

Using multiple tracers to distinguish between municipal drinking water and wastewater inputs to Deer Creek at the Litzsinger Road Ecology Center

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Kayla Lockmiller and Dr. Elizabeth Hasenmueller

Saint Louis University

Environmental Geochemistry Laboratory

1. Introduction and project background

With over half of the world's population living in cities (UNDESA, 2016), municipal water use is leading to significant chemical alteration of urban streams. In urbanized areas there are many opportunities for municipal water (i.e., treated drinking water, treated wastewater, and untreated wastewater) to run-off, leak, or discharge into nearby streams. These losses can profoundly influence the quality and quantity of stream water, leading to deleterious effects on stream ecosystem health. Municipal waters may be released into proximal waterbodies through several mechanisms including: 1) over-irrigation of lawns, 2) discharges of treated wastewater, 3) discharges of untreated wastewater from sewer overflows, and 4) leaks from drinking water and wastewater infrastructure.

Lawn irrigation consumes nearly 34 billion liters of potable water daily in the United States alone, much of which is lost via surface runoff due to excessive application (USEPA, 2017a). Moreover, leakage from pressurized drinking water pipes can release 5 to 50% of the total volume carried to the shallow groundwater (Seiler and Alvarado Rivas, 1999; Lerner, 1986). These losses of drinking water are wasteful, especially when considering the issue of global water scarcity. Similarly, leakage rates of 5 to 52% of the volume carried by wastewater pipes have been observed (Passarello et al., 2012; Eiswirth and Hotzl, 1997). Untreated wastewater can also be discharged directly into streams in many older cities via combined sewer overflows (CSOs), which collect sewage and storm water runoff in the same piping system (USEPA, 2018a). This untreated wastewater can contain pharmaceuticals (e.g., hormones, antibiotics), pathogens (e.g., *E. coli*, cholera), and inorganic contaminants (e.g., heavy metals), which can all negatively affect human and ecosystem health (Rivera-Jaimes et al., 2018; Phillips et al., 2012, Holeton et al., 2011). Due to the potential risks associated with municipal water inputs to urban streams, the goal of this work is to quantify municipal drinking water and wastewater inputs to Deer Creek at the Litzsinger Road Ecology Center in Saint Louis, MO, by using a variety of chemical and biological tracers.

There are many chemical species that have distinctive concentrations in municipal water sources. An ideal tracer for municipal waters in the Saint Louis area is F^- because it is added to drinking water in known concentrations ($662 \pm 112 \mu\text{g/L}$) for dental health, it is not removed in

significant quantities from wastewaters during treatment, and it is not found in high concentrations in local streams (City of Saint Louis Water Division, 2015; Wallis et al., 1996; Stueber and Criss, 2005). Thus, F⁻ represents an effective tracer for municipal water inputs to Deer Creek. Moreover, Saint Louis has a unique drinking water source (i.e., the Missouri River) that is chemically distinct from local streams like Deer Creek. The Missouri River and the municipal water derived from it exhibit naturally high concentrations of B species (i.e., 100 to 150 µg/L) relative to local waters (i.e., 25 µg/L) due to the Missouri River's origin in the western United States (Hasenmueller and Criss, 2013). B concentrations are enhanced further in untreated wastewaters by as much as 137% (i.e., up to 355 µg/L) due to the addition of B-rich detergents during municipal water use. Thus, B is a reliable tracer for both drinking water and wastewater additions to local streams (Hasenmueller and Criss, 2013). Additionally, optical brighteners, which are compounds used in 97% of detergents and toilet paper to enhance the brilliance of clothing and paper products (Tavares et al., 2008), may be used to trace wastewater. *Escherichia coli* (*E. coli*), a bacterial pathogen found in human waste (Jamieson et al., 2004), has also been measured as an indicator of municipal wastewater. Together, we use F⁻, B, optical brighteners, and *E. coli* to: 1) quantify municipal water inputs to Deer Creek during differing flow regimes and 2) observe the extent to which municipal water infrastructure is impacting Deer Creek's chemistry.

2. Methods

2.1 Field methods

Stream samples were collected weekly at Deer Creek from September 2016 to March 2018 ($n = 62$). Additional types of samples were also collected to characterize end-members including: 1) water from a stream minimally affected by municipal water contributions (i.e., the “natural” end-member), 2) Missouri River water prior to drinking water treatment near two drinking water treatment plants ($n = 4$), 3) treated drinking water sourced from the Missouri River from two drinking water treatment plants ($n = 4$), and 4) treated ($n = 6$) and untreated ($n = 6$) wastewater from five wastewater treatment plants in the area that receive drinking water derived from the Missouri River. *In situ* results for standard water quality parameters were measured with a YSI Professional Plus Multiparameter Instrument (i.e., temperature, dissolved oxygen, specific conductivity, pH, and Cl⁻) and Hach 2100P Portable Turbidimeter (i.e., turbidity). Aliquots for ion chromatography (IC) and inductively coupled plasma optical emission spectrometry (ICP-OES) were field-filtered through 0.2 µm cellulose acetate filters into polypropylene (PP) vials; subsamples to be run via ICP-OES were acidified to 1% HNO₃. Both sample types were kept on ice until returning to the lab where they were stored at 4°C until analysis. Starting in September 2017, measurements for optical brighteners and samples for *E. coli* and total coliforms were also collected. Optical brightener measurements were made on site using a Turner Designs AquaFluor Handheld Fluorometer in UV grade methacrylate cuvettes.

Values for optical brighteners are presented in relative fluorescence units (RFU). Samples for *E. coli* and total coliforms were collected in autoclaved high density polyethylene (HDPE) vials and stored on ice until returning to the lab where they were immediately analyzed. Additionally, we acquired stream discharge data from the nearby United States Geological Survey (USGS) gauging station (station number 07020075).

2.2 Lab analyses

A Metrohm 881 Compact IC Pro Ion Chromatograph with a Metrosep A Supp 7 column with suppression was used to measure F^- and other anions (Cl^- , NO_3^- , PO_4^{3-} , SO_4^{2-}) on a conductivity detector. An eluent of 3.6 mM Na_2CO_3 was used at a flow rate of 0.7 mL/min. B-species and major cations were analyzed on a PerkinElmer Optima 8300 ICP-OES with Fluka Analytical Multi-Element Standard Solution 1. Blanks and field and lab duplicates were run on both instruments to test the reliability of field and analytical techniques. Precision was within 4.4% and 2.8% for IC and ICP-OES analytes, respectively.

Colony enumeration for *E. coli* and total coliforms was performed using IDEXX Colilert reagent, 97-well Quanti-Trays®, and autoclaved glassware to prevent bacterial contamination. If bacteria loads above the detection range (1 to 2419.6 cfu/100 mL) of this United States Environmental Protection Agency (USEPA) method were expected (i.e., during high flow or warm temperatures), samples were diluted with autoclaved deionized water before analysis.

2.3 Three Component Mixing Model to Quantify Municipal End-Member Inputs to Deer Creek

In order to quantify the relative contributions of the three end-members to Deer Creek, we used a three component mixing model. We calculated the fractional inputs (X) of natural water (i.e., baseflow contributions; N), drinking water (D), and wastewater (W) as a percentage of the total stream flow simultaneously in a matrix by using two tracers (J and K) in the following equations (after Lee and Krothe, 2001):

$$X_N + X_D + X_W = 1 \quad (1)$$

$$J_N X_N + J_D X_D + J_W X_W = J_S \quad (2)$$

$$K_N X_N + K_D X_D + K_W X_W = K_S \quad (3)$$

where S represents the stream sample. These equations yielded end-member contributions to Deer Creek at the time of sample collection.

3. Results and discussion

3.1 Chemical tracer behavior

F⁻ and B concentrations in Deer Creek fluctuated 96 to 490 µg/L (average = 256 ± 95 µg/L) and 6 to 167 µg/L (average = 49 ± 23 µg/L), respectively, under differing flow conditions that ranged from 0 to 11.07 m³/s between September 2016 to March 2018 (USGS, 2018; Fig. 1A). Optical brightener values fluctuated from 12.51 to 38.04 RFU (average = 21.90 ± 6.63 RFU; Fig. 1B) under flow conditions that ranged from 0 to 0.94 m³/s between September 2017 to March 2018. Note that the F⁻ and B datasets include samples that were taken during higher flow conditions than the samples for the optical brightener dataset. When comparing F⁻, B, and optical brightener data to stream discharge, we observed relatively chemostatic behavior for all of the tracers ($R^2 < 0.01$; Fig. 1). Any apparent negative trends of tracer levels versus discharge were found to be statistically insignificant ($p > 0.28$). No obvious trends were observed in tracer values with changes in season (Fig. 2).

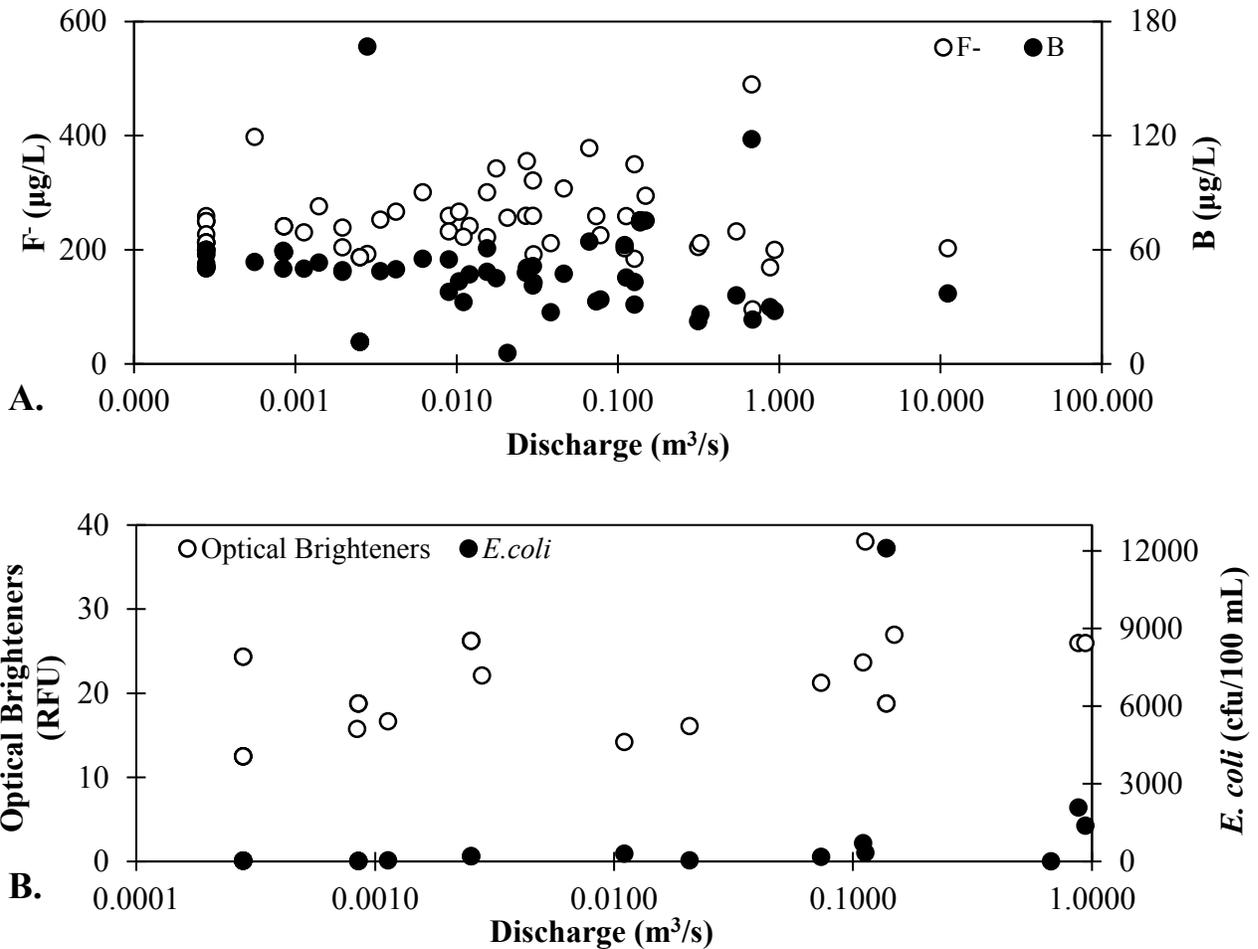


Figure 1. F⁻ (white circles) and B (black circles) concentrations (A.) or optical brightener (white circles) and *E. coli* (black circles) levels (B.) plotted against Deer Creek's discharge. None of the tracers had

statistically significant correlations with discharge ($p > 0.28$). All tracers behave relatively chemostatically ($R^2 < 0.05$) over the sampling period. Note that the F⁻ and B datasets were collected over a larger range of discharge than the optical brightener and *E. coli* datasets.

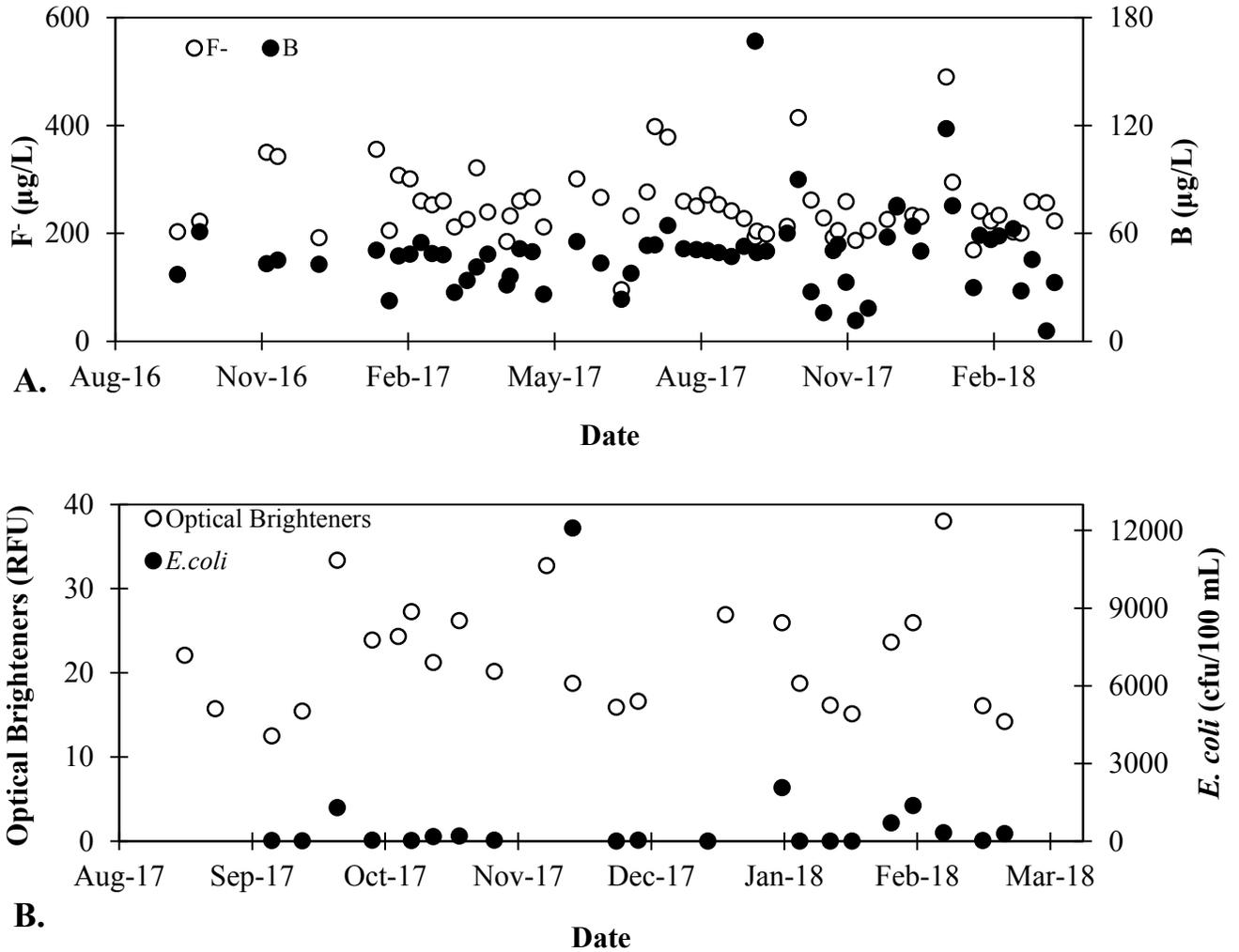


Figure 2. F⁻ (white circles) and B (black circles) concentrations (A.) or optical brightener (white circles) and *E. coli* (black circles) levels (B.) plotted against sample collection date. No seasonal trends were observed for any of the tracers ($R^2 \leq 0.01$; $p > 0.35$). Note that the F⁻ and B datasets were collected from September 2016 to March 2018, while the optical brightener and *E. coli* datasets were collected from September 2017 to March 2018.

3.2 Bacterial loads

Samples were analyzed for *E. coli* and total coliforms from September 2017 through March 2018 generally at or near baseflow conditions (i.e., $< 1 \text{ m}^3/\text{s}$; Table 1). *E. coli* levels were

variable throughout the sampling period, ranging from less than 5 cfu/100 mL to above the detection limit after a 5× dilution (i.e., >12098 cfu/100mL). We observed that 29% of the *E. coli* analyses exceeded the USEPA regulatory limit of 206 cfu/100 mL (MoDNR, 2009). Total coliform levels were also variable, but positively and significantly correlated with *E. coli* values ($R^2 = 0.60$ and $p < 0.001$; the statistical analyses only include data that were within range of our test).

Table 1. Discharge, *E. coli*, and total coliform bacteria levels in Deer Creek.

Date	Discharge (m³/s)	<i>E. coli</i> (cfu/100 mL)	Total Coliform (cfu/100 mL)
9/27/2017	<0.001	31.5	>12098.0
10/4/2017	0.000	21.6	>12098.0
10/12/2017	0.000	1297.5	>12098.0
10/20/2017	0.000	49.0	>12098.0
10/29/2017	0.000	32.0	593.5
11/3/2017	0.073	182.0	4082.0
11/9/2017	0.003	201.0	3850.5
11/17/2017	0.000	43.0	1538.0
12/5/2017	0.138	>12098.0	>12098.0
12/15/2017	0.000	5.0	154.5
12/20/2017	0.001	42.0	890.0
1/5/2018	0.674	<5.0	5.0
1/22/2018	0.878	2080.0	5056.0
1/26/2018	0.001	15.5	408.0
2/2/2018	0.000	<5.0	322.5
2/7/2018	0.000	<5.0	86.5
2/16/2018	0.110	628.0	710.5
2/21/2018	0.937	1377.5	>12098.0
2/28/2018	0.113	331.5	8664.5
3/9/2018	0.021	35.0	411.0
3/14/2018	0.011	10.0	645.5

Unlike previous *E. coli* results from our lab group (Hasenmueller and Shaughnessy, 2016; Hasenmueller, 2017), we did not observe a statistically significant correlation between *E. coli* and discharge ($R^2 = 0.02$; $p = 0.53$; Fig. 3A) or temperature ($R^2 < 0.01$; $p = 0.95$; Fig. 3B). The lack of correlation between *E. coli* and discharge is likely because we did not collect samples during high flow conditions (Fig. 1B). Increased flow in Deer Creek is induced by precipitation events, which increase suspended materials and bacteria levels. High flow can also introduce sewage from the nearby CSO into the stream when the sewer system is overwhelmed by new

runoff, thereby increasing *E. coli* levels due to human waste contributions. The lack of a correlation between *E. coli* and stream temperature can be explained by the duration of our sampling period: we only sampled for bacteria during fall and winter months (Fig. 2B). Hasenmueller (2017) showed that *E. coli* levels in Deer Creek were 80% lower during fall and winter compared to spring and summer months. Since bacterial growth is enhanced with increasing temperature, we believe that continued monitoring into the spring and summer months at Deer Creek would show similar trends as observed by Hasenmueller (2017).

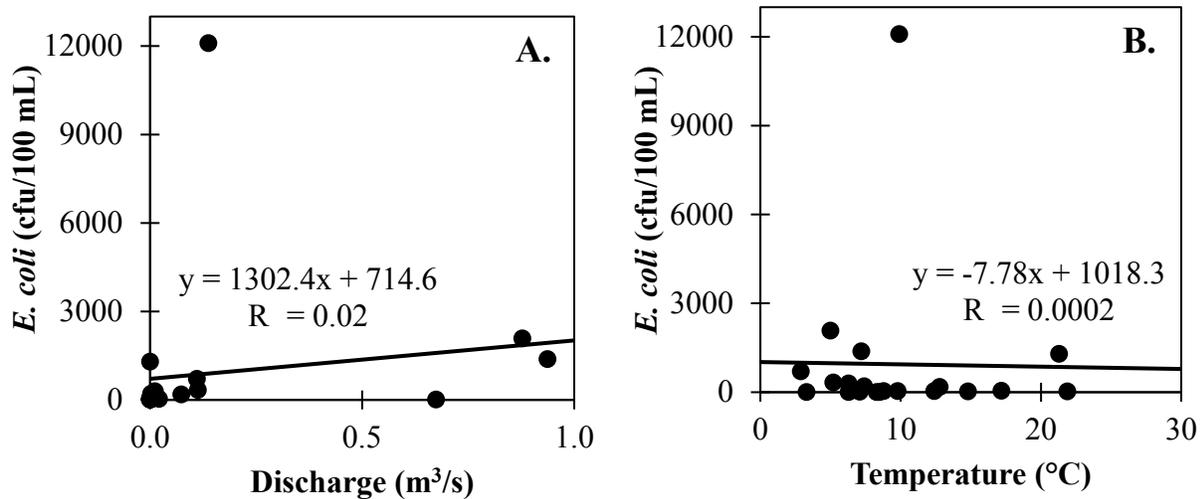


Figure 3. *E. coli* levels plotted against Deer Creek’s discharge (A.) and temperature (B.). Both correlations are statistically insignificant ($p = 0.53$ and 0.93 , respectively). This is likely due to the lack of samples collected during high flow periods and warmer temperatures, which have been shown by past workers to yield the largest bacterial levels in Deer Creek.

3.3 Municipal water inputs to Deer Creek

Results from our three end-member mixing model (Eqs. 1-3) for Deer Creek indicate that drinking water contributions range from 1 to 42% (average = $10 \pm 9\%$) and untreated wastewater contributions range from 9 to 34% (average = $18 \pm 7\%$) of the total stream flow. We compared our results for Deer Creek to studies of municipal water inputs to streams around the Saint Louis area by Lockmiller et al. (2017) and Lockmiller (2018). The highest contributions of drinking water to Deer Creek that we observed during the study period are similar to those in the most urbanized watersheds in Saint Louis sampled by Lockmiller et al. (2017) and Lockmiller (2018). Indeed, drinking water fractions of $>20\%$ of the stream flow were only observed in highly urbanized watersheds with impervious surface areas greater than 40% (compared to Deer Creek’s impervious surface area of only 28%).

Additionally, the highest wastewater inputs seen at Deer Creek are $\sim 18\%$ higher than wastewater inputs to highly urbanized streams during low flow conditions (Lockmiller et al.,

2017 and Lockmiller, 2018). Surprisingly, even the average percentage of Deer Creek's flow derived from wastewaters is 2% higher than that of the most highly urbanized watersheds (i.e., >40% watershed impervious surface area) sampled in Saint Louis by Lockmiller et al. (2017) and Lockmiller (2018). These municipal water contributions likely indicate inputs from the CSO that is just upstream of our sampling site at Deer Creek. With increasing runoff (and, therefore, increasing event water into the combined sewer system), the contributions of municipal waters from the CSO to Deer Creek are also likely to increase. Because of these CSO inputs, the relative fractions of our municipal water tracers remain fairly consistent with variable discharge and we do not see significant tracer dilution due to event water.

Since we did not observe any seasonal changes in municipal water inputs to Deer Creek (Fig. 2), we can infer that drinking water applications for lawn irrigation do not contribute substantially to Deer Creek's flow. If drinking water from irrigation was significantly influencing Deer Creek, we would expect to see higher drinking water contributions during the summer months when homeowners, parks, and golf courses more frequently water their lawns. The lack of seasonal trends in municipal water tracers indicates that leaking drinking water and wastewater infrastructure and the upstream CSO are likely large contributors of municipal waters to Deer Creek. However, the CSO is probably the largest contributor of municipal water to Deer Creek because the average untreated wastewater input to the stream is nearly twice as high as the average drinking water input.

4. Conclusions and need for future work

Our chemical and bacterial tracer results clearly show that Deer Creek is highly influenced by municipal waters, with wastewater contributions as high as 34% of the total flow, which is 18% higher than contributions to the most urbanized streams in Saint Louis. Drinking water contributions were shown to comprise up to 42% of the total flow, which again is similar to more urbanized and impacted stream systems. The lack of seasonal trends in drinking water inputs to Deer Creek may indicate that lawn irrigation is not a substantial contributor to the stream flow. Instead, we suggest that municipal water contributions to Deer Creek are largely controlled by discharges from the CSO as well as leaking municipal water infrastructure. However, more work during high flow periods is necessary to confirm these observations. Continuous monitoring of municipal water tracers throughout a flood could provide interesting information about how CSO inputs alter the stream's chemistry over short time periods. Although untreated wastewater contributions may be high at the onset of a flood event, there is potential for substantial dilution as the flood progresses. Additionally, we found that *E. coli* levels in Deer Creek did not follow expected trends with stream discharge and temperature. These discrepancies from previous work are likely influenced by our sampling routine which occurred during low flow and cooler periods when *E. coli* levels are lower. Future work should focus on collecting stream samples under a more dynamic discharge range, which could help us

better characterize the behavior of wastewater inputs from the nearby CSO. These bacterial data, in combination with the chemical data, could provide a comprehensive understanding of stream response to CSO inputs. These behaviors are important to understand as this CSO is scheduled for removal under the Metropolitan Saint Louis Sewer District's Project Clear. The data shown here act as a baseline and could be compared to future water quality analyses to show how effective CSO removal is in improving overall stream and ecosystem quality.

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