Utilizing Fluorescent Dyes to Identify Meaningful Water-Quality Sampling Locations and Enhance Understanding of Groundwater Flow Near a Hog CAFO on Mantled Karst—Buffalo National River, Southern Ozarks

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Abstract

The karst area of the Springfield Plateau in the southern Ozarks of north-central Arkansas is subject to numerous and varied land-use practices that impact water quality. In this region of the U.S., animal production and human activities have concentrated wastes within environmentally-sensitive karst hydrogeologic settings. Groundwater flow in this region includes aquifers covered by a thin, rocky soil, and a variable thickness of regolith. The karst groundwater system is underlain by thin chert and limestone layers that have been fractured by slight uplift. The carbonate-rock aguifer intervals have been dissolved to form an open network of enlarged fractures, bedding- plane voids, conduits, sinkholes, swallets, sinking streams, caves, and springs. Flow in these aquifers is typically rapid, flow directions are difficult to predict, and interaction between surface water and groundwater is extensive, with little opportunity for contaminant attenuation. Herein, we show dispersive groundwater flow from multiple injection sites where groundwater-basin boundaries can vary with groundwater level. Although the geologic framework appears simple, the results of tracing with fluorescent dyes from April to October 2014 indicates that a meaningful conceptual model is indeed complex, yet essential to use when sampling water quality and fully understanding the movement of groundwater and its close interaction with surface streams and recharge.

INTRODUCTION

The landscape of the Springfield Plateau in the southern Ozarks (fig. 1) is a mantled karst, with few apparent topographic features such as sinkholes on the land surface, yet the region is underlain by a system of well-developed fast-flow pathways and voids which pass water and entrained contaminants downgradient to resurgent springs and streams quickly and with little attenuation of the pollutants. Karst scientists have long been aware and are fully

knowledgeable about this and related areas of mantled karst, covered by insoluble debris weathered from the original carbonate bedrock (White, 1988; Quinlan, 1989; Ford and Williams, 2007).

Unfortunately, consultants, some landowners, and water managers unfamiliar with mantled karst have difficulty in recognizing the vulnerability of groundwater in these settings, and the close interaction with surface water of such areas (Murdoch et al., 2016). This is the case of Big Creek basin, the second largest tributary of the Buffalo National River. Big Creek basin has a total area of xxx hectares (ha), within which permission was recently granted for an industrial hog factory housing 6,500 swine in a concentrated animal feeding operation (CAFO). Waste from this CAFO was permitted to be spread from lagoons onto 252 ha of mantled karst in 2012 using documents that did not discuss groundwater or karst (Pesta, 2012).



Figure 1. General physiographic regions of the Ozark Plateaus, including the Springfield Plateau, an alternating thinly-bedded chert and limestone rock interval in northern Arkansas that develops mantled karst. The approximate area of this study area is shown by the ellipse.

Purpose and Scope

There are two objectives for conducting this research and writing this paper. The first is to present the results of five tracing events using three separate fluorescent dyes in Big Creek in the vicinity of the CAFO and its waste-spreading fields, focusing on point-to-point groundwater flow connections and time of travel. The long duration of the traces was intended to show natural variation of the groundwater flow system in the karst for varying recharge, and establish that the rates of flow do indeed characterize the fast-flow conditions of conduit transport. The

second objective is to provide an explanation of why the groundwater moves in the manner that was measured, and to do so in terminology that will enlighten and educate laypeople and other stakeholders, especially those who have the responsibility of promulgating regulations based on the established karst science. Documenting these karst attributes in peer-reviewed publications represents an important means to further educate all stakeholders.

Study Area

The study area was chosen to include the potential flow boundaries of the groundwater system that are known from previous karst studies in the Ozarks (Aley, 1988; Mott et al., 2000), which includes an area of natural groundwater flow larger than the site-specific location of the CAFO and its spreading fields (fig. 2). The spreading fields extend from Dry Creek to Big Creek, and the confluence of these streams south along Big Creek to slightly north of the CAFO.

The reason for extending the study area boundaries in dye-tracing studies is to evaluate if surface-drainage basin boundaries and groundwater-basin boundaries are coincident or not. It is not uncommon for these boundaries to be different in karst (Quinlan, 1989). In addition to placing dye receptors on Big Creek and the Buffalo National River, Little Buffalo River, Left Fork of Big Creek, Dry Creek, and Cave Creek and the springs that flow into these surface drainages, wells tapping the Boone Formation proximate to the CAFO also were evaluated.

Hydrogeologic and Karst Characterization of the Study Area

Big Creek is one of the largest tributaries to the Buffalo National River, encompassing slightly more than 10% of the total drainage of the entire Buffalo River basin (Scott and Hofer, 1995; Mott and Laurans, 2004). Topographically, tributaries head in uplands on terrigenous

sediments of Pennsylvanian age of the Boston Mountains Plateau (fig. 1) and flow generally toward the north and east with relatively steep gradients, typically in the range of from 3 to 5 meters (m) per kilometer (km).



Figure 2. Expanded study area, showing location of the CAFO and the town of Mt. Judea, and the major surface-water bodies that receive groundwater from springs. The streams are approximately located by the blue lines, which are connected to the stream names. The dashed rectangle shows the approximate boundaries of the focused study area, which has been enlarged in figures 7-9 to show specific details of the dye tracing.

The stratigraphic unit of greatest concern to this study is the Boone Formation (Braden and Ausbrooks, 2003), an impure limestone interval (fig. 3) that contains as much as 70% chert (Liner, 1978). The chert is hypothesized to have formed from atmospheric deposition of volcanic ash that was periodically ejected and carried by prevailing winds. In northern Arkansas, the setting was a shallow carbonate shelf (Brahana, 2014). The carbonate factory operating in this shallow marine setting at that time was hypothesized to have been overwhelmed by massive amounts of silica, which in the study area formed thin but fairly continuous layers of silica gel that typically ranged in thickness from 5 to 30 centimeters (cm). During periods of volcanic quiescence, carbonate sediments were deposited onto the thin layers of silica gel, and with successive sedimentation from these two sources, a sequence of approximately 80 m of chert/limestone couplets were laid down, compressed, and diagenetically altered and indurated into limestone and chert of the middle portion of the Boone Formation (Brahana, 2014).

Structural uplift resulting from compressive closure of the Ouachita orogeny created a foreland bulge. This uplift acted concurrently with the volcanism, causing jointing, faulting, and tilting that allowed and facilitated pathways of weathering and karstification (fig. 4) of the carbonate intervals of the middle Boone.

Big Creek and its major tributary, Left Fork of Big Creek, flow in alleviated valleys on bedrock. Alluvium is composed of nonindurated sediments, primarily chert and terrigenous rock fragments from younger, topographically higher formations. The alluvium in these valleys varies in thickness from a feather-edge to about 8 meters (m). Outcrops of the Boone Formation are common in the streambed and bluffs along Big Creek and the Buffalo. Springs are common along the entire reach of Big Creek, ranging from relatively small discharges in the tens of liters per minute range to large discharges in the tens of liters per second. These larger discharges resurge from relatively pure carbonate lithologies, with caves more commonly found in the lower Boone or in Ordovician-aged limestones and dolomites (Mott et al., 2000).



Figure 3. Stratigraphic column of the Big Creek study area, showing the stratigraphic extent of karst where the Boone Formation (light grey color) occurs at land surface. Arrows on the column bracket approximately 80 m of the chert-rich interval of the chert/limestone couplets of the Boone. Total thickness of the Boone is about 110 m. Figure modified from Braden and Ausbrooks (2003).



Figure 4. Karst dissolution features in limestone interbedded with chert from the middle Boone. The chert acts as an insoluble confining unit for the upper and lower dissolution zone. The size of these voids typically ranges from 2 to more than 5 cm.

METHODOLOGY

Qualitative dye tracing was conducted from April 2014 through October 2014 in Big Creek and contiguous basins using three nontoxic, fluorescent dyes, fluorescein, rhodamine WT, and eosin. A single dye was injected into flowing groundwater in the middle part of the Boone, characterized by chert/limestone couplets (fig. 5). Injection sites included hand-dug wells, a sinking stream in alluvium, and a swallet (table 1). The latter feature was a sinkhole that captured all of the flow of Dry Creek, a tributary that lies upgradient from Big Creek and nearby spreading fields in limestone of the upper Boone. Fluorescein dye was introduced into a dug well with groundwater flowing on the epikarst

overlain by Big Creek alluvium over lower-middle Boone about 500 m downgradient from the CAFO; and eosin was injected into a dug well that was surrounded by waste-spreading fields.

Passive dye receptors similar in appearance to a tea bag were constructed by placing approximately 10 grams of coconut charcoal in a permeable packet that allowed flowing groundwater to contact the charcoal. In most cases, the permeable external layer of the packet was a "milk sock", whose manufactured purpose is to filter milk from automatic milking machines used by dairy barns. This fabric enjoys recent popularity among dye tracers, especially for flow velocities about 2 km/d or less. For greater flow velocities, such as surface streams, an additional packet was made with larger fabric openings approximately one-fourth the size of window screen. In high velocity streams, the milk sock receptor was often too fine a mesh to allow full contact of the flowing water with the charcoal, and thus did not yield meaningful positive dye detections.

Passive dye receptors were placed in flowing groundwater and surface water throughout the study area, based on a previous karst inventory and discussion with local landowners. Receptors were placed in all available springs, wells, streams, and flowing water where we had been granted permission. Inasmuch as groundwater flow directions were not known at the start of the study, such a conservative approach is required (Quinlan, 1989).

If fluorescent dye were in the water, it was sorbed onto the charcoal of the receptor. These were left in place for periods of time varying from one day to one month, and were replaced by new receptors when the original receptors were retrieved. Receptors were identified by plastic tags with station number, date placed, and date retrieved noted in black permanent marker and placed into ziplock bags with additional information as appropriate recorded on the bag. Chain-of-custody forms were prepared and updated for the receptors through each transfer responsible for all remaining actions. Upon receipt from the field, the receptors were rinsed with distilled water in the Hydrogeology Laboratory at the University of Arkansas (Room 240 Gearhart Hall) to remove sediment and related debris. They were allowed to air dry for at least 24 hours, and analyzed on a calibrated Shimadzu scanning spectrofluorophotometer (Model RF 5000). One half of the dried charcoal was placed into plastic containers and an elutant of isopropyl alcohol and potassium hydroxide was added to mobilize any dye present on the charcoal into the residual solution (eluant). This eluant was transferred by disposable polyethylene pipette into a single-use cuvette, and analyzed for the wavelength of fluoresce specific to the three dyes that were used. All analyses were made using the scanning spectrofluoromphotometer. Wavelength maxima for fluorescein were centered at 515 nanometers (nm); for eosin at 540 nm; and for rhodamine WT at 572 nm.

DATA VERIFICATION

Verification of the accuracy of dye tracing is essential, and is documented by a process called quality assurance/quality control (QA/QC). QA/QC is a major component of all dye-tracing studies, and it provides unquestioned verification that the information gained from the passive detectors. QA/QC also verifies that the study is accurate and represents only dye that was injected into the flowing groundwater. For this study, it involved verifying that: 1) the hydraulic head of the groundwater is higher at the point of injection that at the point the dye receptor was placed; 2) that the injection point is part of a dynamic groundwater flow system; 3) that positive attributes of the dye at specific locations are duplicated by other dye analysists through a series of blind testing; 4) that the concept of clean hands/dirty hands (Shelton, 1994) is honored strictly and that receptor retrieval is done by different personnel than those that injected the dye; 5) that cross-contamination of receptors is avoided by means of gloves and ziplock bags; and 6) that duplicate receptors reflect the same results.



Figure 5. This spliced-multiimage photo shows karstified zones in a sequence of limestone/chert couplets in a bluff along Big Creek. The dark, near-horizontal features are incompletely dissolved zones in the limestone, which Figure 3 represents a close-up view. Vertical fractures allow water from above to enter the karst and exit through Big Creek. The gentle dip of the layers reflects slight tilting, typically less than several degrees. Photo credit is John F. Murdoch.



Figure 6. Swallet in Dry Creek in Ozark National Forest capturing all streamflow upgradient from CAFO spreading fields. In karst, surface water and groundwater interact as a single resource, with streams typically being pirated into groundwater as shown here, later resurging from downgradient groundwater springs back to the surface.

As a final note on QA/QC, all dye injections were accomplished using liquid dyes, inasmuch as the powdered dyes (fluorescein and eosin) are easily caught up by air currents, and may cause severe cross-contamination if they are not in liquid form during injection. The liquid dyes were kept in impermeable containers, and dye receptors and personnel were isolated from incidental contact which would give false positive results (Aley, 2003; Quinlan, 1989).

TRACING RESULTS

Five dye traces were undertaken in the study area in 2014, and a summary of specifics of each is summarized in table 1. Dye injection sites are shown in figure 7 overlain on a shaded relief map, and a summary of point-to-point dye connections are shown in figure 8. Important details of each trace are described in the following section.

Table 1. Selected dye injections events in the study area during 2014. Locations of injection sites are shown on figures 7, overlying topography, and 8, overlying geology.

[FL, fluorescein; RWT, rhodamine WT; EO, eosin; v, velocity of groundwater; ~, approximately; m, meters; d, day; outside tracers providing verification of positive traces included Tom Aley, Ozark Underground Lab, Protem, Missouri, and Geary Schindel, Edwards Aquifer Authority, San Antonio, Texas. Instrumental confirmation was conducted with Shimadzu Scanning Spectrophotometers; visual confirmation was assessed by fluorescent color in the resurgence by observers]

Injection Date	Site Number	Hydrologic Setting	Geology	Tracer	GW Flow	Generalized Results
4/22/14	BS-39	Dug well perched	lower cherty Boone epikarst	FL	moderate	multiple visual and instrument confirmations; v ~660 m/d
4/27/14	BS-78	Sinking stream	alluvial gravel over middle Boone	RWT	low	no observable confirmation; likely perched ; v not calculated
5/12/14	BS-36	Dug well perched on chert	middle cherty Boone	EO	very high	widespread instrument and outside tracer confirmations; cross-basin and cross-formation flow; radial flow; v ~800 m/d
7/10/14	BS-71	Swallet perched	upper Boone limestone	RWT	moderate	Visible and instrument confirmation; v ~7000 m/d with surface flow part of way
8/5/14	BS-36	Dug well	middle cherty Boone	FL	very low	no observable confirmation; dye density caused it to sink to lower reservoir; stagnant with no flow; v ~0 m/d



Figure 7. Topography of Big Creek basin near Mt. Judea, in the area of the CAFO, including the locations of dye injection, type of dye injected, location of CAFO structures housing 6,500 hogs and waste lagoons. Symbol for the injection sites are stars. BS-36 also was used to inject fluorescein 3 months later (table 1). Table 1 summarizes the important aspects of each dye-tracing test.

On April 22, five kilograms (kg) of fluorescein dye were injected into BS-39, a hand-dug well 13.17 m deep that had flowing groundwater on an epikarst perched on chert of the lower Boone Formation. BS-39 lies on an alluvial surface between the CAFO and Big Creek, about equidistant from both (fig. 6).

On April 27, two kg of rhodamine WT were injected at BS-78, a sinking stream at the intersected Sycamore Hollow and a county road where a low-water county road crossed

Sycamore Hollow (fig. 7). The dye was emplaced into alluvial gravel that overlaid limestone of the upper part of the middle Boone. No positive instrumental observations of dye were confirmed from this trace. Insofar as passive dye receptors were only placed along Dry Creek and Big Creek for this test, all that can be taken from this test is there was no discernable eastern groundwater flow for the low-flow conditions measured at the time of this test. Positive traces were visually and instrumentally confirmed in an alluvial well downgradient, and and multiple springs that resurged from below a chert layer in the bottom of Big Creek, upwelling about 660 m from the injection site at 24 hours after injection. As with many of the other positive dye traces in the study area, the springs in the middle part of the Boone had multiple orifices that flowed from a discrete karstified layer of a single limestone/chert couplet. This trace established that groundwater flowed from BS-39 to springs in Big Creek at a velocity of at least 660 m/d. Springs associated with this resurgence would be an excellent place to sample for potential contamination from the CAFO , including feeding, waste-handling, and pond leakage.

On May 12, eight kg of eosin dye were was injected into BS-36, a hand-dug well 12.23 m deep in the middle Boone with visible groundwater flow along several zones near the water table that has been intensively studied (Murdoch et al., 2016). Well BS-36 was located within the generalized area of waste spreading, with these fields on three sides and within several hundred meters of the well. One day following dye emplacement, more than 15 cm of rainfall caused a water-level rise of more than one m, mobilizing much of the dye into permeable zones above the pre-injection water level. The dye was dispersed in a radial pattern (fig. 8), with 36 confirmed positive eosin traces (fig. 9) extending to springs and surface streams in Big Creek and different basins other than Big Creek, as well as downstream in the Buffalo National River. One



Base map from Braden and Ausbrooks, 2003

Figure 8. Geologic map showing point-to point dye-tracing results in the area of the CAFO and its spreading fields. Injection points are shown by stars, and the solid arrows that emanate from the injection points show the groundwater sites of recovery on the map. Dashed lines from injection well BS-36 extend beyond the area shown in this figure, with the full observed extent shown in Figure 9. Actual flow paths in the subsurface are significantly more complex than the straight lines shown. Tracing results shown here are groundwater-level dependent.

positive trace to Mitch Hill Spring, on the opposite side of the Buffalo River from injection reflected how complex the karst flow system is and how far flow from the study area could be measured. This positive Mitch Hill Spring trace was reconfirmed by both of the external dye tracers using split receptor samples provided in a blind test. Obviously, some of the flow from the ground-water resurfaced and moved downgradient in Big Creek and other surface channels, but this test documented that groundwater flow from the area of the spreading fields surrounding BS-36 is mobilized under intense rainfall events, and sampling sites at springs along Left Fork of Big Creek, the Buffalo River, and surface streams in contiguous basins would be excellent sites for water quality sampling at high-flow conditions. The radial pattern of flow resulting from this storm (figure 8) is a common feature observed in other dye traces in the middle Boone (Aley, 1988; Mott et al., 2000). The solid arrows of this positive trace with a northwest trend from BS-36 to Left Fork of Big Creek (fig. 8) showed receptors at 7 days, yielding a conservative straightline velocity of about 800 m/d. These values, along with those from the BS-39 injection site, are comparable to the fluorescein trace from BS-36 in the same geologic interval. As a comparison of velocity, later recovery of dye receptors from BS-36 showed a static zone of very little groundwater movement that served as a storage reservoir in the lower part of the well. The remaining dye, which was denser than water, was not flushed from the deeper part of the well for more than three months, and during that time was trapped with a velocity of 0 m/d.

On July 10, five kg of rhodamine WT were injected in to a swallet in the upper Boone that captured the entire discharge of Dry Creek upstream from BS-71 (fig. 7). This site had visual confirmation of dye at the confluence of Dry Creek and Big Creek, as well as positive instrumental confirmation from dye receptors at springs along Dry Creek, and the fastest groundwater velocity, nearly 7000 m/d, although much of the flow path was on the surface.

This is consistent with the larger, more open voids upper Boone limestone (Stanton, 1994), which is chert free.



Figure 9. Flow from BS-36 during high flow on May 12, 2014, when eosin input was positively traced to outflow springs and streams. Letters show recommendations for sites to sample for evaluating contamination in the future. The dye-trace results show the full dispersive extent of karst flow in the subsurface into other surface-water basins, the Buffalo National River, and even beneath the Buffalo River to Mitch Hill Spring, identified by the black circle in the northeast quadrant. The star is the dye input well BS-36, the abstract shape around the star with multiple rectangular patterns (waste spreading fields) outlines the general area of the waste spreading fields. Five positive dye detections were retrieved from the Buffal National River from this test.

Flow velocity based on this test is much greater than determinations made from the karst in the middle Boone, and can be explained by less frictional flow from conduits in the pure-phase upper

limestone of the upper Boone and significant portion of the flow path occurring on the surface in Dry Creek.

On August 5, two kg of fluorescein were injected into BS-36, this time under extremely low-flow conditions. As with the trace at BS-78, no positive confirmation at any dye receptor except within the injection well was observed. The variation of stage in BS-36 at the time of this test was significantly lower than the eosin trace of May 5 and the conditions of groundwater flow were essentially as different from the May 12 test as they possibly could be.

The May 13 test had 36 confirmed positive eosin traces (fig. 9). The August 5 fluorescein trace had no confirmed traces. This result provides good insight for the water-level control on the flow in the middle Boone, and helps explain our observations.

DISCUSSION AND CONCLUSIONS

Based on the results of the dye tracing described herein, the following observations of groundwater flow in the Boone Formation in the study area. Information from the dye traces completed within the Big Creek study area can be used for designing a more reliable and relevant water-quality sampling network to assess the impact of the CAFO on the karst groundwater and to gain further understanding of the karst flow .

1. Although the study area is mantled karst, subsurface flow is very important, and forms a significant part of the hydrologic budget.

2. Groundwater velocities in the chert/limestone portion of the middle Boone Formation were conservatively measured to be in the range of 600-800 m/d. 3. Conduits in pure-phase limestones of the upper and lower Boone have flow velocities that can exceed 5000 m/d.

4. Groundwater flow in the Boone Formation is not limited to the same surface drainage basin, which means that anomalously large springs should be part of the sampling network (Brahana, 1997).

5. Because the Buffalo National River is the main drain from the study area, and the intensive contact of the river water by uses such as canoeing, fishing, swimming, and related activities, large springs and high-yield wells should be included in the sampling network.

6. Potential transport velocities of CAFO wastes from the land surface appears to be most rapid during and shortly after intense precipitation events. Minimum groundwater flow occurs during periods of low flow or during droughts . Sampling should accommodate these considerations.

The chert obviously plays a role as confining layers in the Boone Formation, and adds to the complexity of the flow systems of the karst. Interbasin transport of the dye is consistent with groundwater following faults, which are common in the study area, with many not mapped. Insoluble material can be washed into the fault plane and deflect groundwater flow along the fault. The appearance of linear patterns truncating topography (fig. 7) and geology (fig. 8) are consistent with this interpretation, and can be further tested with additional dye traces. Table 2. Recommended sites for collecting water-quality samples based on the results of dye tracing near

the CAFO and its spreading fields near Big Creek, Newton County, Arkansas. Locations of sites are shown

on figure 9.

 $[C^{l-}, chloride; nutrients, P and NO_3^-; pathogens,$ *E. coli*and fecal coliform; trace metals, isotopes of ³¹P ⁶³Cu, ⁶⁵Cu, and ⁶⁶Zn; DO, dissolved oxygen; major constituents, Na⁺, K⁺, Ca⁺², Mg⁺², C^{l-}, HCO₃⁻, SO₄⁻²; field parameters, temperature, pH, and specific conductance].

Site ID	Hydrologic Setting	Parameters to Sample	Justification for Recommendation
A	springs, wells, surface streams that drain into Big Creek from waste-spreading fields	Cl ⁻ ; nutrients; pathogens; trace metals; DO; algae; major constituents;field parameters	dye tracing; proximity to source
В	perched bedding plane springs upstream on Big Creek	Cl-; nutrients; pathogens; trace metals; DO; algae; major constituents; field parameters	dye tracing; upstream from CAFO source and waste spreading fields
С	perched bedding plane springs upstream on Left Fork of Big Creek	Cl ⁻ ; nutrients; trace metals; DO; algae; major constituents; field parameters	dye tracing; larger spring indicates subsurface capture outside drainage basin; major algal blooms downstream from springs
D	upstream springs and surface streams on Left Fork of Big Creek	Cl ⁻ ; nutrients; trace metals; DO; algae; major constituents; field parameters	dye tracing; major algal blooms downstream from springs
E	Rock Creek upstream from Buffalo National River	nutrients; DO; algae; major constituents; field parameters	dye tracing
F	furthest upstream on Buffalo National River	nutrients; DO; algae; major constituents; field parameters	dye tracing
G	springs and cave streams less than 100 m upstream from Buffalo National River	nutrients; DO; algae; major constituents; field parameters	dye tracing
Н	Big Creek and springs downstream from confluence with Left Fork. Major gaining reach	Cl-; nutrients; trace metals; DO; algae; major constituents; field parameters	dye tracing; downstream from CAFO source and waste spreading fields
I	Mitch Hill Spring and its spring run, on the north side of the Buffalo National River	Cl-; nutrients; pathogens; trace metals; DO; algae; major constituents; field parameters	dye tracing; largest spring in the expanded study area; numerous dye traces discharge here
J	intermediate reach on Buffalo National River	Cl-; nutrients; pathogens; DO; algae; major constituents; field parameters	dye trace
K	below ponded resurgence of major spring on Cave Creek	CI-; nutrients; pathogens; DO; algae; major constituents; field parameters	dye trace
L	furthest downstream location on Buffalo National River	Cl-; nutrients; pathogens; DO; algae; major constituents; field parameters	dye trace

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