5cm and is intended for use anywhere except where well diameter prohibits the use of the normal style samplers. The OUL also supplies samplers that measure about 2cm in diameter by 12cm. These narrower samplers are intended only for small diameter wells.

The OUL will also provide sterile Whirl-Pak® bags for sampler collection and 50ml disposable vials for water sampling.

The OUL routinely tests all materials it provides for use in tracer studies for the presence of tracer dyes or other compounds with similar fluorescence characteristics. One percent of materials purchased ready to use, such as disposable vials and Whirl-Pak® bags, are eluted and the elutant is subjected to fluorescence analysis. Test samples of the materials used to manufacture activated carbon samplers are selected at random, eluted and the elutant is subjected to fluorescence analysis.

All samples will be handled and analyzed in accordance with OUL's established Procedures and Criteria dated March 21, 2005, a copy of which is attached. In addition, OUL personnel will provide training in sampling methods at the approximate same time as the first dye introductions.

Activated carbon samplers have the ability to accumulate small concentrations of dye over time and can sample continuously from placement to recovery. However, activated carbon samplers do not provide data on the actual dye concentration in the water at any single point in time. Water samples have the advantage of providing data on the dye concentration at a single point in time, can provide confirmation of results from activated carbon samplers, and can provide a backup in case there is a problem with the activated carbon sampler. Since water samples can detect only the presence of dye at a specific time, sampling at water-only sites is more frequent than at sites using activated carbon. More frequent sampling minimizes the possibility that a dye pulse might pass the sampling site between sampling events and provides more accurate data on travel time.

Wherever possible, primary sampling reliance will be placed on activated carbon samplers manufactured by the OUL. The samplers will be anchored and left in place at a sampling station for periods of time as defined in the schedule. Reliance will be placed on water samples at stations where activated carbon samplers cannot be used.

From the time of collection to the time of analysis samples will be maintained on ice, packed with Blue-Ice®, or in refrigerators.

Upon collection, activated carbon samples will be placed in a Whirl-Pak® bag and labeled with the sampling station number and name, the date and time the sampler was placed, and the date and time the sampler was collected. Where duplicate activated carbon samplers have been placed at one sampling location, both samplers will be placed in the same Whirl-Pak® bag. At surface water or stormwater sampling stations, it is sometimes noted that one sampler was better placed than the other. For instance, rising and falling water may have left one sampler out of the water. If sample collection personnel believe that one sampler was better placed than the other, they will fold the better sample in half before placing it in the Whirl-Pak® bag and the folded sampler will be selected at the OUL for analysis. Folded samplers will be noted on the COC form.

In open borehole wells, samplers will be placed approximately in the middle of the saturated zone.

At storm sewer and surface water sampling locations, duplicate activated carbon samplers will be placed and collected during each sampling event.

Water samples will be collected at every sampling location. Each water vial will be labeled with the sampling station number and name and the date and time the sample was collected. About 20 ml of water will be collected in each vial; vial capacity is about 50 ml.

At sampling stations where both activated carbon samplers and water samples have been collected, each activated carbon sampler and its corresponding water vial will be placed in a single Ziploc® or equivalent plastic bag. The OUL does not provide these Ziploc® bags.

The collected samples will then be placed in a cooler containing Blue Ice® (or an approved equivalent). If samples cannot be immediately shipped to the OUL, they will be refrigerated until shipment. As soon as possible, the samples will be packed in insulated containers, packed with Blue Ice®, and shipped via Federal Express or UPS overnight service to the OUL. Packed with each shipment, in a plastic bag taped to the inside of the cooler lid, will be one or more completed COC forms that list the entire inventory of samples in that shipping container.

The OUL cannot receive shipments on Saturdays, Sundays, or holidays. Therefore, all shipments will be made on Monday through Thursday with consideration given to any holiday that would not allow delivery to the OUL on the day after shipment. If samples from multiple days are to be shipped together in one container, samples for each day should be grouped in one or more large plastic bags to facilitate check-in, handling and storage of the samples at the OUL.

It is preferred that samples be shipped the day they are collected. If samples cannot be shipped the same day as collected, the samples will be shipped as soon as possible to keep holding times to a minimum. It is permissible to ship part of a day's collection of samples if necessary to meet courier deadlines.

The OUL will analyze at least one activated carbon sampler from each sampling station where these samplers are used. The OUL will analyze the water sample from each sampling station where activated carbon samples are not being collected.

Prior to the start of sampling, GZA will select approximately five percent of the sampling stations for duplicate or replicate analysis. If activated carbon samplers are collected at a station designated for duplicate analysis, the second activated carbon sampler from that station will be analyzed. At stations designated for replicate analysis (where activated carbon samplers are *not* collected), a second water sample will be analyzed. In the case of water samples, there will not be two vials of water. A second aliquot will be taken from the water vial for analysis.

Whenever dye is detected in any activated carbon sampler the corresponding water sample collected on the same date will be analyzed. In addition, the three most recent prior water samples from that station will be analyzed.

The target turnaround time for analysis of carbon samplers and for water samples, where water samples are the primary sampling method, will be five business days. Target turnaround time for water samples to be analyzed due to dye recovery in an activated carbon sampler will be five business days after analysis of the activated carbon sampler. Preliminary analytical results will be provided each week in the form of an Excel spreadsheet delivered by email. Notification of a new dye recovery site will be made by email as soon as possible; typically within two business days of sample analysis that indicates a new detection site has been identified.

The sampling locations and their characteristics are identified in Table 1.

Sampling locations are classified in this workplan as being groundwater-monitoring wells, storm sewers (stormwater sewers), or surface water. When possible, activated carbon samplers will be used as the primary sample type.

The primary sample type, either Activated Carbon or Water-only, determines the sampling schedule referenced in Table 3, Study Schedule.

Four digit OUL station numbers, with leading and trailing zeroes, have been selected for two reasons. The use of a leading zero allows data to be sorted in the correct order under all word processing and spreadsheet applications. The trailing zero allows additional stations to be added to the list without renumbering the entire list.

Table 1: Sampling Stations

OUL Station #	Station Name	Type of Sampling Station	Primary Sample Type
0010	CB5 (control point)	storm sewer	Activated Carbon – With Duplicates
0020	CB24 (control point)	storm sewer	Activated Carbon – With Duplicates
0030	Hudson River downstream	surface water	Activated Carbon – With Duplicates
0040	Hudson River upstream	surface water	Activated Carbon – With Duplicates
0050	MH1	storm sewer	Activated Carbon – With Duplicates
0060	MH2	storm sewer	Activated Carbon – With Duplicates
0070	MH3	storm sewer	Activated Carbon – With Duplicates
0080	MH4	storm sewer	Activated Carbon – With Duplicates
0090	MH4A	storm sewer	Activated Carbon – With Duplicates
0100	MH5	storm sewer	Activated Carbon – With Duplicates
0110	MH5A	storm sewer	Activated Carbon - With Duplicates
0120	MH6	storm sewer	Activated Carbon - With Duplicates
0130	MH7	storm sewer	Activated Carbon - With Duplicates
0140	MH8	storm sewer	Activated Carbon - With Duplicates
0150	MH9 (control point)	storm sewer	Activated Carbon - With Duplicates
0160	MH14	storm sewer	Activated Carbon - With Duplicates
0170	MH15	storm sewer	Activated Carbon - With Duplicates
0180	MH19	storm sewer	Activated Carbon - With Duplicates
0190	MH23	storm sewer	Activated Carbon - With Duplicates
0200	MW30-A at TBD feet	monitoring well	Water-only
0210	MW30-B at TBD feet	monitoring well	Water-only

Continued

Table 1: Sampling Stations (Cont.)

OUL Station #	Station Name	Type of Sampling Station	Primary Sample Type
0220	MW31-A at TBD feet	monitoring well	Water-only
0230	MW31-B at TBD feet	monitoring well	Water-only
0240	MW31-C at TBD feet	monitoring well	Water-only
0250	MW31-D at TBD feet	monitoring well	Water-only
0260	MW32-A at TBD feet	monitoring well	Water-only
0270	MW32-B at TBD feet	monitoring well	Water-only
0280	MW32-C at TBD feet	monitoring well	Water-only
0290	MW32-D at TBD feet	monitoring well	Water-only
0300	MW32-E at TBD feet	monitoring well	Water-only
0310	MW33	monitoring well	Activated Carbon
0320	MW34	monitoring well	Activated Carbon
0330	MW35	monitoring well	Activated Carbon
0340	MW36-A at 26 feet	monitoring well	Activated Carbon
0350	MW36-B at 41 feet	monitoring well	Activated Carbon
0360	MW36-C at 53 feet	monitoring well	Activated Carbon
0370	MW37-A at 22 feet	monitoring well	Activated Carbon
0380	MW37-B at 32 feet	monitoring well	Activated Carbon
0390	MW37-C at 40 feet	monitoring well	Activated Carbon
0400	MW37-D at 57 feet	monitoring well	Activated Carbon
0410	MW38	monitoring well	Activated Carbon
0420	MW39-A at TBD feet	monitoring well	Water-only
0430	MW39-B at TBD feet	monitoring well	Water-only
0440	MW39-C at TBD feet	monitoring well	Water-only
0450	MW39-D at TBD feet	monitoring well	Water-only
0460	MW42-A at 51 feet	monitoring well	Activated Carbon
0470	MW42-B at 79 feet	monitoring well	Activated Carbon
0480	MW47-A at 56 feet	monitoring well	Activated Carbon
0490	MW47-B at 80 feet	monitoring well	Activated Carbon
0510	MW48-A at 23 feet	monitoring well	Activated Carbon
0520	MW48-B at 38 feet	monitoring well	Activated Carbon
0530	MW49-A at 25 feet	monitoring well	Activated Carbon
0540	MW49-B at 42 feet	monitoring well	Activated Carbon
0550	MW49-C at 65 feet	monitoring well	Activated Carbon
0560	MW50-A at 42 feet	monitoring well	Activated Carbon
0570	MW50-B at 67 feet	monitoring well	Activated Carbon
0580	MW52-A at 12 feet	monitoring well	Activated Carbon
0590	MW52-B at TBD feet	monitoring well	Activated Carbon
0600	MW52-C at TBD feet	monitoring well	Activated Carbon

Continued

Table 1: Sampling Stations (Cont.)

OUL Station #	Station Name	Type of Sampling Station	Primary Sample Type
0610	MW52-D at TBD feet	monitoring well	Activated Carbon
0620	MW52-E at TBDfeet	monitoring well	Activated Carbon
0630	MW53-A at TBD feet	monitoring well	Activated Carbon
0640	MW53-B at TBD feet	monitoring well	Activated Carbon
0650	MW53-C at TBD feet	monitoring well	Activated Carbon
0660	MW54-A at TBD feet	monitoring well	Activated Carbon
0670	MW54-B at TBD feet	monitoring well	Activated Carbon
0680	MW54-C at TBD feet	monitoring well	Activated Carbon
0690	MW55-A at TBD feet	monitoring well	Activated Carbon
0700	MW55-B at TBD feet	monitoring well	Activated Carbon
0710	MW55-C at TBD feet	monitoring well	Activated Carbon
0720	MW56-A at TBD feet	monitoring well	Water-only
0730	MW56-B at TBD feet	monitoring well	Water-only
0740	MW56-C at TBD feet	monitoring well	Water-only
0750	MW56-D at TBD feet	monitoring well	Water-only
0760	MW57-A at TBD feet	monitoring well	Activated Carbon
0770	MW57-B at TBD feet	monitoring well	Activated Carbon
0780	MW57-C at TBD feet	monitoring well	Activated Carbon
0790	MW58-A at TBD feet	monitoring well	Water-only
0800	MW58-B at TBD feet	monitoring well	Water-only
0810	MW58-C at TBD feet	monitoring well	Water-only
0820	MW59-A at TBD feet	monitoring well	Activated Carbon
0830	MW59-B at TBD feet	monitoring well	Activated Carbon
0840	MW59-C at TBD feet	monitoring well	Activated Carbon
0850	MW60-A at TBD feet	monitoring well	Water-only
0860	MW60-B at TBD feet	monitoring well	Water-only
0870	MW60-C at TBD feet	monitoring well	Water-only
0880	MW61-A at TBD feet	monitoring well	Water-only
0890	MW61-B at TBD feet	monitoring well	Water-only
0900	MW61-C at TBD feet	monitoring well	Water-only
0910	MW61-D at TBD feet	monitoring well	Water-only
0920	MW61-E at TBD feet	monitoring well	Water-only
0930	MW61-F at TBD feet	monitoring well	Water-only
0940	MW62	monitoring well	Activated Carbon
0950	MW63-A at TBD feet	monitoring well	Water-only
0960	MW63-B at TBD feet	monitoring well	Water-only
0970	MW63-C at TBD feet	monitoring well	Water-only
0980	MW63-D at TBD feet	monitoring well	Water-only

Continued

Table 1: Sampling Stations (Cont.)

OUL Station #	Station Name	Type of Sampling Station	Primary Sample Type
0990	MW63-E at TBD feet	monitoring well	Water-only
1000	MW63-F at TBD feet	monitoring well	Water-only
1010	MW65-A at TBD feet (upgradient control)	monitoring well	Water-only
1020	MW65-B at TBD feet (upgradient control)	monitoring well	Water-only
1030	MW65-C at TBD feet (upgradient control)	monitoring well	Water-only
1040	MW65-D at TBD feet (upgradient control)	monitoring well	Water-only
1050	MW107 (open hole control)	monitoring well	Activated Carbon
1060	MW108	monitoring well	Activated Carbon
1070	MW109	monitoring well	Activated Carbon
1080	MW111	monitoring well	Activated Carbon
1090	U3-1	monitoring well	Activated Carbon
1100	U3-2	monitoring well	Activated Carbon
1110	U3-3	monitoring well	Activated Carbon
1120	U3-4D	monitoring well	Activated Carbon
1130	U3-4S	monitoring well	Activated Carbon

TBD = To Be Determined.

Dye Introduction Methodology

The introduction of tracer dyes always presents an opportunity to unintentionally spread low concentrations of dyes across the study area. As detection limits are in the parts per trillion range we will use appropriate caution when handling these dyes.

Powdered dyes (eosine and fluorescein), will be shipped to the site pre-measured in durable Nalgene® containers (carboys) to facilitate minimum handling of the dyes. OUL personnel will be on site to mix the dyes and participate in the first two dye introductions.

Rhodamine WT is a liquid dye and will be shipped to the site ready for introduction.

Although final determination of tracer dyes to be used will not be finalized until the second round of background samples have been analyzed, the workplan anticipates that eosine, fluorescein, and rhodamine WT dyes will be the three dyes used in this investigation. Possible alternatives include sulforhodamine B and pyranine dyes.

Prior to dye introduction, tap water will be introduced into each DIP to moisten underground surfaces. In consultation with GZA personnel, it was determined that as little water as practical should be used to minimize impact to existing groundwater conditions. Based on OUL's experience, about 30 gallons of water will be sufficient to adequately moisten the underground surfaces prior to dye introduction.

Following each introduction of dye, and consistent with the need to minimize impact to existing groundwater conditions, about 170 gallons of water will be used to flush dye from underground surfaces and into the groundwater system.

Both before and after dye introduction, the rate at which water is introduced will also be controlled to minimize impact to existing groundwater conditions.

The first dye introduction will be ten pounds of fluorescein dye mixture (CAS Number 518-47-8), dissolved in approximately ten gallons of distilled water. The mixture consists of 75% dye equivalent and 25% diluent. The dye solution will be introduced beneath the failed fuel pool at Reactor #1 through DIP TI-U1-2.

The second dye introduction will be made on the same day as the first dye introduction. Fifteen pounds of eosine dye mixture (CAS Number 17372-87-1), dissolved in approximately fifteen gallons of distilled water will be introduced through DIP TI-U2-1. The mixture consists of 75% dye equivalent and 25% diluent.

If fluorescein dye from the initial dye introduction is not detected at well MW42 within five to seven days of dye introduction, thirty pounds of rhodamine WT dye will be introduced into DIP TI-U1-1. Rhodamine WT dye (CAS Number 37299-86-8) is supplied as a liquid and need not be mixed with water prior to introduction. The liquid is 20% dye equivalent and 80% diluent. This dye introduction would occur about eight to ten days after the fluorescein dye introduction.

As discussed above, immediately after dye is introduced into each introduction site, water will be introduced into the well to flush (or "chase") the dye out of the well and into the groundwater system.

Injection rates will be slow to avoid local groundwater mounding that could cause unintentional spreading of the dyes.

The dyes, quantities, introduction sites, and chase water details are listed in Table 2.

Table 2: Dye Introduction Details

Introduction #	Location	Dye and Quantity	Pre-Introduction Wetting Water	Post Introduction Flush Water
06-01	Well TI-U1-2	10 pounds of fluorescein	30 gal, at about 1 gpm	170 gal. at about 1 gpm
06-02	Well TI-U2-1	15 pounds of eosine	30 gal, at about 1 gpm	170 gal. at about 1 gpm
06-03	Well TI-U1-1	30 pounds of rhodamine WT	30 gal, at about 5 gpm	170 gal. at less than 5 gpm

Sample Holding

Unanalyzed activated carbon samplers will be kept refrigerated at least until three subsequent rounds of samplers have been analyzed. Thereafter, they may be stored in the dark and at room temperature.

Activated carbon sampler elutants will be kept refrigerated at least until three subsequent rounds of samplers have been analyzed. Thereafter, they may be stored in the dark and at room temperature.

Unanalyzed water samples from activated carbon sampler locations will be kept refrigerated at least until three subsequent rounds of samplers have been analyzed. Thereafter, they may be stored in the dark and at room temperature.

Water samples from locations where water samples are the primary sampling method will be kept refrigerated at least until three subsequent rounds of water samples have been analyzed. Thereafter, they may be stored in the dark and at room temperature.

Study Duration

The study is designed to last approximately thirteen weeks after the first dye introduction. However, sampling and analysis will not end until:

- There have been no new detection sites for three consecutive weeks. Any new detection in a location very close to a previous detection of the same dye will be reviewed jointly by GZA and OUL and may be discounted as a cause for continuing the study.
- Dye concentrations have declined for three consecutive weeks at most, and preferably all, detections sites.
- GZA and the OUL conclude that no other conditions exist that indicate the sampling period should be extended.

Sample Analysis

All analysis will be performed on a Shimadzu RF5301-PC using a synchronous scan protocol developed by OUL. The protocols for the analysis of water samples and activated carbon sampler elutants are described in OUL's Procedures and Criteria for the Analysis of Fluorescein, Eosine, Rhodamine WT, Sulforhodamine B, and Pyranine Dyes in Water and Charcoal Samplers dated March 21, 2005, a copy of which is included as Attachment A.

Disposal of Sampling Materials

Once the sampling materials are no longer needed for sample analysis, the following materials will be shipped from OUL to Indian Point Energy Center(IPEC) for disposal:

- Any water samples still in their original sampling vials will be shipped in those same vials.
- The portion of water samples used in the analysis process will be accumulated in plastic containers during the study and shipped in these same containers.
- Eluted activated carbon will be accumulated in plastic containers during the study and shipped in these same containers.
- The portion of the activated carbon sampler elutants not used in the analysis process will be returned in the disposable vials in which they are initially stored.
- The portion of the activated carbon sampler elutants used in the analysis process will be accumulated in plastic containers during the study and shipped in these same containers.

OUL will dispose of the empty sampler packets, plastic bags, cuvettes, pipettes, gloves, and similar lab materials.

Reports

- Preliminary laboratory results will be provided every week in the form of an emailed spreadsheet.
- Email notification will be provided for each apparent new detection site. Typically, this notification will occur within 2 days of sample analysis and prior to OUL's full QA/QC review of analysis results. The purpose is to identify stations of special interest in the event GZA may wish to sample the station more intensively.
- A Draft Final report detailing the study purpose, methods, analytical results, and hydrogeological findings will be prepared.
- A Final report will be prepared from the Draft Final report based on review comments provided to the OUL by GZA.

Schedule

A detailed schedule is shown in Table 1. Day 0 is the date on which background sampling will begin. Negative numbers represent activities necessary prior to sampling. If necessary, minor adjustments may be made to accommodate holidays or for reasonable logistical reasons. A column is left open for dates; the dates will be filled in once the sampling begins.

Table 1. Study Schedule

Day #	Date	Activity
>-35		GZA approves workplan.
-35		OUL will: ♦ Order vials. ♦ Order a spare Shimadzu Xenon lamp. ♦ Begin preparation of Chain of Custody (COC) sheets and sample labels. ♦ Begin assembly of 2000 regular style activated carbon samplers. ♦ Begin assembly of 1400 small diameter style activated carbon samplers.
-21		OUL will: Conduct QA tests on material to be shipped.
-14		OUL will: ♦ Ship 10 boxes (4950 vials) of disposable vials to GZA. ♦ Ship 7 boxes of Whirl-Pac® bags (3465 bags) to GZA. ♦ Ship 2000 regular style activated carbon samplers to GZA. ♦ Ship 1400 small diameter style activated carbon samplers to GZA. ♦ Ship COC forms and prepared labels for samples to GZA.
-1 to 7		OUL will: Install a new lamp in the spectrofluorophotometer and calibrate the instrument using the Raman peak of distilled water.
		Continued

Table 1: Study Schedule (cont.)

Day #	Date	Activity
0		**Begin sampling;** GZA will: ♦ Place activated carbon samplers at all stations where activated carbon samplers will be used. ♦ Place one activated carbon sampler at each well horizon or, where wells are open hole wells, place sampler in the middle of the saturated zone. ♦ Two wells will be selected for duplicate activated carbon samplers; place two samplers in each of these wells and collect and replace both samplers each time these wells are sampled. ♦ Place two activated carbon samplers in each manhole or surface water sampling location and collect and replace both samplers each time these locations are sampled.
7		GZA will: ♦ Collect and replace activated carbon samplers at all stations where activated carbon samplers are used. ♦ Collect water samples at *all* sampling stations. ♦ Complete COC form and ship samples to OUL.
9-15		OUL will: Analyze first week of background samples.
14		GZA will: ♦ Collect and replace activated carbon samplers at all stations where activated carbon samplers are used. ♦ Collect water samples at all sampling stations. ♦ Complete COC form and ship samples to OUL.
16-18		OUL will: ♦ Analyze second week of background samples. ♦ In consultation with GZA, make final determination on dye choices and quantities. ♦ Ship dyes to GZA
21		End of background sampling: GZA will: ♦ Collect and replace activated carbon samplers at all stations where activated carbon samplers will be used. ♦ Collect water samples at all sampling stations. ♦ Complete COC form and ship samples to OUL. An OUL staff member will be on site to review field sampling and recommend any modifications warranted.
22		**Introduce tracer dyes:** An OUL staff member will be present to assist GZA staff in the two initial dye introductions.

Continued

Table 1: Study Schedule (cont.)

Day #	Date	Activity
Target dates for analysis are included above in this table since the choice of dyes is dependent on analysis completion. From this point on in this table, the target turnaround time for sample analysis will be five business days from receipt of samples at OUL. For brevity, these dates will not be included in the remainder of this table.		
23-27 Wk 1		GZA will collect water samples as often as possible, but at least morning and evening, at MW42.
23-29		GZA will: ♦ Seven days per week (daily), collect and replace activated carbon samplers at all stations where activated carbon samplers will be used ♦ Daily, collect water samples at all sampling stations. ♦ Monday Tuesday, Wednesday, and Thursday (MTWT), complete COC form and ship samples to OUL, never ship on Friday.
30		OUL will: Evaluate dye detections (if any) at MW42 samples from Days 23-27. Introduce dye if there were no detections at MW42.
30-36 Wk 2		GZA will: ♦ Daily, collect water samples at water-only sampling stations. ♦ Monday, Wednesday, and Friday (MWF), collect and replace activated carbon samplers at all stations where activated carbon samplers are used. ♦ MWF, collect water samples at all stations where activated carbon samplers are used. ♦ MTWT, complete COC form and ship samples to OUL.
37-43 Wk 3		GZA will: ♦ Monday, Tuesday, Wednesday, Thursday, and Friday (MTWTF), collect water samples at water-only sampling stations. ♦ MWF, collect and replace activated carbon samplers at all stations where activated carbon samplers are used. ♦ MWF, collect water samples at all stations where activated carbon samplers are used. ♦ MTWT, complete COC form and ship samples to OUL.
		Continued

Table 1: Study Schedule (cont.)

Day #	Date	Activity
44-50 Wk 4		GZA will: ♦ MTWTF, collect water samples at water-only sampling stations. ♦ MWF, collect and replace activated carbon samplers at all stations where activated carbon samplers are used. ♦ MWF, collect water samples at all stations where activated carbon samplers are used. ♦ MTWT, complete COC form and ship samples to OUL.
51-57 Wk 5		GZA will: ♦ MTWTF, collect water samples at water-only sampling stations. ♦ MWF, collect and replace activated carbon samplers at all stations where activated carbon samplers are used. ♦ MWF, collect water samples at all stations where activated carbon samplers are used. ♦ MTWT, complete COC form and ship samples to OUL.
58-64 Wk 6		GZA will: ♦ MTWTF, collect water samples at water-only sampling stations. ♦ Monday and Friday (MF), collect and replace activated carbon samplers at all stations where activated carbon samplers are used. ♦ MF, collect water samples at all stations where activated carbon samplers are used. ♦ MTWT, complete COC form and ship samples to OUL.
65-71 Wk 7		GZA will: ♦ MWF, collect water samples at water-only sampling stations. ♦ MF, collect and replace activated carbon samplers at all stations where activated carbon samplers are used. ♦ MF, collect water samples at all stations where activated carbon samplers are used. ♦ Monday, and Wednesday (MW), complete COC form and ship samples to OUL.
		Continued

Table 1: Study Schedule (cont.)

Day #	Date	Activity
72-78 Wk 8		GZA will: ♦ MWF, collect water samples at water-only sampling stations. ♦ MF, collect and replace activated carbon samplers at all stations where activated carbon samplers are used. ♦ MF, collect water samples at all stations where activated carbon samplers are used. ♦ MW, complete COC form and ship samples to OUL.
79-85 Wk 9		GZA will: ♦ MWF, collect water samples at water-only sampling stations. ♦ MF, collect and replace activated carbon samplers at all stations where activated carbon samplers are used. ♦ MF, collect water samples at all stations where activated carbon samplers are used. ♦ MW, complete COC form and ship samples to OUL.
86-92 Wk 10		GZA will: ♦ MWF, collect water samples at water-only sampling stations. ♦ Monday, collect and replace activated carbon samplers at all stations where activated carbon samplers are used. ♦ Monday, collect water samples at all stations where activated carbon samplers are used. ♦ MW, complete COC form and ship samples to OUL.
93-99 Wk 11		Same as Days 86-93
100-106 Wk 12		Same as Days 86-93
107-113 Wk 13		GZA will: ♦ MWF, collect water samples at water-only sampling stations. ♦ Monday, collect activated carbon samplers at all stations where activated carbon samplers are used. DO not place more activated carbon samplers unless the study has been extended. ♦ Monday, collect water samples at all stations where activated carbon samplers are used. ♦ MW, complete COC form and ship samples to OUL.
163		OUL will: Prepare the draft report for review and comment.

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Submitted:

Thomas Aley, PHG & PG
President, Ozark Underground Laboratory Inc.

Ozark
UNDERGROUND
LABORATORY
1572 Aley Lane Protem, MO 65733 (417) 785-4289 fax (417) 785-4290 oul@tri-lakes.net

Attachment A

PROCEDURES AND CRITERIA
ANALYSIS OF FLUORESCEIN, EOSINE, RHODAMINE WT, SULFORHODAMINE B, AND PYRANINE DYES IN WATER AND CHARCOAL SAMPLERS

March 21, 2005

Thomas Aley, PHG 179
President
Ozark Underground Laboratory, Inc.

PROCEDURES

Introduction

This document describes standard procedures and criteria currently in use at the Ozark Underground Laboratory as of the date shown on the title page. Some samples may be subjected to different procedures and criteria because of unique conditions; such non-standard procedures and criteria are identified in reports for those samples. Standard procedures and criteria change as knowledge and experience increases and as equipment is improved or up-graded. The Ozark Underground Laboratory maintains a summary of changes in standard procedures and criteria.

Dye Nomenclature

Fluorescein is C.I. Acid yellow 73, Color Index Number 45350. Rhodamine WT is Acid Red 388; there is no assigned Color Index Number for this dye. Eosine (sometimes called eosin) is Acid Red 87, Color Index Number 45380. Sulforhodamine B is C.I. Acid Red 52, Color Index Number 45100. Pyranine is Solvent Green 7 (also called D&C Green 8), Color Index Number 59040.

Description of the Samplers

The charcoal samplers are packets of fiberglass screening partially filled with approximately 4.25 grams of activated coconut charcoal. The charcoal used by the Ozark Underground Laboratory is Barnebey and Sutcliffe coconut shell carbon, 6 to 12 mesh, catalog type AC.

The most commonly used samplers are about 4 inches long by two inches wide. A cigar-shaped sampler is made for use in very small diameter wells (such as 1 inch diameter wells); this is a special order item and should be specifically requested when it is needed. All of the samplers are closed by heat sealing.

Placement of Samplers

Samplers (also called charcoal packets) are placed so as to be exposed to as much water as possible. In springs and streams they are typically attached to a rock or other anchor in a riffle area. Attachment of the packets often uses plastic tie wires. In swifter water galvanized wire (such as electric fence wire) is often used. Other types of anchoring wire can be used. Electrical wire with plastic insulation is also good. Packets are attached so that they extend outward from the anchor rather than being flat against it. Two or more separately anchored packets are typically used for sampling springs and streams. The use of fewer packets is discouraged except when the spring or stream is so small that there is not appropriate space for placing multiple packets.

When pumping wells are being sampled, the samplers are placed in sample holders made of PVC pipe fittings. Brass hose fittings are installed at the end of the sample holders so that the sample holders can be installed on outside hose bibs and water which has run through the samplers can be directed to waste through a connected garden hose. The samplers can be unscrewed in the middle so that charcoal packets can be

changed. The middle portions of the samplers consists of 1.5 inch diameter pipe and pipe fittings.

Charcoal packets can also be lowered into monitoring wells for sampling purposes. In general, if the well is screened, samplers should be placed approximately in the middle of the screened interval. Some sort of weight should be added near the charcoal packet to insure that it will not float. The weight should be of such a nature that it will not affect water quality. One common approach is to anchor the packets with a plastic cable tie to the top of a dedicated weighted disposable bailer. We typically run nylon cord from the top of the well to the charcoal packet and its weight. Nylon fishing line should not be used since it can be readily cut by a sharp projection in the well.

In some cases, especially with narrow wells and appreciable well depths, the weighted disposable bailers sink very slowly or may even fail to sink because of friction and floating of the anchoring cord. In such cases a stainless steel weight may be added to the top of the disposable bailer. We have had good success with two to three ounce segments of stainless steel pipe which have an outside diameter of 1.315 inches and an inside diameter of 1.049 inches; such pipe weighs about 1.7 pounds per linear foot. The weight of the stainless steel is approximately 497 pounds per cubic foot. The pipe segments can be attached over the anchoring cord at the top of the bailer. All weights should be cleaned prior to use; the cleaning approach should comply with decontamination procedures in use at the project site.

Placement of samplers requires adjustment to field conditions. The above placement comments are intended as guidance, not firm requirements.

Rinsing of Charcoal Packets Prior to Sampling

Charcoal packets routinely contain some fine powder that washes off rapidly when they are placed in water. Since such material could remain in monitoring wells, charcoal packets to be placed in such wells are triple rinsed with distilled, demineralized, or reagent water known to be free of tracer dyes. This rinsing is typically done by soaking. With this approach, approximately 25 packets are placed in one gallon of water and soaked for at least 10 minutes. The packets are then removed from the water and excess water is shaken off the packets. The packets are then placed in a second gallon of water and again soaked for at least 10 minutes. After this soaking they are removed from the water and excess water is shaken off the packets. The packets are then placed in a third gallon of water and the procedure is again repeated. Rinsed packets are placed in plastic bags and are placed at sampling stations within three days. Packets can also be rinsed in jets of water for about one minute; this requires more water and is typically difficult to do in the field with water known to be free of tracer dyes.

Collection and Replacement of Samplers

Samplers are routinely collected and replaced from each of the sampling stations. The frequency of sampler collection and replacement is determined by the nature of the study. Collections at one week intervals are common, but shorter or longer collection frequencies are acceptable and sometimes more appropriate. Shorter sampling frequencies are often used in the early phases of a study to better characterize time of

travel. As an illustration, we often collect and change charcoal packets 1, 2, 4, and 7 days after dye injection. Subsequent sampling is then weekly.

Where convenient, the collected samplers should be briefly rinsed in the water being sampled. This is typically not necessary with well samples. The packets are shaken to remove excess water. Next, the packet (or packets) are placed in a plastic bag (Whirl-Pak bags are ideal). The bag is labeled on the outside with a permanent type felt marker pen. Use only pens that have black ink; colored inks may contain fluorescent dyes. The notations include station name or number and the date and time of collection. Labels are not inserted inside the sample bags.

For most projects the Ozark Underground Laboratory supplies the Whirl-Pak bags. Prior to use, 1% of the new bags are randomly selected. Each bag is soaked in the standard eluting solution and then analyzed for the presence of any of the tracer dyes being used.

Collected samplers are kept in the dark to minimize algal growth on the charcoal prior to analysis work. We prefer (and in some studies require) that samples be placed on "blue ice" or ice upon collection and that they be shipped refrigerated with "blue ice" by overnight express. Do not ship samplers packed in ice since this can create a potential for cross contamination when the ice melts. Our experience indicates that it is not essential for samplers to be maintained under refrigeration, yet maintaining them under refrigeration clearly minimizes some potential problems. A product known as "green ice" should not be used for maintaining the samples in a refrigerated condition since this product contains a dye which could contaminate samples if the "green ice" container were to break or leak.

New charcoal samplers are routinely placed when used charcoal packets are collected. The last set of samplers placed at a stream or spring is commonly not collected.

Water samples are often collected. They should be collected in either glass or plastic; the Ozark Underground Laboratory routinely uses 50 ml research grade polypropylene copolymer Perfector Scientific vials (Catalog Number 2650) for such water samples. The vials should be placed in the dark and refrigerated immediately after collection. They should be refrigerated until shipment. For most projects the Ozark Underground Laboratory supplies the vials. Prior to use, 1% of the new vials are randomly selected. Each vial is soaked in the standard eluting solution and then analyzed for the presence of any of the tracer dyes being used.

When water or charcoal samplers are collected for shipment to the Ozark Underground Laboratory they should be shipped promptly. We receive good overnight and second day air service from both UPS and Fed Ex; Airborne Service is excessively slow, and the Postal Service does not provide next day service to us.

Each shipment of charcoal samplers or water samples must be accompanied by a sample tracking sheet. These sheets (which bear the title "Samples for Fluorescence Analysis") are provided by the Ozark Underground Laboratory and summarize placement

and collection data. These sheets can be augmented by a client's chain of custody forms or any other relevant documentation. Figure 1 is one of our blank sample forms.

Receipt of Samplers

Samplers shipped to the Ozark Underground Laboratory are refrigerated upon receipt. Prior to cleaning and analysis, samplers are assigned a laboratory identification number. All samples are logged in upon receipt.

It sometimes occurs that there are discrepancies between the chain-of-custody sheets and the actual samples received. When this occurs, a "Discrepancy Sheet" form is completed and sent to the shipper of the sample for resolution. A copy of this form is enclosed as Figure 2. The purpose of the form is to help resolve discrepancies, even when they may be minor.

Cleaning of Samplers

Samplers are cleaned by spraying them with jets of clean water. At the Laboratory we use unchlorinated water for the cleansing to minimize dye deterioration. Effective cleansing cannot generally be accomplished simply by washing in a conventional laboratory sink even if the sink is equipped with a spray unit.

The duration of packet washing depends upon the condition of the sampler. Very clean samplers may require less than a minute of washing; dirtier samplers may require several minutes of washing.

After washing, the packets are shaken to remove excess water. Next, the packets are cut open and the charcoal is emptied into a new disposable plastic beaker. The beaker has been pre-labeled with the laboratory identification number. The charcoal is now ready for elution. The emptied fiberglass screen packet is discarded. At stations where two or more charcoal packets are collected, one is selected for analysis and the other is frozen and retained until the end of the study. In some studies the analysis protocol stipulates that a fixed percentage (often 5%) of the samples should be duplicates; in these cases the second charcoal packet is separately analyzed. Note that these are duplicate samples, not replicate samples since each packet is, of necessity, placed in a somewhat different location and is therefore exposed to somewhat different conditions.

Cleaning of Glassware

Most of our work uses disposable plastic containers. A small amount of glassware is occasionally used for preparation of standards. It is dedicated to this use. In the event that any glassware does come in contact with tracer dyes it will be carefully cleaned before re-use. To do this cleaning, containers are rinsed several times in clean water. Glassware that may be contaminated with dyes is washed with detergent, and then again rinsed. Next, the glassware is soaked for one hour or more in a bleach and water solution. Upon removal from this soaking, the glassware is rinsed again and allowed to air dry.

Figure 1. Sample Collection Data Sheet

OZARK UNDERGROUND LABORATORY, INC.

1572 Aley Lane Protem, MO 65733 (417) 785-4289 fax (417) 785-4290 email: oul@tri-lakes.net

SAMPLE COLLECTION DATA SHEET for FLUORESCENCE ANALYSIS

Project:_____ Week No:_____ Samples Collected By:_____

Samples Shipped By:_____ Samples Received By:_____

Date Samples Shipped:___/___/___ Date Samples Received:___/___/___ Time Samples Received:____:____ Return Cooler? Yes_____No_____

Bill to:_____ Send Results to: _____

Analyze for: Fluorescein____Eosine____Rhodamine WT____Other_____Ship cooler to: _____

OUL use only		*Please indicate stations where dye was visible in the field for field technician use - use black ink only*						*OUL use only*
# CHAR REC'D	LAB NUMBER	STATION NUMBER 1-4 Numbers	STATION NAME	PLACED		COLLECTED		# WATER REC'D
				DATE	TIME	DATE	TIME	

COMMENTS:_____

This sheet filled out by OUL staff? Yes_____No_____Charts for samples on this page proofed by OUL:_____

Page _____ of _____

Figure 2. Discrepancy Sheet

OZARK UNDERGROUND LABORATORY, INC.

DISCREPANCIES BETWEEN CHAIN-OF-CUSTODY SHEETS AND ACTUAL SAMPLES RECEIVED **Page _____ of _____**

Company & Project Name: **Date Rec'd by OUL:** **Wk # _____**

Lab #	Sta #	Station Name	Date Pulled	Problem	Solution

Comments:

Elution of the Charcoal

There are various eluting solutions that can be used for the recovery of tracer dyes. The solutions typically include an alcohol, some water, and a strong basic solution such as aqueous ammonia.

The standard elution solution now used at the Ozark Underground Laboratory is a mixture of 5% aqua ammonia and 95% isopropyl alcohol solution and sufficient potassium hydroxide flakes to saturate the solution. The isopropyl alcohol is 70% alcohol and 30% water. The aqua ammonia solution is 29% ammonia. The potassium hydroxide is added until a super-saturated layer is visible in the bottom of the container. This super-saturated layer is not used for elution. Preparation of eluting solutions uses dedicated glassware which is never used in contact with dyes or dye solutions.

The eluting solution we use will elute fluorescein, eosine, rhodamine WT, sulforhodamine B, and pyranine dyes. It is also suitable for separating fluorescein peaks from peaks of some naturally present materials found in some samplers.

Fifteen ml of the eluting solution is poured over the washed charcoal in a disposable sample beaker. The sample beaker is capped. The sample is allowed to stand for 60 minutes. After this time, the liquid is carefully poured off the charcoal into a new disposable beaker which has been appropriately labeled with the laboratory identification number. A few grains of charcoal may inadvertently pass into the second beaker; no attempt is made to remove these from the second sample beaker. After the pouring, a small amount of the elutant will remain in the initial sample beaker. After the transfer of the elutant to the second sample beaker, the contents of the first sample beaker (the eluted charcoal) are discarded.

Analysis on the Shimadzu RF-5000U or RF-5301

The Laboratory uses two Shimadzu spectrofluorophotometers. One is a model RF-5000U, and the other is a model RF-5301. Both of these instruments are capable of synchronous scanning. The RF-5301 is the primary instrument used; the RF-5000U is primarily used as a back-up instrument except for tracing studies which were begun using this instrument. The OUL also owns a Shimadzu RF-540 spectrofluorometer which is occasionally used for special purposes.

A sample of the elutant is withdrawn from the sample container using a disposable polyethylene pipette. Approximately 3 ml of the elutant is then placed in disposable rectangular polystyrene cuvette. The cuvette has a maximum capacity of 3.5 ml. The cuvette is designed for fluorometric analysis; all four sides and the bottom are clear. The spectral range of the cuvettes is 340 to 800 nm. The pipettes and cuvettes are discarded after one use.

The cuvette is then placed in the RF-5000U or the RF-5301. Both instruments are controlled by a programmable computer. Each instrument is capable of conducting substantial data analysis.

Our instruments are operated and maintained in accordance with the manufacturer's recommendations. On-site installation of the instruments and a training

session on the use of spectrofluorophotometers was provided by Delta Instrument Company.

Our typical analysis of an elutant sample where fluorescein, eosine, rhodamine WT, or sulforhodamine B dyes may be present includes synchronous scanning of excitation and emission spectra with a 17 nm separation between excitation and emission wavelengths. For these dyes, the excitation scan is from 443 to 613 nm; the emission scan is from 460 to 630 nm. The emission fluorescence from the scan is plotted on a graph. The typical scan speed setting is "very fast" on the RF-5000U; it is "fast" on the RF-5301. The typical sensitivity setting used on both instruments is "high."

Our typical analysis of an elutant sample where pyranine dye may be present includes a synchronous scanning of excitation and emission spectra with a 35 nm separation between excitation and emission wavelengths. For this dye, the excitation scan is from 360 to 600 nm; the emission scan is from 395 to 635 nm. The emission fluorescence from the scan is plotted on a graph. The typical scan speed setting is "very fast" on the RF-5000U; it is "fast" on the RF-5301. The typical sensitivity setting on both instruments is "high."

Excitation and emission slit width settings vary between the two instruments. The widths vary with the dyes for which we are sampling and for the matrix in which the dyes may be present. Excitation and emission slit width settings are summarized in Table 1.

Table 1. Excitation and emission slit width settings routinely used for dye analysis. Units are nanometers (nm)

Parameter	**RF5000U**	**RF5301**
Excitation slit for Eos, Fl, RWT, and SRB in elutant	5	3
Emission slit for Eos, Fl, RWT, and SRB in elutant	3	1.5
Excitation slit for Eos, Fl, RWT, and SRB in water	5	5
Emission slit for Eos, Fl, RWT, and SRB in water	10	3
Excitation slit for Pyranine in elutant	5	5
Emission slit for Pyranine in elutant	3	3
Excitation slit for Pyranine in pH adjusted water	5	5
Emission slit for Pyranine in pH adjusted water	3	3

Eos = Eosine. Fl = Fluorescein. RWT = Rhodamine WT. SRB = Sulforhodamine B.

The instrument produces a plot of the synchronous scan for each sample; the plot shows emission fluorescence only. The synchronous scans are subjected to computer peak picks; peaks are picked to the nearest 0.1 nm. All samples run on the RF-5000U and RF-5301 are stored on disk and printed on normal typing paper with a laser printer; sample information is printed on the chart.

All samples analyzed are recorded in a bound journal.

Quantification

We calculate the magnitude of fluorescence peaks for fluorescein, eosine, rhodamine WT, sulforhodamine B, and pyranine dyes. Dye quantities are expressed in microgram per liter (parts per billion; ppb). On the RF-5000U and RF-5301 the dye concentrations are calculated by separating fluorescence peaks due to dyes from background fluorescence on the charts, and then calculating the area within the fluorescence peak. This area is proportional to areas obtained from standard solutions.

Where there are multiple fluorescence peaks it is sometimes necessary to calculate dye concentrations based upon the height of the fluorescence peak rather that the area. The heights of the peaks are also proportional to dye concentrations.

We run dye concentration standards each day the machine is used. Ten separate standards are used; the standard or standards appropriate for the analysis work being conducted are selected. All standards are based upon the as-sold weights of the dyes. The standards are as follows:

1) 10 ppb fluorescein and 100 ppb rhodamine WT in well water from the Jefferson City-Cotter Formation
2) 10 ppb eosine in well water from the Jefferson City-Cotter Formation
3) 100 ppb sulforhodamine B in well water from the Jefferson City-Cotter Formation.
4) 10 ppb pyranine in well water from the Jefferson City-Cotter Formation. A sample of the standard is placed for at least two hours in a high ammonia atmosphere to adjust the pH to a value of 9.5 or greater.
5) 10 ppb fluorescein and 100 ppb rhodamine WT in elutant.
6) 10 ppb eosine in elutant.
7) 100 ppb sulforhodamine B in elutant.
8) 10 ppb pyranine in elutant.

Preparation of Standards

Dye standards are prepared as follows:

Step 1. A small sample of the as-sold dye is placed in a pre-weighed sample vial and the vial is again weighed to determine the weight of the dye. We attempt to use a sample weighing between 1 and 5 grams. This sample is then diluted with well water to make a 1% dye solution by weight (based upon the as-sold weight of the dye). The resulting dye solution is allowed to sit for at least four hours to insure that all dye is fully dissolved.

Step 2. One part of each dye solution from Step 1 is placed in a mixing container with 99 parts of well water. Separate mixtures are made for fluorescein, rhodamine WT, eosine, sulforhodamine B, and pyranine. The resulting solutions contain 100 mg/l dye (100 parts per million dye). The typical prepared volume of this mixture is appropriate for the sample bottles being used; we commonly prepare about 50 ml. of the Step 2 solutions. The dye solution from Step 1 that is used in making the Step 2 solution

is withdrawn with a digital Finnpipette which is capable of measuring volumes between 0.200 and 1.000 ml at intervals of 0.005 ml. The calibration certificate with this instrument indicates that the accuracy (in percent) is as follows:

At 0.200 ml, 0.90%

At 0.300 ml, 0.28%

At 1.000 ml, 0.30%

The Step 2 solution is called the long term standard. Ozark Underground Laboratory experience indicates that Step 2 solutions, if kept refrigerated, will not deteriorate appreciably over periods of less than a year. Furthermore, these Step 2 solutions may last substantially longer than one year.

Step 3. A series of intermediate-term dye solutions are made. Approximately 45 ml. of each intermediate-term dye solution is made. All volume measurements of less than 5 ml are made with a digital Finnpipette. (see description in Step 2). All other volume measurements are made with Rheinland Kohn Geprufte Sicherheit 50 ml. capacity pump dispenser which will pump within plus or minus 1% of the set value. The following solutions are made; all concentrations are based on the as-sold weight of the dyes:

1) A solution containing 1 ppm fluorescein dye and 10 ppm rhodamine WT dye.

2) A solution containing 1 ppm eosine.

3) A solution containing 10 ppm sulforhodamine B dye.

4) A solution containing 1 ppm pyranine.

Step 4. A series of eight short-term dye standards are made from solutions in Step 3. These standards were identified earlier in this section. In the experience of the Ozark Underground Laboratory these standards have a useful shelf life in excess of one week. However, in practice, they are kept under refrigeration and new standards are made weekly.

Dilution of Samples

Samples with peaks that have arbitrary fluorescence unit values of 500 or more are diluted a hundred fold to ensure accurate quantification.

Some water samples have high turbidity or color which interferes with accurate detection and measurement of dye concentrations. It is often possible to dilute these samples and then measure the dye concentration in the diluted sample.

The typical dilution is 100 fold. One part of the test sample is combined with 99 parts of water (if the test sample is water) or with 99 parts of the standard elutant (if the test sample is elutant). Typically, 0.300 ml of the test solution is combined with 29.700 ml of water (or elutant as appropriate) to yield a new test solution. All volume measurements of less than 5 ml are made with a digital Finnpipette. which is capable of measuring volumes between 0.200 and 1.000 ml at intervals of 0.005 ml. The calibration certificate with this instrument indicates that the accuracy (in percent) is as follows:

At 0.200 ml, 0.90%

At 0.300 ml, 0.28%

At 1.000 ml, 0.30%

All other volume measurements are made with Rheinland Kohn Geprufte Sicherheit 50 ml. capacity pump dispenser which will pump within plus or minus 1% of the set value.

Quality Control

Laboratory blanks are run for every sample where the last two digits of the laboratory numbers are 00, 20, 40, 60, or 80. A charcoal packet is placed in a pumping well sampler and at least 25 gallons of unchlorinated water is passed through the sampler at a rate of about 2.5 gallons per minute. The sampler is then subjected to the same analytical protocol as all other samplers.

System functioning tests of the analytical instruments are conducted in accordance with the manufacturer's recommendations.

All materials used in sampling and analysis work are routinely analyzed for the presence of any compounds that might create fluorescence peaks in or near the acceptable wavelength ranges for any of the tracer dyes. This testing typically includes approximately 1% of materials used.

Reports

Reports are provided in accordance with the needs of the client. At a minimum we provide copies of the analysis graphs and a listing of stations and samples where dye was detected. The reports indicate dye concentrations.

Work at the Ozark Underground Laboratory is directed by Mr. Thomas Aley. Mr. Aley has 40 years of professional experience in hydrology and hydrogeology. He is certified as a Professional Hydrogeologist (Certificate #179) by the American Institute of Hydrology. Mr. Aley has 35 years of professional experience in groundwater tracing with fluorescent tracing agents.

CRITERIA FOR DETERMINATION OF POSITIVE DYE RECOVERIES

Normal Emission Ranges and Detection Limits

The OUL has established normal emission fluorescence wavelength ranges for each of the five dyes. The normal acceptable range equals mean values plus and minus two standard deviations. These values are derived from actual groundwater tracing studies conducted by the OUL.

The detection limits are based upon concentrations of dye necessary to produce emission fluorescence peaks where the signal to noise ratio is 3. The detection limits are realistic for most field studies since they are based upon results from actual field samples rather than being based upon values from spiked samples in a matrix of reagent water or the elutants from unused activated carbon samplers. In some cases detection limits may be smaller than reported if the water being sampled has very little fluorescent material in it. In some cases detection limits may be greater than reported; this most commonly occurs if the sample is turbid due to suspended material or a coloring agent such as tannic compounds. Turbid samples are typically centrifuged or, if this is not effective, diluted prior to analysis.

Table 2 provides normal emission wavelength ranges and detection limits for the five dyes when analyzed on the OUL's RF-5000U spectrofluorophotometer. Table 3 provides similar data for the OUL's RF-5301. As indicated earlier in Table 1, the analytical protocols used on the two instruments are somewhat different, especially in regard to the widths of excitation and emission slit settings.

Table 2. RF-5000U Spectrofluorophotometer. Normal emission wavelength ranges and detection limits for fluorescein, eosine, rhodamine WT, sulforhodamine B, and pyranine dyes in water and elutant samples. Detection limits are based upon the as-sold weight of the dye mixtures normally used by the OUL.

Dye and Matrix	Normal Acceptable Emission Wavelength Range (nm)	Detection Limit (ppb)
Eosine in Elutant	533.0 to 539.6	0.035
Eosine in Water	529.6 to 538.4	0.008
Fluorescein in Elutant	510.7 to 515.0	0.010
Fluorescein in Water	505.6 to 510.5	0.0005
Pyranine in Elutant	500.4 to 504.6	0.055
Pyranine in Water*	501.2 to 505.2	0.030
Rhodamine WT in Elutant	561.7 to 568.9	0.275
Rhodamine WT in Water	569.4 to 574.8	0.050
Sulforhodamine B in Elutant	567.5 to 577.5	0.150
Sulforhodamine B in Water	576.2 to 579.7	0.040

* pH adjusted water with pH of 9.5 or greater.

Note: The protocols for the analysis of pyranine dye are substantially different than those for the other dyes. As a result, there is less potential interference between pyranine and fluorescein than might otherwise be indicated by the emission wavelength values shown in the table.

Table 3. RF-5301 Spectrofluorophotometer. Normal emission wavelength ranges and detection limits for fluorescein, eosine, rhodamine WT, sulforhodamine B, and pyranine dyes in water and elutant samples. Detection limits are based upon the as-sold weight of the dye mixtures normally used by the OUL.

Dye and Matrix	Normal Acceptable Emission Wavelength Range (nm)	Detection Limit (ppb)
Eosine in Elutant	538.1 to 543.9	0.050
Eosine in Water	533.4 to 537.9	0.015
Fluorescein in Elutant	514.0 to 518.1	0.025
Fluorescein in Water	508.0 to 511.7	0.002
Pyranine in Elutant	502.1 to 508.1	0.015
Pyranine in Water*	504.1 to 510.1	0.010
Rhodamine WT in Elutant	565.4 to 572.0	0.170
Rhodamine WT in Water	572.7 to 578.0	0.015
Sulforhodamine B in Elutant	572.8 to 579.6	0.080
Sulforhodamine B in Water	580.1 to 583.7	0.008

* pH adjusted water with pH of 9.5 or greater.

Note: The protocols for the analysis of pyranine dye are substantially different than those for the other dyes. As a result, there is less potential interference between pyranine and fluorescein than might otherwise be indicated by the emission wavelength values shown in the table.

Criteria for Determining Positive Dye Recoveries

The following sections identify normal criteria used by the OUL for determining positive dye recoveries. Beginning January 1, 2001, the primary analytical instrument in use at the OUL was the RF-5301; the RF-5000U was the principal backup instrument. Studies which were in progress prior to January 1, 2001 continued to have samples analyzed on the RF-5000U.

Except for pyranine dye, the analytical protocol used for the RF-5301 provides for the use of narrower excitation and/or emission slit settings than the RF-5000U protocol. This enhances our ability to discriminate between dyes and other fluorescent compounds. The protocol which is possible with the RF-5301 (as contrasted with the RF-5000U) also provides for a better balance in the sizes of the fluorescence peaks associated with an equal concentration of all of the dyes.

Normal Criteria Used by the Ozark Underground Laboratory for Determining Positive Eosine Dye Recoveries in Elutants from Charcoal Samplers.

There is generally little or no detectable fluorescence background in the general range of eosine dye encountered in most groundwater tracing studies. The following four criteria are used to identify fluorescence peaks which are deemed to be eosine dye.

Criterion 1. There must be at least one fluorescence peak at the station in question in the range of 538.1 to 543.9 nm for samples analyzed by the RF-5301. The range must be 533.0 to 539.6 nm for samples analyzed by the RF-5000U.

Criterion 2. The dye concentration associated with the fluorescence peak must be at least 3 times the detection limit. For the RF-5301, the eosine detection limit in elutant samples is 0.050 ppb, thus this dye concentration limit equals 0.150 ppb. For the RF-5000U the eosine detection limit in elutant samples is 0.035 ppb, thus this dye concentration limit equals 0.105 ppb.

Criterion 3. The dye concentration must be at least 10 times greater than any other concentration reflective of background at the sampling station in question.

Criterion 4. The shape of the fluorescence peak must be typical of eosine. Much background fluorescence yields low, broad, and asymmetrical fluorescence peaks rather than the more narrow and symmetrical fluorescence peaks typical of eosine. In addition, there must be no other factors which suggest that the fluorescence peak may not be eosine dye from our groundwater tracing work.

Normal Criteria Used by the Ozark Underground Laboratory for Determining Positive Eosine Dye Recoveries in Water Samples.

There is generally little or no detectable fluorescence background in the general range of eosine dye encountered in most groundwater tracing studies. The following three criteria are used to identify fluorescence peaks which are deemed to be eosine dye.

Criterion 1. The associated charcoal samplers for the station should also contain eosine dye in accordance with the criteria listed above. These criteria may be waived if no charcoal sampler exists.

Criterion 2. There must be no factors which suggest that the fluorescence peak may not be eosine dye from our groundwater tracing work. For samples analyzed on the RF-5301, the fluorescence peak should generally be in the range of 533.4 to 537.9 nm. For samples analyzed on the RF-5000U, the fluorescence peak should generally be in the range of 529.6 to 538.4 nm.

Criterion 3. The dye concentration associated with the fluorescence peak must be at least three times the detection limit. Our eosine detection limit in water samples analyzed on the RF-5301 is 0.015 ppb, thus this dye concentration limit equals 0.045 ppb. For samples analyzed on the 5000U the detection limit is 0.008 ppb, thus this dye concentration limit equals 0.024 ppb.

Normal Criteria Used by the Ozark Underground Laboratory for Determining Positive Fluorescein Dye Recoveries in Elutants from Charcoal Samplers.

There is often some fluorescence background in the range of fluorescein dye present at some of the stations used in groundwater tracing studies. We routinely conduct background sampling prior to the introduction of any tracer dyes to characterize this background fluorescence and to identify the existence of any tracer dyes which may be present in the area. The fact that a fluorescence peak is identified in our analytical results is not proof that it is fluorescein dye or that it is fluorescein dye from the trace of concern. The following 4 criteria are used to identify fluorescence peaks which are deemed to be fluorescein dye recoveries from our tracing work.

Criterion 1. There must be at least one fluorescence peak at the station in question in the range of 514.0 to 518.1 nm for samples analyzed by the RF-5301. The range must be 510.7 to 515.0 for samples analyzed by the RF-5000U.

Criterion 2. The dye concentration associated with the fluorescence peak must be at least 3 times the detection limit. For the RF-5301, the fluorescein detection limit in elutant samples is 0.025 ppb, thus this dye concentration limit equals 0.075 ppb. For the RF-5000U, the fluorescein detection limit in elutant samples is 0.010 ppb, thus this dye concentration limit equals 0.030 ppb.

Criterion 3. The dye concentration must be at least 10 times greater than any other concentration reflective of background at the sampling station in question.

Criterion 4. The shape of the fluorescence peak must be typical of fluorescein. Much background fluorescence yields low, broad, and asymmetrical fluorescence peaks rather than the more narrow and symmetrical fluorescence peaks typical of fluorescein. In addition, there must be no other factors which suggest that the fluorescence peak may not be fluorescein dye from our groundwater tracing work.

Normal Criteria Used by the Ozark Underground Laboratory for Determining Positive Fluorescein Dye Recoveries in Water Samples.

There is commonly some fluorescence background in the general range of fluorescein dye at some sampling stations used in groundwater tracing studies. The following criteria are used to identify fluorescence peaks which are deemed to be fluorescein dye in water.

Criterion 1. The associated charcoal samplers for the station should also contain fluorescein dye in accordance with the criteria listed above. These criteria may be waived if no charcoal sampler exists.

Criterion 2. There must be no factors which suggest that the fluorescence peak may not be fluorescein dye from our groundwater tracing work. For samples analyzed on the RF-5301, the fluorescence peak should generally be in the range of 508.0 to 511.7 nm. For samples analyzed on the RF-5000U, the fluorescence peak should generally be in the range of 505.6 to 510.5 nm.

Criterion 3. The dye concentration associated with the fluorescence peak must be at least three times the detection limit. Our fluorescein detection limit in water samples analyzed on the RF-5301 is 0.002 ppb, thus this dye concentration limit equals 0.006 ppb. For the RF-5000U the detection limit is 0.0005 ppb, thus this dye concentration limit equals 0.0015 ppb.

Normal Criteria Used by the Ozark Underground Laboratory for Determining Positive Rhodamine WT Dye Recoveries in Elutants from Charcoal Samplers.

There is generally little or no detectable fluorescence background in the general range of Rhodamine WT dye encountered in most groundwater tracing studies. The following four criteria are used to identify fluorescence peaks which are deemed to be Rhodamine WT.

Criterion 1. For samples analyzed on the RF-5301, there must be at least one fluorescence peak at the station in question in the range of 565.4 to 572.0 nm. For samples analyzed on the RF-5000U, there must be at least one fluorescence peak at the station in question in the range of 561.7 to 568.9 nm.

Criterion 2. The dye concentration associated with the Rhodamine WT peak must be at least 3 times the detection limit. For the RF-5301, the detection limit in elutant samples is 0.170 ppb, thus this dye concentration limit equals 0.510 ppb. For the RF-5000U, the detection limit in elutant samples is 0.275 ppb, thus this dye concentration limit equals 0.825 ppb.

Criterion 3. The dye concentration must be at least 10 times greater than any other concentration reflective of background at the sampling station in question.

Criterion 4. The shape of the fluorescence peak must be typical of Rhodamine WT. In addition, there must be no other factors which suggest that the fluorescence peak may not be dye from the groundwater tracing work under investigation.

Normal Criteria Used by the Ozark Underground Laboratory for Determining Positive Rhodamine WT Dye Recoveries in Water Samples.

The following criteria are used to identify fluorescence peaks which are deemed to be Rhodamine WT dye in water.

Criterion 1. The associated charcoal samplers for the station should also contain Rhodamine WT dye in accordance with the criteria listed above. These criteria may be waived if no charcoal sampler exists.

Criterion 2. There must be no factors which suggest that the fluorescence peak may not be Rhodamine WT dye from the tracing work under investigation. For samples analyzed with the RF-5301, the fluorescence peak should generally be in the range of 572.7 to 578.0 nm. For samples analyzed with the RF-5000U, the fluorescence peak should generally be in the range of 569.4 to 574.8 nm.

Criterion 3. The dye concentration associated with the fluorescence peak must be at least three times the detection limit. Our Rhodamine WT detection limit in water samples analyzed on the RF-5301 is 0.015 ppb, thus this dye concentration limit is 0.045 ppb. For samples analyzed on the RF-5000U the detection limit is 0.050 ppb, thus this dye concentration limit equals 0.150 ppb.

Normal Criteria Used by the Ozark Underground Laboratory for Determining Positive Sulforhodamine B Dye Recoveries in Elutants from Charcoal Samplers.

There is generally little or no detectable fluorescence background in the general range of sulforhodamine B dye encountered in most groundwater tracing studies. The following four criteria are used to identify fluorescence peaks which are deemed to be sulforhodamine B.

Criterion 1. For samples analyzed on the RF-5000U, there must be at least one fluorescence peak at the station in question in the range of 567.5 to 577.5 nm. The acceptable range for samples analyzed on the RF-5301 is 572.8 to 579.6 nm.

Criterion 2. The dye concentration associated with the sulforhodamine B peak must be at least 3 times the detection limit. For the RF-5000U, the detection limit in elutant samples is 0.150 ppb, thus this dye concentration limit equals 0.450 ppb. For the RF-5301, the detection limit in elutant samples is 0.080 ppb, thus this dye concentration limit equals 0.240 ppb.

Criterion 3. The dye concentration must be at least 10 times greater than any other concentration reflective of background at the sampling station in question.

Criterion 4. The shape of the fluorescence peak must be typical of sulforhodamine B. In addition, there must be no other factors which suggest that the fluorescence peak may not be dye from the groundwater tracing work under investigation.

Normal Criteria Used by the Ozark Underground Laboratory for Determining Positive Sulforhodamine B dye Recoveries in Water Samples.

The following criteria are used to identify fluorescence peaks which are deemed to be sulforhodamine B dye in water.

Criterion 1. The associated charcoal samplers for the station should also contain sulforhodamine B dye in accordance with the criteria listed earlier. These criteria may be waived if no charcoal sampler exists.

Criterion 2. There must be no factors which suggest that the fluorescence peak may not be sulforhodamine B dye from the tracing work under investigation. For samples analyzed with the RF-5000U, the fluorescence peak should generally be in the range of 576.2 to 579.7 nm. For samples analyzed with the RF-5301, the fluorescence peak should generally be in the range of 580.1 to 583.7 nm.

Criterion 3. The dye concentration associated with the fluorescence peak must be at least three times the detection limit. For samples analyzed on the RF-5301 the detection limit in water is 0.008 ppb, thus this dye concentration limit equals 0.024 ppb. For samples analyzed on the RF-5000U the detection limit in water samples is 0.040 ppb, thus this dye concentration limit equals 0.120 ppb.

Normal Criteria Used by the Ozark Underground Laboratory for Determining Positive Pyranine Dye Recoveries in Elutants from Charcoal Samplers.

It must be remembered that the analysis protocol for pyranine dye is different than the protocol for the other four dyes discussed in this document. If the other dyes are present in a sample analyzed for pyranine dye their emission fluorescence peaks (if any) will be appreciably different than the values presented above. Because of this, there is very little analytical interference between fluorescein and pyranine dyes when both are present in a sample.

There is often some detectable fluorescence background encountered in the general range of pyranine dye in groundwater tracing studies. The following four criteria are used to identify fluorescence peaks which are deemed to be pyranine.

Criterion 1. For samples analyzed on the RF-5000U, there must be at least one fluorescence peak at the station in question in the range of 500.4 to 504.6 nm. The acceptable range for samples analyzed on the RF-5301 is 502.1 to 508.1 nm.

Criterion 2. The dye concentration associated with the pyranine dye peak must be at least 3 times the detection limit. For the RF-5000U, the detection limit in elutant samples is 0.055 ppb, thus this dye concentration limit equals 0.165 ppb. For the RF-5301, the detection limit in elutant samples is 0.015 ppb, thus this dye concentration limit equals 0.045 ppb.

Criterion 3. The dye concentration must be at least 10 times greater than any other concentration reflective of background at the sampling station in question.

Criterion 4. The shape of the fluorescence peak must be typical of pyranine dye. In addition, there must be no other factors which suggest that the fluorescence peak may not be dye from the groundwater tracing work under investigation.

Normal Criteria Used by the Ozark Underground Laboratory for Determining Positive Pyranine Dye Recoveries in Water Samples.

It must be remembered that the analysis protocol for pyranine dye is different than the protocol for the other four dyes discussed in this document. If the other dyes are present in a sample analyzed for pyranine dye their emission fluorescence peaks (if any) will be appreciably different than the values presented above. Because of this, there is very little analytical interference between fluorescein and pyranine dyes when both are present in a sample.

The fluorescence of pyranine decreases below a pH of about 9.5. Prior to analysis water samples are placed in a high ammonia atmosphere for at least two hours. A pyranine dye in water standard is placed in the same atmosphere as the samples. Prior to analysis samples are tested to insure that their pH is 9.5 or greater. If pyranine dye concentrations in a sample are so great as to require dilution for quantification of the dye concentration the diluting water used is OUL reagent water which has been pH adjusted in a high ammonia atmosphere.

The following criteria are used to identify fluorescence peaks which are deemed to be pyranine dye in water.

Criterion 1. The associated charcoal samplers for the station should also contain pyranine dye in accordance with the criteria listed earlier. These criteria may be waived if no charcoal sampler exists.

Criterion 2. There must be no factors which suggest that the fluorescence peak may not be pyranine dye from the tracing work under investigation. For samples analyzed with the RF-5000U, the fluorescence peak should generally be in the range of 501.2 to 505.2 nm. For samples analyzed with the RF-5301, the fluorescence peak should generally be in the range of 504.1 to 510.1 nm.

Criterion 3. The dye concentration associated with the fluorescence peak must be at least three times the detection limit. For samples analyzed on the RF-5301 the detection limit in water is 0.010 ppb, thus this dye concentration limit equals 0.030 ppb. For samples analyzed on the RF-5000U the detection limit in water samples is 0.030 ppb, thus this dye concentration limit equals 0.090 ppb.