

A KARST GROUNDWATER STUDY TO DELINEATE THE QUARRY SPRING BASIN GROUNDWATERS NEAR THE LEMON LANE LANDFILL, WEST-CENTRAL BLOOMINGTON, INDIANA

Ву

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Objectives:

The purpose of this study is to better understand the flow pathways and hydrogeologic conditions within the groundwater basin of the Lemon Lane Landfill sinkhole complex and drainage basin, and to seek hydrochemical evidence of groundwater storage in the epikarst portion of underlying bedrock. Several tracer studies of the Lemon Lane area groundwater complex have been carried out by Westinghouse Electric Corporation, including one in 1987, 1989 and a third in 1990. These tracer tests involved injection of dye into wells drilled around the perimeter of the landfill/sinkhole complex with the purpose of locating the primary groundwater flow paths. Conductivity readings were also taken as an aid to understanding groundwater flow conditions. Rather than using wells immediately around the landfill proper, this study was designed to use natural sinkhole connections to the groundwater system. More importantly, these injection sinks are located further out -400 to 3500 feet (122 to 1067 meters) from the perimeter helping to further define the groundwater drainage basin.

Two springs, Illinois Central and Quarry, have been shown in the Westinghouse studies to receive the majority of groundwater flowing from the Lemon Lane sinkhole complex; therefore, this basin is the primary focus for dye and chemical parameter monitoring. Measurements of specific conductivity, pH, temperature, dissolved oxygen, and major ions are used to understand groundwater flow and possible storage of waters in the epikarstic bedrock zone. This is accomplished through interpretation of spring chemographs.

Introduction:

The study area, which is located on the west side of the city of Bloomington in Monroe County, Indiana (Figure 1.), includes the drainage of the groundwater basin that contains the Lemon Lane Landfill and focuses on Illinois Central and Quarry springs' drainage. The geology beneath and surrounding the Lemon Lane Landfill is typical of much of Southern Indiana's karst terrane found in the Mitchell Plain physiographic unit. A thin clay mantle overlies formations consisting chiefly of Mississippian Age limestones. The hydrology of karst terranes is influenced and controlled by the dissolution features found in the carbonate bedrock. Groundwater flow occurs along bedding planes, joints, and conduits rather than through a more or less homogeneous, isotropic granular and unfractured rock, and therefore, special methods and protocols have been developed to characterize flow paths.

EPA recommendations (Quinlan, 1989) for monitoring the progression of groundwater flow in karst terranes call for injection of a suitable tracer (usually fluorescent dye) at



an upgradient recharge point. All springs located within a 5 to 15 mile (8 to 24 kilometers) radius should be monitored for the tracer during and after injection; the possibility of radial flow is assumed.

The ideal recommended injection points are perennial sinking streams followed by sinkholes which have a hole at the bottom and wells drilled on fracture traces or fracturetrace intersections (Quinlan, 1989). Perennial sinking streams are not present in the immediate Lemon Lane site area; however, the other two options are available. Previous studies by Westinghouse were conducted by injecting dye into wells under "high" and "low" flow conditions, primarily to trace flow away from the Lemon Lane Landfill sinkhole complex. In the present study, sinkholes were used rather than injection wells to trace area groundwater flow and an effort was made to locate injection sinks well beyond the perimeter of the landfill to provide better definition of the surrounding groundwater basins. Particular attention was paid to the basin containing Illinois Central and Quarry springs, by placing injection points concentrated around the south and east side of Lemon Lane Landfill.

Numerous candidate sinkholes were located by using 1" = 200' and 1" = 500' scale topography maps, sketches from early twentieth century aerial photos, and field reconnaissance. Also long term residents living adjacent to nearby sinkholes were questioned about the ability of the

sinkholes to swallow storm waters.

Five sinkholes located along a topographic high around the Lemon Lane Landfill were selected as dye injection points (Figure 2.). Three of these sinkholes in particular are located between the Illinois Central and Quarry springs and adjacent spring basins. Four of the sinkholes were about 2300 feet (700 meters) or less from the perimeter of the landfill, while the fifth was found about 3,500 feet (1070 meters) away.



Figure 2. Map of injection sink locations.

The Lemon Lane North sink, a sinkhole with several large openings, lies 700 feet (214 meters) directly north of the landfill.

The 11th & Adams Street sink is an open hole lying in a local topographic low about 2,300 feet (700 meters) due east of the landfill. This sinkhole readily takes copious amounts of surface runoff which drains from a low lying field about one square block in area.

The sinkhole, which lies in a deep depression, was cleared of debris and trash, and a 4-inch (10 cm) PVC pipe was placed into a small cave at the bottom. The sink is located about 400 feet (122 meters) southwest of the landfill, off the east end of Evergreen Drive and on the east side of the **Evergreen Drive** and on the

The sink is located 2,100 feet (640 meters) south-southwest of the landfill. It is a shallow sinkhole located in the backyard of the sector and sectors.

property on Le Jac Lane. This sink, which is located in a low flat area, is reported to swallow water readily and becomes ponded after large rainfalls (1.5 inches (38mm) or more).

The Cory Lane sink is the swallow of an ephemeral sinking creek that only flows after storm events. It has been observed to be ponded after as little as 0.5 inches (13 mm) of rain. The Cory lane sink is located 3,500 feet (1067 meters) due south of the landfill. In addition to identifying flow paths and delineating groundwater basins, this study was designed to seek any evidence of epikarst stored waters by examining various water chemical parameters of spring discharge during a rain event.

In karst terranes, groundwater is stored in the saturated and unsaturated zones of the bedrock (Figure 3.).



Figure 3. Model of water storage compartments of the vadose and phreatic zones (modified from Gruver, 1991).

In the saturated zone, water lies in phreatic conduits which have been enlarged by solution activity, and in small joints, fractures and bedding planes. A great deal of enlargement occurs in the saturated rock mass. However, some 50 to 80 percent of carbonate rock solution occurs in the top 33 feet (10 meters) below the surface (Smith &

Atkinson, 1976), which is generally unsaturated, resulting in heavy corrosion.

The epikarst, also called the subcutaneous zone, refers to the upper 10 to 33 feet (3 to 10 meters) of unsaturated rock mass and includes the soil/bedrock interface (Williams, 1983). Intense, near-surface solution activity enlarges fractures and bedding planes. Any voids created below the surface may also collapse, further fracturing the nearsurface carbonate rocks. The resulting high secondary porosity is a primary characteristic of the epikarst.

Solution activity decreases with depth within the epikarstic zone due to less available CO₂ and carbonic acid, causing a bottleneck and subsequent retarded downward flow (Figure 4.). While water infiltration into this highly



Figure 4. Schematic relationship between CO_2 , rate of limestone solution, and fissuring beneath the soil (from Williams, 1983).

porous zone can be rapid, percolation down to phreatic conduits and the saturated rock mass is much slower, causing significant amounts of water storage in the epikarst, particularly after rain storms. The baseflow of springs may be sustained for many weeks by epikarst stored water (Smith & Atkinson, 1976).

A primary method for identifying sources of spring discharge waters is the interpretation of spring chemographs, which plot specific water quality parameters occurring over time relative to discharge. Water quality parameters such as major ions in solution, electrical conductivity, pH, temperature, dissolved oxygen, and stable isotopes may all be potential indicators of water sources. Specific conductance has been particularly useful in defining sources of spring waters. While defining the relationship between specific conductance, ion concentrations and dissolved solids in natural waters is not simple, strong correlations among these parameters have been demonstrated. For example, a reliable correlation between dissolved solids and specific conductance was obtained in a study of daily samples from the Gila River at Bylas, Arizona (Hem, 1985). Similar results may be found by observing conductance, dissolved solids, and additionally some ions.

Krothe and Libra (1983) found an association between the amount of total dissolved solids (TDS) and residence time in several springs in southern Indiana. Springs characterized as having conduit flow and shorter residence times had predominately low TDS, while those described as having diffuse flow typically maintained much higher values. In addition, springs dominated by conduit flow exhibited greater variability in ionic concentrations, among other parameters, whereas diffuse springs displayed ionic concentration values which were more constant.

A further study pointing to the value of assessing water quality in locating spring sources took place in Hungary (Jakucs, 1959). Jakucs utilized chemographs to plot calcium (Ca) concentration and discharge against time; samples were taken from the Komlos spring during and after heavy rainfall. Ashton (1966) later hypothesized that the increase of Ca concentration found by Jakucs at the start of the flood hydrograph is caused when long residence water in the deeper phreatic zone is flushed out. Recharging water forces the phreatic water out in what he calls a "pistonlike" process. Ashton describes the process as "pulses of water coming from different input points and passing through essentially discrete sections of phreas."

Williams (1983) went a step further in explaining the Ca concentration changes found by Jakucs by studying subcutaneous karst hydrogeology in mixed lithology basins. In his study calling the first part of the rising limb of the hydrograph "quick flow", he noted that the "quick flow" had been commonly interpreted as resulting from phreatic

water being flushed out by the incoming recharge wave. This interpretation had been based on examining both constant or temporary increase in calcium hardness (i.e., conductivity) seen before the hydrograph peaks. It has been commonly assumed that there is only one major source of high conductivity water, that is phreatic conduit storage. Williams argued that this assumption would lead to an over estimation in the volume of water displaced from this Instead, realizing that water stored in the vadose source. zone has characteristically high hardness values, this second major source also needed to be considered. Taking this into account, Williams (1983) hypothesized that the initial rise in the spring hydrograph is caused by phreatic water displaced by arriving stream water and a pulse from what is mostly subcutaneous storage. This pulse is indicated by an increase in water hardness or conductivity. As the hardness levels drop off, the subcutaneous source water is replaced by incoming allogenic stream waters (i.e., storm and stream water originating from a non-carbonate source rock of the mixed lithology basin). Based on this analysis, a generalized interpretation of the karst spring hydrograph and chemographs is presented (Figure 5.).

Quarry spring examined in the present study, has been shown by recent dye traces (McCann & Krothe, 1991) to be included in the same groundwater flow system as Illinois Central spring. Waters resurging at Illinois Central spring



Figure 5. Interpretation of a karst spring hydrograph and chemographs (from Williams, 1983).

flow a short distance overland, submerge, and then resurge again at Quarry spring. Chemistry data from both springs is used in this study to investigate epikarst storage for the same groundwater system.

As mentioned earlier, springs may be influenced by both conduit and diffuse flow, both of which represent two end points of a continuum of flow type. While both types are present in springs, one usually dominates. The Quarry system responds rapidly to storm events and is dominated by conduit flow.

McCann (1990) analyzed specific conductivity readings from Quarry Spring discharge during a 1990 rainstorm. The



QUARRY SPRING

Figure 6. Interpretation of Quarry spring hydrograph and chemograph (from McCann, 1990).

peaks in the chemograph presented in Figure 6 were

representative of pulses of water arriving in stages. Based on conductivity values, the initial rise in conductivity was attributed to storage water being forced out of the conduits by storm water. This is followed by a drop in conductivity as the hydrograph begins to rise, showing storm water arriving from concentrated recharge by way of conduits. A sharp rise in conductivity occurs with peak discharge as stored epikarst water is forced out by rapid, discrete recharge. Where the hydrograph falls off, conductivity drops, showing that storm waters are discharged from the conduits. Conductivity then rises and returns to higher values, representing replacement of storm waters by phreatic storage water.

The purpose of the present study is to delineate the Quarry spring basin using dye tracing techniques and to seek evidence of epikarst groundwater storage by examining chemical parameters relative to spring discharge. In addition to using conductivity as evidence of epikarst groundwater storage, other parameters are examined: major ions, temperature, dissolved oxygen and pH. Analysis of oxygen isotopes is not included because the proper weather conditions did not occur before the sampling event. An extended dry period of a week or longer prior to the sampling event would increase the likelihood of maintaining isotopically unique epikarst and storm waters.

Location:

The study area, which includes injection sinks and all monitoring stations, is located on the west central side of

Bloomington in Monroe County, Indiana (Figure 7.). Bloomington lies about 45 miles (72 kilometers) southwest of Indianapolis in the Mitchell Plain, a low plateau underlain by Mississippian carbonates and characterized by karst developed terrane. The site area is comprised of approximately 16 square miles (41 square kilometers) and is entirely located on the Bloomington 7.5 minute topographic quadrangle U.S.G.S map. It is bounded on the east by Walnut Street, which runs north-south through downtown Bloomington, and on the west by Hartstraight Road (north of Whitehall Pike/Hwy 48) and Kirby Road (south of Whitehall Pike/Hwy 48). Highway 45/46 bypass, Highway 46, and the western portion of Woodyard Road run along the northern edge of the study area, while Airport Road (westward) and Tapp Road (eastward) form the southern boundary.

Site Geology:

The study area is underlain by Mississippian limestones comprised of two major formations: the St. Louis and Salem Limestones (Figure 8.). Nearest the surface is the St. Louis Limestone, which is approximately 100 to 120 feet (30 to 37 meters) thick locally, and 80 to 400 feet (24 to 122 meters) thick throughout southern Indiana. It is a thinly bedded microcrystalline, dolomitic limestone with clay-rich and shale zones throughout the formation (Cutler, 1987).



PERIOD	EPOCH	THICKNESS (FEET)	LITHOLOGY	FORMATION	GROUP	17
PENN-1 SYL-1 VANIAN	POTTS-	150 - 300		MANSFIELD FM.	"RACCOON CREEK"	-
		20-30		GLEN DEAN LS.		
	ļ	30-40		HARDINSBURG SS.		
		40-50		GOLCONDA LS.	STEPHENS - PORT	
	CHESTER	25-40	[=====	BIG CLIFTY FM.		
	1ES	15-25		BEECH CREEK LS.]	1
	5	20-40		ELWREN FM.	4	}
		0-5 20-40		REELSVILLE LS. SAMPLE FM.	WEST BADEN	
		10-20		BEAVER BEND LS.		
		12-30		BETHEL FM.		
		15-20		PAOLI LS.		
MISSISSIPPIAN		100- 120		STE. GENEVIEVE LS.	BLUE RIVER	
WIS	MERAMEC	120 1.		ST. LOUIS LS.		
	2	90- 100		SALEM LS.	SANDERS	
	• {	50-80		HARRODSBURG LS.		
	OSAGE	600- 800 -		MULDRAUGH FM.	BORDEN	

Figure 8. Stratigraphic column (from Palmer, 1969).

The Salem Limestone is located beneath the St. Louis Limestone. The Salem Limestone is a thickly bedded, porous, granular, massive calcarenite composed mainly of oolites and small calcareous fossils (Palmer, 1969). Both formations have similar lithologic characteristics near the contact, which is not well-defined lithologically. Below the Salem Limestone is the Harrodsburg Limestone - a medium to thinly bedded, coarse-grained limestone - and the Ramp Creek Formation, which is a cherty shaley limestone.

The bedrock formations dip west-southwest at about 30 feet per mile toward the center of the Illinois Basin (Gates, 1962). Monroe County lies just off of the southeast rim of the Illinois Basin. Due to the highly jointed, thinly bedded nature of the St. Louis Limestone, sinkholes are well developed and abundant wherever this formation lies at or near the surface. Ritter (1986) noted that most of the joints in the St. Louis are vertical. The presence of vertical joints further augments the development of sinkholes, as evidenced on the west side of Bloomington.

Field Methods:

To analyze fluorescing dyes in karst groundwater, grab samples must be obtained from spring resurgences prior to injection to assess background levels. Samples must be taken during the tracer test at regular intervals and

passive detectors are used to ensure that any dye pulse missed by regular grab sampling rounds is still detected.

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Grab samples were collected in new 2 or 4 oz. (60 or 120 ml) polyethylene bottles and stored in the dark in coolers until analyzed at the laboratory on a scanning spectrofluorophotometer. Each bottle was rinsed several times with sample water before obtaining the sample.

Passive charcoal detectors were constructed of nylon screen stapled into 2x3 inch (5x8 cm) pouches and filled with 2 to 3 tablespoons (30 to 40 ml) of activated charcoal made from dried coconut shell. Passive cotton detectors were also placed in the springs during the tracer test to check for optical brightener later in the laboratory with an ultraviolet light source. These detectors were constructed of similar nylon screen pouches, each containing several unbleached, pharmaceutical grade cotton balls.

Passive detectors were submerged and held in place with concrete anchors. The anchors were made by pouring concrete into styrofoam bowls and embedding a wire loop in the concrete before it hardened. Paper clips were looped through the nylon screen mesh of detectors and clipped onto the wire loop embedded in the concrete anchor. At collection time, each charcoal or cotton detector was placed into a small plastic bag which was labeled with the date of collection and the sample location.

Injection of fluorescing dyes in the field required

special precautions to reduce the risk of contaminating equipment or clothing and thus any samples. The dye was handled by one person, who was outfitted with a splash proof Serenac coverall, rubber boot covers and gloves (inner and outer), which were all sealed with duct tape. Direct Yellow 96 (DY96), which was one of the dyes shipped in powder form, had to be mixed in the field because of its tendency to cake in stored solutions. DY96 was mixed with water which was ponded at the Cory Lane injection site using a new 30 gallon (114 liter) plastic garbage can.

Each of the four remaining sinkholes did not generate sufficient runoff to flush dyes thoroughly into the bedrock groundwater system, Two 1500 gallon (5680 liter) tanks were set up on two of the injection sites and filled to capacity. Two inch diameter (5 cm) flexible plastic pipe was run from each tank to an adjacent injection sink. The two sinks,

the tanks simultaneously. During injection, water was flushed down the hole with the valve partially open while liquid dye was poured into the sink. After all of the dye was emptied, the valve was opened wide until all 1500 gallons (5680) of water was flushed down. After the tanks were completely drained, they were moved, refilled and used to flush dye down the remaining sinks, Lemon Lane North and 11th & Adams.

The selected sinks were prepared ahead of time, where

necessary, to receive the injection. Two of the sinks,

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and were full of gravel or debris which might interfere or absorb dye; therefore they were excavated down to bedrock, where a 3 inch (8 cm) PVC pipe was installed and afterward the hole backfilled. Of the remaining three injection sites, two had sinks with an open hole at the bottom (Lemon Lane North and 11th & Adams) and the third (Cory Lane) had a swallet which ponded stormwater at the terminus of an intermittent sinking stream.

Measurements of discharge, rainfall, specific conductivity, temperature, dissolved oxygen and pH were taken in the field.

Continuous average hourly discharge readings of Quarry (May 1991 - June 1992) and Illinois Central (July 1991 -June 1992) springs were accomplished using Omnidata Datapod II data recorders with Druck 5.0 psi (0.34 atm) transducers. Each data recorder transducer was calibrated to measure the depth of the water approximately four feet (1.2 meters) behind a 90 degree V-notch weir. Discharge (Q) in cubic feet per second (CFS) was computed using the depth of water over the base of the V-notch (Head or H) by the following formula: $Q = 2.5H^{2.5}$ (Grant, 1988). Note: Discharge values are also reported in cubic meters per second (CMS) in the text; figures and graphs report discharge in cubic feet per second only. Hourly rainfall data was continuously recorded using the second channel of the data recorder located at the Quarry spring weir connected to a Sierra-Misco model 2502 tipping bucket rain gauge. The rain gauge was factory calibrated and rechecked in the lab to measure 1/100th of an inch of rain (0.25 mm) for each tip of the bucket. The data recorder was set to count the number of tips per hour and record the sum. Alternate sources of hourly rainfall data were rain gauges in the vicinity operated by Westinghouse Electric Corporation and I.U. Physical Plant, which were consulted when the field recorder was down for repairs.

Specific conductivity measurements were taken using a Cole-Parmer model 4070 hand held meter at Illinois Central spring and a Hanna Instruments model HI8033 hand held meter at Quarry spring.

Dissolved oxygen was read using a Cole-Parmer model 9070 hand held meter at Illinois Central spring and an Orion Research, Inc. model 820 hand held meter at Quarry spring.

Temperature and pH were read with two Orion Research model SA250 Eh/pH/Temperature hand held meters.

Two and four ounce (60 and 120 ml) white opaque polyethylene bottles were used to gather water samples for analyzing dye concentration and major ions back in the laboratory. New bottles were rinsed with sample water several times before being filled and they were transported and stored in coolers. The samples obtained for analyzing major ions were filtered using 0.2 micron filter paper within 48 hours and refrigerated. Cation samples were acidified with nitric acid for preservation at the same time.

Laboratory Methods:

The Indiana University Department of Geological Sciences Water Research Laboratory was the location used for preparation of dyes, field materials and all analysis of water samples except cation concentration, which were conducted at the Indiana Geological Survey on the Jerrell-Ash ICP model 975 Plasma Atomcomp inductively coupled plasma atomic emissions spectrometer.

Two of the dyes which were in powder form were mixed in the laboratory well ahead of the tracer test to reduce any possibility of contamination. Plastic jugs used to contain the dissolved dye powders were filled with deionized water, allowed to stand for several hours, after which the water was checked for any dye contamination using the scanning spectrofluorophotometer. All jugs used were found to have dyes just at or below the detection limit. Sixteen ounces (454 grams) of Fluorescein (C.I.# Acid Yellow 73; AY73) powder were obtained at 75% concentration level, yielding 12.0 ounces (341 grams) of pure Fluorescein. The AY73 powder was divided into two equal parts, each mixed with

approximately a one half gallon (2 liters) of deionized water under a fume hood in a plastic milk jug. Similarly, about 16.0 ounces (454 grams) of Eosine (C.I.# Acid Red 87; AR87) dye at 80% concentration, yielding 12.8 ounces (363 grams), were divided into equal parts and mixed with deionized water in two one gallon plastic jugs, each half full. Because of the tendency for Direct Yellow (C.I.# Direct Yellow 96; DY96) to cake and because DY96 requires larger quantities of water to dissolve, it was mixed in the field at the injection site in a new 30 gallon (114 liter) plastic garbage can. Concentration data for DY96 are not available from the manufacturer so there was no possibility to compute concentration values or mass balance data for the DY96. Rhodamine WT (C.I.# Acid Red 388; AR388, or also RWT) and Optical Brightener (C.I.# Fluorescent Brightener 28; FB28) were both in liquid form and therefore required no special preparation prior to injection. The 9 pounds (4.1 kilograms) of AR388 came as a 20% concentration solution for an actual total of 1.8 pounds (817 grams) used. Again, concentration data are not available from the manufacturer for FB28, so only relative intensity values are reported.

A Shimadzu RF5000U scanning spectrofluorophotometer (SSFP) with a 150 watt xenon source lamp was used to scan samples for presence of the fluorescing dyes and identify them based on the peak emission wavelength in nanometers (nm). A calibration curve set was available in the

laboratory to convert the raw intensity numbers into parts per billion (ppb) values for the AY73, AR87 and AR388 dyes. (Note: ppb units are nearly equivalent to milligrams per liter (mg/l).) Concentration data for FB28 and DY96 were not available from the manufacturer; therefore, only relative intensity values are reported.

 Prior to the actual tracer test, samples of all dyes were run on the SSFP to verify the characteristic average peak wavelength of fluorescence. The wavelengths for each dye were as follows: FB28 - 405 nm, DY96 - 455 nm, AY73 -512 nm, AR87 - 537 nm, AR 388 - 577 nm (see Table 1.). Peaks from sample runs falling within +/- 5 nm of the above values were identified as the respective dye and recorded as such.

TABLE	1.	DYE	FLUORES	CENCE (+,	/-5rm)
FB28	DY9	-	AY73	AR87	AR388
405nm	4551		512nm	537nm	577nm

Samples brought back from the field for dye analysis were stored in coolers out of direct light in the laboratory at room temperature. All samples were analyzed using the SSFP. Sample water was decanted into plastic fluorometric cells (cuvettes), which were placed into the SSFP scanning chamber. A printed graphical report was produced for each sample run and was labeled by the analyst with the sample number, location name, date, time and analyst's initials. The same information was also recorded into a log book at the time of the scan along with identified peak wavelength, intensity and analysis date and time.

Charcoal and cotton detectors that were brought in from the field were immediately rinsed thoroughly under tap water to remove clay, silt, algae and foreign particles. They were placed back into their respective labeled plastic bag and refrigerated until analysis time.

At analysis time the charcoal was emptied into new 4 oz. (120 ml) clear plastic cups. Charcoal elutant made from ethanol, ammonium hydroxide, and distilled water in a 5:2:3 volumetric ratio was poured onto the charcoal, covering the top by about 1.0 oz. (30 ml). The containers were capped and stored out of direct light for approximately 2 hours. The elutant was then decanted into cuvettes and analyzed on the SSFP.

Cotton detectors were checked by placing them on brown packing paper, labeling with the location name and illuminating them in a dark room with a long wave UV lamp. Only detectors with the entire cotton mass that evenly fluoresced the characteristic blue-white were considered to be a positive indication of Optical Brightener. Cotton detectors were judged visually as being anywhere from strongly to weakly positive cr negative. Specks fluorescing

were not judged as a positive indication.

To analyze for anions, Cl.,NO₃ and SO₄²⁻, a Dionex Corporation, Series 4000i aqueous ion chromatograph was used. All samples were prefiltered through 0.2 micron cellulose nitrate filter paper. A syringe, which was rinsed 3 times with double deionized water, was used to inject each sample into the ion chromatograph. Prior to running a set of samples, the chromatograph was calibrated using a series of 3 ionic solution standards (each with Chloride, Nitrate and Sulfate at three concentration levels). The calibration was then verified with 2 check standards at two intermediate concentration levels. A graphical plot accompanied by a report of concentration values was produced for each sample. Runs of both check standards were performed at the end of each session to bracket the sample set as a verification of correct concentration readings.

A Jerrell-Ash ICP Model 975 Plasma Atomcomp inductively coupled plasma atomic emissions spectrometer was used to scan for four major cations: Ca^{2+} , Na^+ , Mg^{2+} , K^+ . Calibration was accomplished using 2 standards, each containing all four cations at concentrations bracketing the minimum and maximum anticipated sample levels. Each sample was drawn into the analyzer by a tube and scanned 4 separate times in sequence, each scan recording the concentrations for all four cations. The values from all four scans were then averaged to produce

concentration values. A report for each sample was produced by an IBM personal computer interfaced to the spectrometer.

Background and Procedure:

In preparation for the dye trace, background concentrations of existing tracers had to be established; therefore, taking a series of water samples from all sampling locations was necessary. The stations sampled in this investigation were previously located and chosen for the Westinghouse tracer tests conducted around the Lemon Lane sinkhole complex, and are listed in Table 2 and shown in Figure 7. Because numerous tracers have been injected within the last five years, low residual concentrations were expected to be present in the spring waters of at least some, if not most, of all area resurgences.

Tracer tests were conducted by Westinghouse Electric Corporation in 1987, 1989 and 1990 (McCann and Krothe, 1991). All tracers were injected into monitoring wells placed immediately around the perimeter of the Lemon Lane Landfill. The 1987 tracer test used Lithium Bromide as a tracing agent under dry fall conditions. Subsequently, background samples taken during the summer of 1991 included analysis for Lithium Bromide on the Dionex chromatograph. It was later determined that sample analysis could be greatly expedited if only fluorescing dyes were used, which
TABLE 2 MONITORING STATIONS

Station is near a Primary Spring ------Illinois Central Quarry ICG-1 ICG-2 (D) ICG-3 (D) ICG-6 (D) Fell Iron (D) **Crestmont East Crestmont West Pumping Station** 17th Street Urban **Slaughter House Packinghouse Road** Packinghouse Culvert Robertson (D) Detmer East (D) Detmer West Stoney East Stoney West WN-1

Station is downstream of a Primary Spring Bypass 37 Snoddy A & B 7th and Adams Clear Cr. @ 1st. St. Clear Cr. @ 7th. St. Defeat Cr. East Defeat Cr. West (D) Kirby Road Sinking Creek Station is a backup point downstream of several primary Springs

Cascade Branch (D) Stouts Cr. East (D) Stouts Cr. West (D) Il Cen. @ Allen St. (D) Weimer Road (D)

D - Charcoal/Cotton detectors only, no grab samples taken during the tracer test. All other stations were monitored with detectors and grab samples. could all be identified on a scanning spectrofluorophotometer (SSFP). In addition to Lithium Bromide, the 1989 tracer test used three different fluorescing dyes, one for each of three injection wells. Dyes used during this high flow test after a 1.35" (34.3 mm) rainfall were: Fluorescent Brightener 28 (FB28), Fluorescein (Acid Yellow 73; AY73), and Direct Yellow 96 (DY96). Another high flow tracer test was performed in 1990; however in this case Rhodamine WT (Acid Red 388; AR388 or RWT) was used to provide the least interference with background dyes present from the prior tests.

Because a variety of the most commonly used fluorescing dyes had already been used in the karst groundwater system of the Lemon Lane Landfill, care had to be taken in evaluating background occurrence of these and any other dyes. Results from the previous traces showed that the springs receiving the highest concentrations of injected dyes were Quarry and Illinois Central springs. Both of these springs were sampled at least six times during the summer and fall of 1991, between July and October. In order to best determine the residual presence of the dyes for the remaining springs, four complete grab sampling rounds were carried out. The first three rounds were made during August and September of 1991, during which dry weather conditions prevailed. A number of the springs were dry and could not be sampled on one or more rounds. Sampling also occurred on

October 28 and November 20, 1991. The fourth complete background sampling round was collected on April 20, 1992, when baseflow conditions were elevated from recent rainfall. At that time, all springs were flowing.

Passive detectors in the form of activated charcoal packets were prepared for the tracer test. A set of the charcoal detectors was submerged in all flowing resurgences for background level sampling during the period October 8 -21, 1991. Using passive detectors ensured that any tracer missed by grab sampling rounds would be adsorbed by the activated charcoal. The elutant prepared from these detectors was scanned using the SSFP.

All of the necessary preparations were made by the end of 1991; the next step was to wait for a rain storm of sufficient precipitation to occur. The ideal circumstance needed for injection required more than 1 inch (25 mm) of rain to fall within a three to six hour period in order to cause high base flow conditions and generate the necessary surface runoff to flush tracers into the injection sinks. The rainy season occurs in the spring months of March, April and May, when frequent high precipitation storms occur in southern Indiana. In addition to needing a certain magnitude of storm event, the tracer test required that sufficient persons were available to assist with dye injection and make frequent sampling rounds.

The first large rain event occurred on March 18, 1992,

during which slightly more than 1 inch (25 mm) of rain fell. Conducting the test was not possible at that time because surface runoff was not generated at 3 of the 5 injection sinks, and a sustained runoff was necessary to completely flush tracer dye into the bedrock system. Also, there were not enough field assistants available to perform the test properly.

After the March 18 rain event, it was realized that water tanks would be needed at two or more of the injection sites to flush the dyes into the bedrock. At least three of the sinks - Lemon Lane North, **March and March -** would require substantially more than 1 inch (25 mm) of rainfall to generate sufficient inflow to flush the dyes. Two 1500 gallon (5680 liter) tanks were situated and filled at the two. sink holes deemed least likely to develop surface inflow during a storm event: **March and American**

Rain events occurring in April and early May were about two-thirds of an inch (17 mm) or less in magnitude. Typical spring rainy seasons provide numerous rains nearing or exceeding 1 inch (25mm).

On May 12, 1992, 0.74 inches (19 mm) of rain fell between 12:00 and 17:00 hours. Quarry spring reached its maximum discharge of 0.561 CFS (0.0157 CMS) at 21:00 hours. Field chemistry stations were set up and active at Illinois Central and Quarry springs between 13:30 and 22:30 hours on May 12. Field measurements and bottled water samples were taken during that time interval. However, it was decided to wait for a larger rain event to perform the dye trace.

Six days later, on May 18, a rain event occurred during which about 0.7 inches (18 mm) of rain fell within three hours. The Cory Lane sink became ponded and the 11th & Adams sink received runoff. Also, enough suitable field assistants were available to help inject dyes and collect grab samples from all needed stations. Because the rainy season was nearly over and there was a risk of not having any better opportunities later, the decision was made to use this rain event for the dye trace.

Quarry spring reached a maximum discharge of 0.727 CFS (0.0204 CMS) at 17:14 hours on May 18. This exceeded the 0.561 CFS (0.0157 CMS) discharge occurring on May 12 after a slightly smaller rain event. A 0.30 inch (8 mm) rainfall occurring on May 17 between 14:00 and 16:14 hours helped to saturate the ground and raise the baseflow level slightly. Discharge in Quarry spring had returned to 0.169 CFS (0.0047 CMS) just prior to the rain event occurring on May 18.

All five fluorescing dyes were injected on May 18, 1992, beginning after noon, after the rainfall had ceased. The first injection was made at the Cory Lane sink at 12:32 hours. It consisted of 4 pounds (1.8 kg) of DY96 which was mixed on site and poured into the water ponded over the sink. The second injection was made at the **Example 1** sink at 12:45 hours using 1500 gallons (5680 liters) of water

from a tank to flush 25 gallons (94.6 liters) of FB28 solution down a 4 inch (10 cm) PVC pipe into bedrock. Another water tank had been set up at the sink, about 400 ft. (122 meters) South-west of the Lemon Lane Landfill. The sink was the third site injected. Approximately 12.0 ounces (341 grams) of powder AY73 mixed into solution (see Methods section) was injected into the sink at 13:20 hours, followed by 1500 gallons (5680 liters) of water.

At this time both water tanks were moved to the remaining two injection sites and refilled. As soon as the next water tank was ready at the 11th & Adams Street sink, 12.8 ounces (363 grams) of powder AR87 mixed in solution was injected and flushed with 1500 gallons (5680 liters) of water; this occurred at 16:02 hours. The fifth and final injection occurred at 17:05 hours at the Lemon Lane North sink, where 28.8 ounces (817 grams) of AR388 solution was injected followed by 1500 gallons of water.

Sampling of springs and backup stations began on May 18, 1992, when the dye tracers were injected and concluded on June 12, 1992, when the last passive detector was retrieved. Analysis of all grab samples and passive detectors was completed in the weeks that followed.

Results:

There have been previous dye traces performed around the Lemon Lane Landfill, so it was not surprising that significant residual dyes were detected by analysis of Illinois Central and Quarry spring background grab samples (see Table 3). Illinois Central spring waters contained levels of AY73 between 0.22 and 8.7 ppb and AR388 between 3.1 and 15.7 ppb. Quarry spring waters contained similar concentration levels of background dye: AY73 between 0.23 and 1.8 ppb and AR388 between 2.7 and 10.1 ppb. These levels are relatively high; therefore injecting the same dyes again required that large quantities be used in order to overwhelm the background and provide a positive indication.

Fluorescein (AY73) was present in the background of virtually all of the other surrounding springs. Only Defeat Creek West, Detmer East and 7th & Adams were negative for AY73, but they were also dry for most of the sampling runs.

Rhodamine WT (AR388), showed up in fewer of the remaining springs. Stouts East, Bypass 37, Packinghouse Culvert, Snoddy A & B, Kirby Rd., Stoney East, Stoney West, Weimer Rd., ICG-1, ICG-2, ICG-3, Clear Creek @ 7th St., Clear Creek @ 1st St., and Illinois Central @ Allen St. contained background levels of AR388.

There is no known report of Eosine (AR87) being used as

	During Low Flow (Maximum Value)		During High Flow (Maximum Value)		Charcoal
Station	Tracer	Conc (ppb)	Tracer	Conc (ppb)	Bug Tracer
Illinois Central	AY73 AR388	8.70 15.7	-na-		-na-
Quarry	AX388 AY73	1.80	AY73	0.093	- 22.
Quarry	AR388	10.1	AR388	0.85	-na-
7th & Adams	-dry-	10.1	ACJOU	0.05	-na-
Urban	AY73	0.025	AY73	0.037	-na-
17th Street	-dry-		AY73	0.024	-na-
Crestmont East	AY73	0.038			AY73**
Crestmont West	AY73	0.019	AY73	0.013	AR388**
	AR87	0.015			
Pumping Station	AY73	0.014			AY73
	AR87	0.020			DY96
Cascade	AY73	0.150			AY73
Stouts Creek East	AY73	0.018			AY73
	AR388	0.046			
Stouts Creek West	AY73	0.025			AY73
Bypass & 37	AY73	0.051			-na-
	AR388	0.087			
Packinghouse Road	AY73	0.018			AY
Packinghouse Culvert	AY73	0.014			AY73
	AR388	0.046			
Slaughterhouse	AY73	0.075	AY73	0.0003	AY 73
Snoddy A & B	AY73	0.015	AY73	0.001	AY73
	AR388	0.048			
Detmer East	-dry-		DY96	9.33*	-na-
Detmer West	AY73	0.024	AY73	0.0004	AY73
- • •			DY96	12.54*	
Robertson	AY73	0.023	DY96	10.08*	AY73
Defeat Creek East	AY73	0.037	AY73	0.001	AY73
	3		DY96	17.98*	
Defeat Creek West	-dry-	0.000	****	0 007	-na-
Kirby Road	AY73 Ar388	0.020 0.140	AY73 DY96	0.003 21.73*	AY73
Sinking Creek	AK388 AY73	0.068	D196	21.73-	AY73
Stoney East	AY73	0.015	DY96	9.12*	AY73
Sconey East	A175 AR388	0.036	0190	9.12~	AI / S
Stoney West	AY73	0.042	DY96	15.55*	AY73
Beomey West	AR388	0.080	DIJU	10.00	DY96
Weimer Road	AY73	0.023	DY96	15.29*	AY73
Weimer Noad	AR388	0.078	0190	23.25	n1 / J
WN-1	-dry-	••••	AY73	0.002	-na-
ICG-1	AY73	810	AY73	0.486	AY73
	AR388	4.6	DY96	15.29*	AR388
ICG-2	AY73	0.025	AY73	0.004	AY73
	AR388	0.058			
ICG-3	AY73	0.063	AY73	0.044	AY73
	AR388	0.160			
ICG-6	-na-		AY73	0.003	-na-
Clear Cr. @ 7th St.	AY73	0.040	AY73	0.011	AY73
	AR388	0.064	DY96	25.40*	
Clear Cr. @ 1st St.	AY73	0.054	AY73	0.005	AY73
	AR388	0.095	AR388	0.052	
			DY96	21.69*	
Il. Cen. @ Allen St.	AY73	1.25	AY73	0.009	AY73
	AR388	3.80	AR388	0.188	AR388
			DY96	15.62*	
Fell Iron	AY73	0.034	AY73	0.001	AY73
	AR87	0.036	DY96	10.30*	AR388

* - Value represents peak intensity.
** - Charcoal bug monitored Chrestmont A & B combined.
na - Charcoal bug or grab sample not available.
Note: Values reported are maximum available from sample flow regime. In many cases only one was available.

a tracer in the Lemon Lane Landfill area. Nevertheless, background scans revealed peaks identifying Eosine at Crestmont West, Pumping Station and Fell Iron springs.

Fluorescent Brightener peaks may be scanned at wavelengths anywhere from 400 nm to 450 nm. Most of the springs, including Illinois Central and Quarry, contained background levels of brightening agents falling within that range. The brightener agent used for this tracing study actually scanned at a wavelength of 405 nm average during preliminary lab tests. However, due to the meta-stable nature of Fluorescent Brightener 28, peaks scanned from water samples may vary considerably from the 405 nm value, perhaps +/-25 nm or more.

Direct Yellow (DY96) was present in approximately one third of the springs. They include Detmer West, Detmer East, Robertson, Defeat Creek East, Kirby Rd., Stoney East, Stoney West, Weimer Rd., ICG-1, Clear Cr. @ 7th St., Clear Cr. @ 1st St., Illinois Central @ Allen St., and Fell Iron.

A summary of dye detection results from the tracer test is presented in Table 4 and graphically in Figure 9. First occurrence and maximum occurrence of detected dyes are presented in tables 5 and 6 respectively.

Illinois Central spring grab samples were noted to contain the highest levels of detection in major dye pulses (See Figure 10.). Eosine dye first occurred at the May 19 TABLE 4

SUMMARY OF DYE TRACER DETECTION

STATION	TRACER	DATE & TIME OF FIRST DETECTION		DATE & TIME OF MAXIMUM CONCENTRATION		METHOD OF DETECT
Illinois Central	AY73	5/19	0800	5/19	1130	GR
	AR87	5/19	0200	5/19	0400	GR
	AR388	5/19	1500	5/19	2030	GR
Quarry	AY73	5/19	1000	5/19	1640	GR
-	AR87	5/19	0410	5/19	0555	GR
	AR388	5/19	1800	5/19	2135	GR
7th & Adams	AY73	5/19	0725	5/20	1840	GR
	AR8 7	5/19	1055	5/19	1055	GR
Urban	FB28*	5/12-19		5/19-29		СО
17th Street	FB28*	5/12-19		5/12-19		СО
Cascade	AY73*	5/12-19		5/12-19		СН
Stouts Creek East	AY73	5/29-6/12		5/29-6/12		СН
	AR388	5/12-19		5/19-29		СН
Packinghouse Road	AR87*	5/14-19		5/14-19		СН
	AR388	5/19	0150	5/19	0830	GR
Packinghouse Culvert	AY73	5/19	0145	5/19	0145	GR
<u>.</u>	AR87*	5/14-19		5/14-19		СН
	AR388	5/19	0145	5/19	0145	GR
Slaughter House	AY73*	5/14-19		5/19-6/12		СН
Snoddy A & B	AY73	5/29	2021	5/29	2021	GR
Detmer West	AY73	5/19	2002	5/19	2002	GR
	FB28*	5/19-29		5/19-29		СО
Stoney East	DY96	5/18	1525	5/18	1605	GR
	FB28	5/18	1950	5/18	1950	GR
Weimer Road	AY73*	5/14-19		5/19-29		СН
	FB28	5/14-19		5/14-19		CO
ICG-1	AY73	5/19	2015	5/19	2015	GR
	AR87	5/19	1045	5/19	1045	GR
	AR388	5/19	2015	5/20	0735	GR
ICG-3	AY73*	5/12-19		5/12-19		СН
Clear Creek @ 7th St	FB28	5/14-19		5/14-19		СО
Clear Creek @ 1st St	AY73	5/22	1930	5/22	1930	GR
	FB28*	5/12-22or27		5/12-22or27		СО
Ill Cen @ Allen St.	AY73	5/12-19		5/19-29		СН
	AR87	5/12-19		5/12-19		СН
	AR388	5/12-19		5/19-29		СН

AY73 is Acid Yellow 73 or Fluorescein AR87 is Acid Red 87 or Eosine AR388 is Acid Red 388 or Rhodamine WT (RWT) DY96 is Direct Yellow 96 FB28 is Fluorescent Brightener 28 an optical brightener GR - grab sample CH - charcoal bug (date indicates interval at station) CO - cotton bug (date indicates interval at station)

CO - Cotton Dug (date indicates interval at sta

* - indicates trace is not definite



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TABLE 5 - FIRST OCCURANCE OF DYE IN GRAB SAMPLES

	AY73	AR87	AR388	DY96	FB28
STATION	CONC DATE TIME (PPB)	CONC DATE TIME (PPB)	CONC DATE TIME (PPB)	CONC DATE TIME (INT)	CONC DATE TIME (INT)
Illinois Central Quarry 7th & Adams Packinghouse Road Packinghouse Culvert Snoddy A & B Detmer West Stoney East ICG-1	17.03 5/19 0800 7.75 5/19 1000 0.017 5/19 0725 0.051 5/19 0145 0.381 5/29 2021 0.064 5/19 2002 1644 5/19 2015	395.3 5/19 0200 390.1 5/19 0410 2.19 5/19 1055 12.4 5/19 1045	23.8 5/19 1500 24.8 5/19 1800 6.33 5/19 0150 209.4 5/19 0145	64.2 5/18 1525	4174 5/18 1950
Clear Cr. @ 1st St	0.173 5/22 1930	12.4 5/15 1045	0.75 5/15 2015		

TABLE 6 - MAXIMUM OCCURANCE OF DYE IN GRAB SAMPLES

	AY73	AR87	AR388	DY 9 6	FB28
STATION	CONC DATE TIME (PPB)	CONC DATE TIME (PPB)	CONC DATE TIME (PPB)	CONC DATE TIME (INT)	CONC DATE TIME (INT)
Illinois Central	964 5/14 1130	1549 5/19 0400	639 5/19 2030		
Quarry	542 5/19 1640	987 5/19 0555	303 5/19 2135		
7th & Adams	0.33 5/20 1840	2.19 5/19 1055			
Packinghouse Road			43.4 5/19 0830		
Fackinghouse Culvert	0.051 5/19 0145		209.4 5/19 0145		
Shoddy A & B	0.38 5/24 2021				
Detmer West	0.064 5/19 2002				
Stoney East				3615 5/1> 1605	4174 5/18 1950
ICG-1	1644 5/19 2015	12.4 5/19 1045	2.2 5/20 0735		
Clear Cr. @ 1st St	0.173 5/22 1930				

AY73 is Acid Yellow 73 or Fluorescein AR87 is Acid Red 87 or Eosine AR388 is Acid Red 388 or Rhodamine WT (RWT) DY96 is Direct Yellow 96 FB28 is Fluorescent Brightener 28 an optical brightener

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ILLINOIS CENTRAL SPRING DYE CONCENTRATION & DISCHARGE 5/18/92 - 5/25/92



(5/19) 02:00 hour sample at 395 ppb (10 hours after injection time = AIT). Peak Eosine concentration, 1549 ppb, occurred in the 5/19 04:00 hour sample (12 hrs AIT). AY73 was first detected at 17 ppb in the 5/19 08:00 hour sample (18.5 hrs AIT). Peak AY73 concentration, 964 ppb, occurred at 5/19 11:30 hours, 22 hours after injection. AR388 was the last dye to be detected at Illinois Central. It was first found 5/19 15:00 hours at 23.8 ppb (22 hrs. AIT) and reached a maximum of 639 ppb at 5/19 20:30 hours (25.5 hrs. AIT).

Quarry spring received all three of the above dyes delayed approximately 2 to 3 hours after Illinois Central spring, and peak concentration values were slightly attenuated in comparison (See Figure 11.). Eosine was first detected in the 5/19 04:10 hour sample at 390 ppb and peaked at the 5/19 05:55 hour sample with 988 ppb. AY73 followed at 5/19 10:00 hours with 7.8 ppb and reached its highest level at 5/19 16:40 hours with 542 ppb. Lastly, the AR388 pulse began at 5/19 18:00 hours at 24.8 ppb and reached a maximum at 5/19 21:35 hours reading 303 ppb.

None of the remaining stations revealed fluorescing dyes in the order of magnitude to which Illinois Central and Quarry springs did, except for ICG-1. A sample from ICG-1 on 5/19 at 20:15 contained AY73 at 1644 ppb, 31 hrs. AIT, the first and maximum occurrence.

Fluorescein (AY73) occurred as a minor detection at 7th



& Adams spring at 0.33 ppb, 2 days AIT. Backup stations Illinois Central @ Allen St. and Clear Creek @ 1st St. had charcoal detectors which adsorbed AY73 above background levels. A number of other stations had sporadic, nearbackground levels of AY73 which are difficult to judge as positive traces; they are listed in Table 4.

Eosine (AR87) was detected at moderate concentration levels in ICG-1 (12.4 ppb, 19 hrs. AIT) and 7th & Adams (2.19 ppb, 19 hrs. AIT). Charcoal detectors adsorbed Eosine at Packinghouse Culvert, Packinghouse Road and Urban springs, and at backup stations Stouts East and Illinois Central @ Allen Street.

Rhodamine (AR388) was detected in moderate levels in two springs. Packinghouse Culvert had the most AR388 on 5/19 at 08:30 hours (72.8 ppb, 15 hrs. AIT), with initial detection on 5/19 at 01:45 hours. Packinghouse Road showed the most dye also on 5/19 at 08:30 hours (43.5 ppb, 15 hrs. AIT) with first detection on 5/19 at 01:50 hours. Charcoal detectors adsorbed AR388 at Urban, Crestmont A & B, Detmer East, Detmer West, Robertson, Defeat East, Defeat West, ICG-6 and W-1, and backup stations Stouts East, Stouts West, Illinois Central @ Allen St. and Clear Creek @ 1st St.

Fluorescent Brightener (FB28) reached its highest concentration level at Stoney East with initial and highest detection (intensity of 5174.2 on the SSFP) on 5/18 at 19:50 hours, 7 hours after injection. Charcoal detectors did not

reveal any positive detections of FB28, aside from Stoney Bast. The only scans showing FB28 at 405 nm were near the detection limit: Detmer East, Detmer West, ICG-2, ICG-6 and Clear Creek @ 7th St., and slightly higher for Stoney West. Sporadic, near-background levels were detected in grab samples at Defeat Creek East and Sinking Creek, again with no traces which can be positively identified with much certainty.

Direct Yellow (DY96) also had its highest concentration level (intensity 3372 on the SSFP) at Stoney East with breakthrough first appearing on 5/18 at 15:50 hours, just 3.3 hours after injection time. The charcoal detector elutant scans revealed no concentration levels high enough to be considered a positive trace apart from at Stoney East.

Cotton detectors were used for backup identification of FB28. They may be considered a more reliable means of identification when SSFP scans reveal no clear peaks. Although there was some overlap, the cotton detectors were placed out for 3 time periods during the dye trace. Period 1 covered May 14 - May 19, Period 2 covered May 19 - May 29 and Period 3 covered May 29 - June 7, 8, 11 or 12, depending on pickup date by the field assistants. Period 1 shows strongly positive detections of FB28 at Stoney East and Clear Cr. @ 7th St., and backup station Weimer Rd. (See Table 7.). Weak to very weak indications occurred at Urban, 17th St. and Clear Cr. @ 1st Street. Period 2 continued to

TABLE 7 - COTTON BUG DETECTION OF FLUORESCENT BRIGHTENER

SPRING	SAMPLE INTERVAL	UV DETECT	SAMPLE INTERVAL	UV DETECT	SAMPLE INTERVAL	UV DETECT
IC	none		none		none	
QUARRY	5/19-21/92		5/21-29/92		none	
7TH&ADAMS	5/14-19/92		5/19-29/92		5/29-6/11/92	
URBAN	5/12-19/92	VWP	5/19-29/92	WP	5/29-6/7/92	-
17TH ST	5/12-19/92	WP	5/19-29/92	WP	5/29-6/7/92	
CRESTMT E&W	5/12- NF		5/??-30/92		5/30-6/7/92	
PUMPING STA	5/12-19/92		5/19-29/92		5/29-6/7/92	
CASCADE	5/12-19/92		5/19-29/92		5/29-6/12/92	1
STOUTS E	5/12-19/92		5/19-29/92		5/29-6/12/92	
STOUTS W	5/12-19/92		5/19-29/92		5/29-6/12/92	
BYPASS&37	5/14-19/92		5/19-29/92		5/29-6/7/92	-
PH ROAD	5/14-19/92		5/19-29/92		5/29-6/8/92	
PH CULVERT	5/14-19/92		5/19-29/92		5/29-6/8/92	
SL HOUSE	5/14-19/92		5/19-29/92		5/29-6/8/92	
SNODDY A&B	5/14-19/92		5/19-29/92		5/29-6/8/92	
DETMER E	5/12-19/92		5/19-29/92		none-dry	
DETMER W	5/12-19/92		5/19-29/92	WP	5/29-6/8/92	
ROBERTSON	5/12-19/92		5/19-29/92		5/29-6/8/92	
DEFEAT CR E	5/14-19/92		5/19-29/92		5/29-6/8/92	
DEFEAT CR W	5/14-19/92		5/19-29/92		none-dry	
KIRBY RD	5/14-19/92		5/19-29/92		5/29-6/11/92	
SINKING CR	5/12-19/92		5/19-29/92		5/29-6/11/92	
STONEY E	5/12-19/92*	SP	5/19-29/92	SP	5/29-6/11/92	SP
STONEY W	5/12-19/92*		5/19-29/92		5/29-6/11/92	
WEIMER RD	5/14-19/92	SP	5/19-29/92	SP	5/29-6/12/92	
WN-1	5/14-19/92		5/19-29/92		5/29-6/12/92	
ICG-1	5/12-19/92		5/19-29/92		5/29-6/11/92	·
ICG-2	5/12-19/92		5/19-29/92		5/29-6/12/92	
ICG-3	5/12-19/92		5/19-29/92		5/29-6/12/92	
ICG-6	5/12-21/92		5/21-29/92		none	
CC 🤮 7TH ST	5/14-19/92	SP	5/19-29/92		5/29-6/11/92	VWP
CC 🤮 1ST ST	5/12-22or27	? WP	5/??-6/1/92	1	6/1 -11/92	
ICQALLEN ST	5/12-19/92		5/19- NF		5/29-6/12/92	
FELL IRON	5/14-19/92		5/19- NF		5/29-6/11/92	
BLANK - no	UV fluoresc	ence.				

BLANK ·	- no UV fluorescence.
SP ·	- Strongly positive (mass fluoresced brightly).
WP -	- Weakly positive (mass fluoresced only dimly).
	- Very weakly positive (mass fluoresced but barely visible)
NF ·	- cotton bug not found in placement location.
* •	- removed at 0030 hours.
	dete e ter
All co	tton bugs were place and removed in the afternoon (3-7pm)
except	where noted.

show strong indications at Stoney East and backup station Weimer Rd., while a weakly positive indication occurred at Detmer West. Weakly positive readings continued at Urban and 17th St. springs. Third period indications of FB28 narrowed to Stoney East (strongly positive) and Clear Creek @ 7th St. (weakly positive).

Background cotton detectors were not placed in any springs prior to the tracer test. However, previous Westinghouse analyses for background showed FB28 repeatedly occurring at Urban, Detmer, Robertson and ICG-1, ICG-2, ICG-3 and ICG-6 springs, and often at Slaughterhouse. Therefore, anything short of a strongly positive indication of FB28 verified in water samples by the SSFP and in the cotton detectors by UV fluorescence, not achieved at the above eight locations, is suspect. In addition, the Clear Creek @ 7th. St. station, which strongly fluoresced, is located in a storm sewer behind large buildings near downtown. Water here may be contaminated by sewage, which often contains brightening agents. Since the grab samples were negative, this station is also suspect. Positive traces of FB28 from this dye trace can only be judged to have occurred at Stoney East, and at Weimer Road, based on strongly positive results from the cotton detectors.

Results of the chemical parameters taken on May 12 and 18 for Illinois Central and Quarry springs are presented in

chemographs (See Figures 12 - 33). Conductivity is the only chemical parameter which was measured on both May 12 and 18. All other parameter measurements were limited to May 12.

Conductivity for Illinois Central (I.C.) and Quarry springs both followed a similar trend during the dye trace beginning on May 18 (See Figures 12. and 13.). Levels dropped rapidly to 630 microsiemens (μ S) at I.C. and 528 μ S at Quarry during the rise in discharge. But conductivity suddenly increased with peak levels (794 μ S at I.C. and 581 μ S at Quarry) which lagged slightly behind the hydrograph peak. Following the hydrograph peak, conductivity quickly dropped off. Then as discharge fell off, conductivity levels rose back to values of about 750 μ S at Illinois Central and 620 μ S at Quarry.

The chemical parameters of Illinois Central and Quarry springs were monitored on May 12 for shortly over 9 hours. At Illinois Central, the duration of monitoring covered both the rise and fall of spring discharge. Sampling at Quarry was concluded approximately an hour before spring discharge began to fall off.

The conductivity measured at Illinois Central on May 12 shows an attenuated version of the response observed at the same spring during the May 18 and 19 monitoring period (See Figure 14.). Conductivity values dropped off immediately preceding the rise in discharge and increased again to a peak value which lagged behind the maximum discharge.









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Following peak conductivity, the levels dropped briefly and then began to rise again as discharge fell off. Quarry spring conductivity on May 12 also followed the same trend as during the May 18 and 19 measurement period, until the time when monitoring was ceased; it appears that conductivity values were approaching peak level during the sustained maximum recorded spring discharge (Figure 16.).

To varying degrees, cation concentrations at Illinois Central spring all displayed a similar pattern (See Figures 18 - 21.). Concentrations decreased during the rise in spring discharge, and the peaks each occurred approximately two hours following maximum discharge. Cation concentrations for Quarry showed a different trend. Calcium, Magnesium, and Sodium all increased in concentration as discharge rose, while Potassium generally dropped, except for two intermittent peaks (See Figures 22 -25.).

Anion concentrations at Illinois Central were quite variable, with concentration peaks occurring shortly before and following maximum discharge (Figure 26). Anion concentrations at Quarry decreased quickly early during the rise in discharge and rose until maximum discharge occurred (Figure 27). A slight peak occurred in chloride and nitrate concentrations prior to maximum discharge at Quarry spring.

Temperature decreased throughout the monitoring period on both springs (See Figures 30 and 32.). Dissolved oxygen





















was variable, with a slight rising trend in both springs as flow increased (Figures 31 and 33.). PH and Ca:Mg ratios are presented in Figures 15 and 17, and 27 and 29, respectively.

Discussion:

In cases where the dye concentration found in the springs was not high, criteria needed to be established to determine whether a dye could be said to have reached a spring with a high level of certainty. In order to conclude that a dye has been traced to a spring, several factors are considered. First, the concentration had to be at least one order of magnitude higher than the level of dye detected in the background samples, if any. However, background level concentration can vary with discharge; more specifically, elevated flow background samples generally contained lower levels of dye than low flow background samples. Because of this, dye concentrations from the actual tracer test measured during high flow at the pre-dye pulse phase were used as the standard of comparison in some cases, rather than the background concentration levels obtained before the tracer test. Finally, the distinctiveness of a peak was considered, in addition to its absolute intensity, when judging SSFP scans for dye traces identified as resulting from the present dye injection. If a peak was not clearly

distinct from the raman water curve on the SSFP, detection could not be considered positive.

In consideration of the previous Westinghouse Lemon Lane Landfill dye traces (McCann & Krothe, 1991), the current study does not seem to present surprising results. In terms of relative concentrations, Illinois Central and Quarry springs received most of the dye injected into the three sinks immediately surrounding the Lemon Lane Landfill: Lemon Lane North, 11th & Adams and Packinghouse Road and Packinghouse Culvert also received high concentration levels of Rhodamine WT from the Lemon Lane North sink. This is not surprising, because the Lemon Lane North sink lies in close proximity to the north side of the major topographic divide.

Both Fluorescent Brightener (FB28) and Direct Yellow (DY96) drained to Stoney East with no positive traces to Stoney West. This may seem surprising considering the locations of the two springs. However, this is the same result found in previous trace studies. Stoney West received DY96 concentrations approximately twice that of the background reading. This indicates that Stoney West has little or no hydraulic connectivity to the source waters feeding Stoney East. ICG-2, ICG-3 and ICG-6 received indications of DY96 slightly above the detection limit as measured through the charcoal detectors, showing perhaps a very minor connection to the Corey Lane sink, but by no

means a trace which can be said to be positive with certainty.

The major hydraulic connections around the Lemon Lane Landfill seem to be easily identifiable given the results of this study. The more difficult question to answer is whether dyes are spreading across drainage divides, and if so by what mechanism. The proposed mechanism of flooding the epikarst with waters (McCann and Krothe, 1991), would be one possibility explaining that drainage divide could be positively shown to be bridged. Widespread occurrences of Fluorescein (AY73) in the background samples support the notion that at least minor quantities of dye are being carried across divides as groundwater repeatedly floods to higher levels. Alternate flow pathways are created by the flooding, diverting some water (with dye) across the divides.

Dye trace water samples from Detmer West spring showed some interesting trends in AY73 concentrations, possibly illustrating cross drainage divide spreading. While there was no single strong detection, AY73 concentrations jumped at least one order of magnitude in two samples: the first was on 5/19 at 20:02 hours at 0.064 ppb (previous two readings were 0.001 ppb), and the second was on 5/23 at 18:53 hours at 0.012 ppb (previous two readings were below the detection limit at 0.0001 and 0.003 ppb).

Packinghouse Road and Packinghouse Culvert samples also

revealed some interesting results. Both springs did not show any Eosine (AR87) in background grab samples or background charcoal detectors. During the tracer test grab samples also were not observed to have any detectable Eosine. However, elutants from charcoal detectors were scanned positively for Eosine. Values of 41.5 and 14.9 ppb from Periods 1 and 2 (respectively) were read at Packinghouse Road. Similarly, values of 85.0 and 28.0 ppb were taken during Periods 1 and 2 at Packinghouse Culvert. These concentrations represent accumulated dye on charcoal over time, but the scans from the elutant were distinct from the raman water curve in all four cases.

Snoddy A & B grab samples also provided some interesting data. On three occasions the concentration sporadically jumped one to three orders of magnitude over the typical readings taken during the tracer test.

These examples suggest that even during this relatively moderate flow tracer test, perhaps minor quantities of dye mass are migrating across the major drainage divide. While not strong, there is at least some evidence to support the notion that dyes are being pirated over to springs on the west side of the north-south major topographic high. It would be reasonable to expect that at much higher flow conditions, more examples of minor dye diversion could occur, as seen in earlier tracer tests performed at the Lemon Lane Landfill site. During any single dye tracer test, it is probable that very little dye is spread across the major divide; rather it is likely that repeated epikarst flooding events are required.

The dye trace results of this study together with results of dye flow in the literature suggest an epikarst storage mechanism with respect to dye movement. The present chemical data gathered and presented in chemograph format also may add credence to the notion of epikarst groundwater storage.

The most important evidence for epikarst storage comes from the conductivity measurements taken during the dye trace beginning on May 18. Trends from both Illinois Central and Quarry springs are similar to those shown by the Westinghouse chemograph produced in 1990 (See Figure 6.). The drop in conductivity level during the rise in discharge represents phreatic water giving way to water from concentrated recharge via conduit flow. The sharp peak lagging slightly behind maximum flow indicates that epikarst water is being flushed out by rising flood water. As flow drops off and conductivity first drops, conduits again begin discharging floodwaters. Finally, conductivity rises as baseflow, phreatic waters begin to increase and become the main source of the discharging spring water.

An anomalous peak in conductivity occurred (920 μ S) at 11:30 hours on May 19 at Illinois Central spring. This peak corresponds almost precisely to the maximum value of Fluorescein measured in that spring as the dye front moved through. It is therefore likely that the dye front was also detected in conductivity readings as it passed. This peak was not observed in Quarry spring. However, Fluorescein peaked after the conductivity measurement frequency was reduced to twice daily, and so could have been missed in the readings. Although monitoring conductivity during the passage of dye fronts was not a goal of this study, it would be interesting to observe conductivity response through entire dye pulse passages in future tests.

Trends in May 12 conductivity readings from Illinois Central and Quarry springs, while not as well defined, display the same pattern as readings from May 18 and 19. They substantiate the usefulness of conductivity to help identify the sources of discharge spring water. Individual sources can have a characteristic high or low values which can be observed together with spring discharge over time.

Ionic concentration chemographs, as pointed out earlier, have also been used in addition to conductivity and Total Dissolved Solids (TDS) to help define water sources; specifically, calcium ions have been discussed. In the cation chemographs from Illinois Central (Figures 18 - 21), values for all four ions (Calcium, Magnesium, Sodium and Potassium) show a general decreasing trend during rise in discharge. At first glance, this might be interpreted as a

dilution of phreatic water with incoming flood water, which is lower in ionic content. Earlier, it was pointed out that cation concentrations such as calcium normally show changes relative to discharge similar to those of specific conductivity and TDS. However, on May 12 all four cations from Illinois Central spring actually show an overall decreasing trend while conductivity increases during the rise in discharge. There is at present no explanation for these cation data. Calcium, Magnesium, Sodium and Potassium all peak immediately following maximum flow and then drop again. This portion of the data parallels the conductivity response, indicating that a pulse of epikarst storage water may be discharging from the spring slightly after the hydrograph peak.

Anion values from Illinois Central are more variable and exhibit a much weaker overall decreasing trend (See Figure 26.). Two peaks occur: one shortly prior to maximum discharge and one following. It is unclear what caused the first peak, but the second peak closely corresponds to the one registered by cation concentrations and is likely caused by the passage of epikarst storage water.

Curiously, at Quarry spring Calcium, Magnesium and Sodium values increase during the rise in flow level (Figures 22 - 25.). Perhaps this may be caused by mixing of phreatic water or epikarstic water with incoming flood water inside the conduits between Illinois Central and the

resurgence at Quarry. The Quarry anion and cation measurements both exhibit very similar patterns.

There are no clear indications of source waters from pH, temperature or dissolved oxygen readings. Dissolved oxygen generally increases and temperature decreases through both the rise and fall of the hydrograph. PH readings, only available from Quarry spring, show weakly elevated values which occur simultaneously with a pre-peak discharge plateau on the hydrograph. Elevated pH may be associated with recharging waters but more measurements during storm events would be required to demonstrate a clear association.

Conclusions:

In this investigation, dye tracing and chemical parameter monitoring were effective tools for learning about hydrogeologic groundwater behavior in karst terranes.

The dye trace was carried out under moderate, rather than high, flow conditions and used open sinkholes widely spaced around the large Lemon Lane sinkhole complex as entry points into the underlying bedrock. Yet the results generally agree well with those obtained by previous investigations under high flow conditions with injection into wells on the Lemon Lane Landfill perimeter. Flow conditions were much lower during this test, probably contributing to the lower incidence of dye detections. However, the slightly more conservative approach to interpreting the dye results used in this study may, in part, also explain the lower number of positive traces found. The interpretation of individual dye fluorograms was developed from observing the distinctiveness of the peaks above the raman water curve, and also comparing the concentration levels with previous background measurements. Each spring was considered individually when interpreting the data.

The widespread occurrence of previously used dyes in the spring background samples indicates that spreading may be occurring across a major groundwater divide by repeated high level flushing of the epikarstic zone. This wide migration of dyes complicates the ability to discern any minor flow paths during subsequent tracer tests. For this reason, selection of alternative dyes in future studies would be helpful in locating these possible paths. Also, it would be instructive to repeat a study of this type using the same injection points during a high flow event with more than 1.5 inches of rainfall.

The chemographs illustrate that conductivity and additionally also ionic measurements of spring waters during a storm event may be useful in determining their sources. The conductivity and cation chemograph trends generally showed the same pattern as those observed from the previous studies and literature. The parameters pH, dissolved oxygen

and temperature did not produce any clear data which aided understanding the sources of spring discharge water, and so may be of little use. However, a greater duration and higher frequency of sampling chemical parameters would benefit any future study, and possibly reveal even more useful chemograph trends.

Optimal conditions did not exist for sampling oxygen and deuterium isotopes as originally proposed. Tracking the isotopic composition of Illinois Central and Quarry spring waters during a future high flow event may add another line of evidence supporting the existence of stored water in the epikarstic zone in the subsurface of the Lemon Lane sinkhole complex.

Environmental applications of this study may be viewed in two main areas. First, dye tracing the primary flow pathways will help to predict the direction of contaminants transported away from the site in karst terranes. Second, the evidence indicates that large volumes of water may stored in the epikarst for many weeks, and possibly years (if residual dyes are any indications). This illustrates that perhaps low levels of contaminants might also be stored in the epikarst and transported in much the same way as the dyes have been. Therefore, a large contaminant plume released into a karst groundwater environment may have residual concentration levels which last well after the main body has been flushed down gradient though conduits and

fractures. The chemical and physical properties of a contaminant will also greatly influence its mobility. The results of this study show how important the application of dye tracing and chemical parameter monitoring is to karst terrain environmental hydrogeology.

APPENDICES

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