Water quality monitoring of Deer Creek at the Litzsinger Road Ecology Center to determine groundwater contributions to stream flow and pollutant loads

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1. Introduction and project background

Urban land use leads to problems with both water quantity and quality, yet the mechanisms that control urban stream water volumes and pollutant loads are still poorly understood. Few studies have examined the relative contributions of "newer" surface runoff vs. "older" groundwater to these urban systems. Increased impervious surface area and historical alterations of streams to become engineered channels can exacerbate local flooding that is followed by periods of low water retention (Criss and Shock, 2001). Moreover, there are frequently many potential sources of contaminants with complex pathways that lead to low water quality in urban streams (Wong et al., 2006; Hasenmueller and Criss, 2013).

It is well known that in forested watersheds a high proportion of the total discharge during a flooding event is from "older" groundwater contributions (i.e., baseflow; Buttle et al., 1995; Genereux and Hooper, 1998; Burns, 2002). However, rainfall-runoff response in urban watersheds has received little attention despite their proximity to humans, risk as flood hazards, and importance as ecological refuges. While urban watershed studies often assume that floodwaters are generated from impervious surface runoff during most rainfall events (Rose, 2003; Rodriguez et al., 2004), high baseflow contributions have been shown to account for a substantial fraction of the total flow in some urban streams (Buttle et al., 1995; Sidle and Lee, 1999; Gremillion et al., 2000). Therefore, the relative importance of impervious surface runoff and baseflow to urban stormflow generation is surprisingly unclear. Of particular concern is that the substantial runoff produced during floods in urban streams can mobilize and transport pollutants at rates that can dwarf their delivery during normal flows.

We monitored Deer Creek from June 2 to September 12, 2015 to determine overall water quality in a small urban stream. Water quality monitoring efforts were conducted at the Litzsinger Road Ecology Center (LREC), and are of interest since Deer Creek drains much of the western suburbs of Saint Louis and the LREC promotes education and outreach in the area. We also quantified the relative contributions of "newer" event water and "older" groundwater during flooding events using hydrograph separations. Deer Creek at the LREC is an ideal site to test urban stream response to flooding because of extensive monitoring already conducted at the site (Intuition and Logic, 2005; Lopez, 2009; Haake, 2011; Chott, 2013; Rinne, 2013), rapid perturbations in flow (USGS, 2016), easily accessible monitoring locations, and the education mission of the LREC.

2. Methods

We combined weekly field sampling, high frequency sampling during storm perturbations, and continuous *in situ* monitoring to understand water quality and groundwater contributions to Deer

Creek. During weekly field visits, point measurements of temperature, conductivity (measured as specific conductance), dissolved oxygen (DO), pH, and turbidity were measured with handheld meters and grab samples were collected for laboratory analysis. An *in situ* continuous monitoring device (i.e., YSI 6600 V2 sonde) was deployed from June 22 to September 12, 2015. This instrument continuously measured (5-minute data intervals) a suite of water quality parameters, including temperature, conductivity, pH, and DO. In addition, an automatic sampling device (i.e., ISCO model 6712) was used to collect physical samples at the monitoring site during floods; generally 10 – 50 samples were obtained to characterize these events. Discharge data was provided by USGS gaging station 07010075 located only 50 m downstream (USGS, 2016). Rain water samples were collected for chemical and isotopic analysis to determine the proportion of "new" water contributed to stream flow during flooding. Rainfall amounts were characterized with rain gauges located at Saint Louis University and LREC. Rainfall samples included total rainfall during a storm event as well as time series samples every 4 to 6 hours from the Saint Louis University gauge.

We separated field samples into subsamples for geochemical analyses. Untreated waters were analyzed with a Picarro L2130-i cavity ring-down spectrometer for hydrogen (H) and oxygen (O) isotopes. Values are reported in the conventional manner as $\delta^{18}O$ and $\delta^{2}H$ values relative to V-SMOW; precision is respectively ± 0.1‰ and ± 1.0‰. Subsamples for major element analysis were field-filtered (0.20 µm acetate filters) and field-acidified (trace metal grade HNO_3) into pre-cleaned high density polyethylene (HDPE) bottles. Major element (calcium, Ca; magnesium, Mg; potassium, K; and sodium, Na) concentrations were measured with an Inductively Coupled Plasma Optical Emissions Spectrometer (ICP-OES; Perkin-Elmer Optima 7300DV ICP-OES) in accordance with the techniques outlined in U.S. Environmental Protection Agency (USEPA) Method 200.7 (USEPA, 1990). Instrument operation and data processing were completed with the WinLab32™ (ICP-OES) software package. Blanks, reference standards (Sigma-Aldrich TraceCERT®), and duplicate and triplicate samples were also analyzed to check the precision and accuracy of analytical procedures; laboratory accuracy was ± 5%. Chloride (Cl) subsamples were also collected in pre-cleaned HDPE bottles, and concentrations were determined using USEPA-approved titration techniques (Hach, 2005). Additional stream water samples were collected in pre-cleaned, autoclaved HDPE bottles to measure *Escherichia coli* (*E. coli*) and total coliform levels. We used the IDEXX Colilert reagent and 51-well or 97-well Quanti-Tray® to enumerate colonies; all labware for bacterial analyses was autoclaved. This USEPA-approved method has a most probable number range limit of 1 to 802 (51-well tray) or 2,420 cfu 100 mL^{-1} (97-well tray). If we expected high bacteria levels, we diluted the samples with autoclaved deionized water.

Isotope and conductivity data were used to calculate the relative contributions of groundwater (baseflow through the hyporheic zone into the channel) and event water (from recent rainfall) to stream flow during flooding (i.e., hydrograph separations; Sklash and Farvolden, 1979). The relationship for two end-member mixing takes the form of equation (1),

$$Q_t C_t = Q_b C_b + Q_e C_e \qquad (1)$$

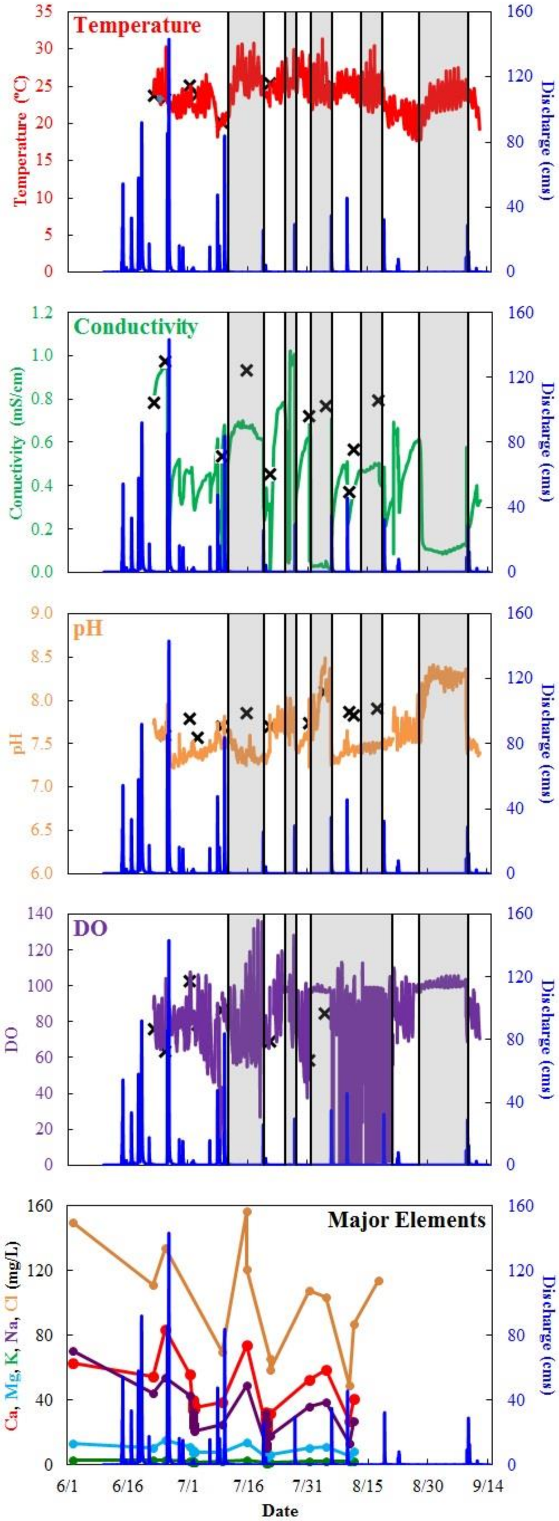

Figure 1. Deer Creek water quality data for June 2, 2015 through September 12, 2015. Measured parameters include temperature (ºC), conductivity (mS/cm), pH, DO (%), and major elements (Ca, Mg, K, Na, and Cl in mg/L). Crosses indicate point measurements of water quality parameters collected during field visits. These data were used to correct any drift in the monitoring sensors. During some periods of low flow, the monitoring equipment was not fully submerged in the stream; these events are marked with gray boxes.

where Q is the discharge, C is the concentration, and the subscripts represent the total (t), baseflow (b), or event water (e) discharge or concentration value. This relationship can be solved to obtain the fraction of discharge derived from baseflow (X_b), which is equal to Q_b/Q_t. The result is equation (2):

$$X_b = \frac{C_t - C_e}{C_b - C_e} \quad (2)$$

For our study, baseflow was defined by samples with (1) isotope values close to the weighted, long-term average of local meteoric precipitation (i.e., -7.0‰ and -45‰; see Criss, 1999), (2) conductivity values near the seasonal average for the stream, and (3) low stage. In contrast, event water features relatively low conductivity compared to baseflow, has variable isotopic composition, and occurs during high flow.

Statistical analyses included paired t-tests that were calculated using Microsoft Excel.

3. Results and discussion

3.1. Deer Creek water quality

We monitored a suite of water quality parameters over the summer of 2015 (Fig. 1; Table 1). Results of these monitoring efforts are discussed below. At times during the monitoring period, the water levels in Deer Creek were low enough that on several occasions our monitoring sensors were not fully submerged in the stream. We observed erroneous data during these periods, which are highlighted in gray in Fig. 1.

3.1.1. Temperature

Water temperature in Deer Creek varied from 17.7 to 31.4ºC (Fig. 1). We observed both diurnal and flood-induced fluctuations in temperature, with flood water temperature being a stronger control on stream temperature than daily oscillations in air temperature. In detail, there was an increasing difference between the daily high and low temperature of the stream water as the time from the most recent flood event increased.

3.1.2. Conductivity

The conductivity in Deer Creek was highly variable through the monitoring period, ranging from less than 0.10 mS/cm during flooding conditions up 1.02 mS/cm during prolonged low flow conditions (Fig. 1). Deer Creek had elevated salinity levels compared to unimpacted east-central Missouri streams, where conductivity values typically range from 0.2 to 0.5 mS/cm. Elevated conductivity in Deer Creek is primarily the result of road salting in the winter months (Shock et al., 2003; Hasenmueller and Robinson, 2016).

Conductivity decreased rapidly during flooding events then slowly increased during periods of low flow. Average baseflow conductivity was ~0.6 mS/cm. At the onset of flood events, the conductivity often initially increased due to the "first flush effect," when salts were flushed from the soils, but then decreased due to dilution by rainwater. Thus, in general, we observed a strong negative correlation between rainfall amount and conductivity during flooding. For example, conductivity decreased by less than 1% during small flood events (< 1.5 cms change in discharge) to 85% during the largest flood event (~ 150 cms).

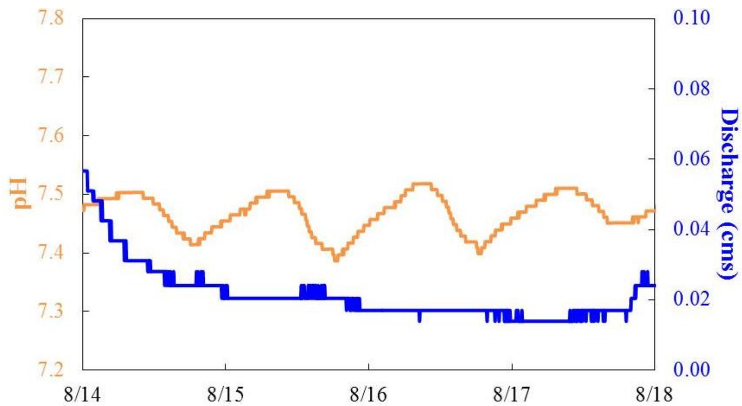

Figure 2. Daily oscillations in pH during low flow conditions.

3.1.3. pH

The pH of Deer Creek ranged from 7.2 to 8.5 (Fig. 1); these circum-neutral pH values are typical of Ca-Mg-bicarbonate-type waters. Stream pH fluctuated daily, with pH values peaking at approximately 9:00 and with lowest values observed around 18:00 (Fig. 2). These oscillations are due to lower dissolved CO_2 content causing higher pH during the day when photosynthetic organisms uptake CO_2 for photosynthesis. Higher dissolved CO_2 content and lower pH values occurred during the evening when photosynthetic organisms are less active.

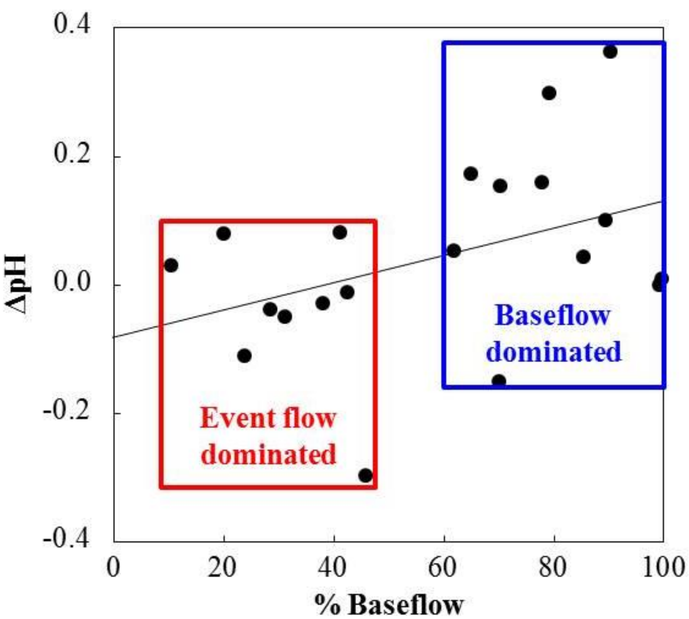

Figure 3. The difference in pH from baseflow (pre-flood conditions) to peak flow plotted against the total percentage of water from baseflow during flood events. Note that floods dominated by event water (< 50% baseflow) have lower pH than those dominated by baseflow (> 50% baseflow).

The pH also changed substantially during flooding events. During the rising limb of every flooding event observed during the study period, the pH of the stream increased. Interestingly, there was a significant difference ($p = 0.02$; Fig. 3) between the pH at peak flow for baseflow-dominated events compared to event water-dominated events. At the peak flow, most of the flooding events dominated by baseflow (> 50% baseflow) exhibited higher pH than initial pre-event pH conditions. On the other hand, the majority of event water-dominated floods (< 50% baseflow) exhibited lower pH than initial pre-event pH conditions. We suspect that the lower pH values observed in event water-dominated floods is due to a higher proportion of relatively acidic rainwater. The cause of higher pH values during peak flow compared to low flow for baseflow-dominated events is less clear and will require further study.

3.1.4. DO

The DO ranged from less than 50% up to 110% during the monitoring period (Fig. 1). Like pH, DO experienced diurnal oscillations due to the dominance of photosynthesis during the daylight hours and respiration during the night. At times, photosynthetic activities were so high that they supersaturated the water with DO (> 100% saturation). The largest variations in DO tended to occur during low flow periods. Though we did not measure stream nutrient contents for this study, we suspect that high concentrations of dissolved nitrogen (N) and phosphorus (P) species, similar to those observed in the region by Hasenmueller and Criss (2013), enhance biological activity in Deer Creek, leading to highly variable DO. The DO also changed substantially during flooding events. In general, the DO increased during these events due to water turbulence.

3.1.5. Major elements

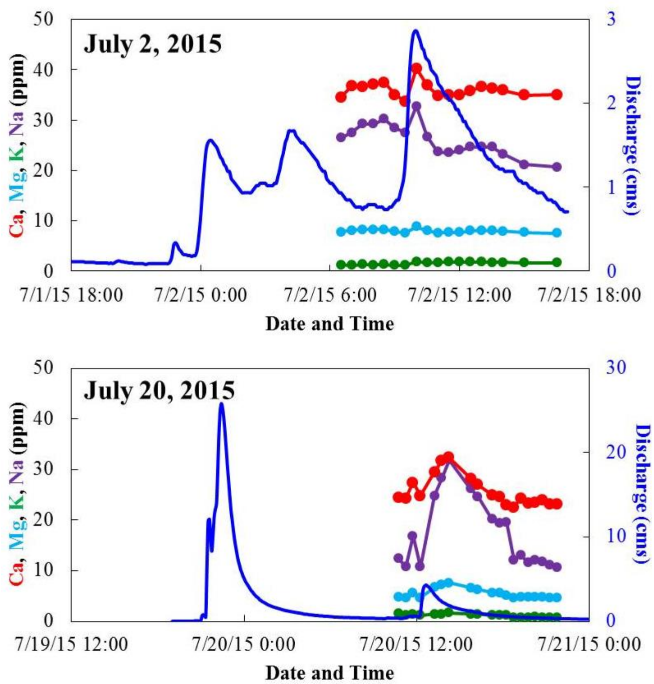

Figure 4. Major element concentrations during flooding events on July 2, 2015 (top) and July 20, 2015 (bottom). Note that both events were preceded by flooding.

Major elements, including Ca, Mg, K, Na, and Cl, were measured in samples collected during regular field visits and by the autosampler during flood events (Figs. 1, 4). Expectedly, the major elements had a strong ($R^2 > 0.7$), positive correlation with conductivity, as these elements are the major source of salinity in the stream. Indeed, like conductivity, the major element concentrations were highest during low flow conditions (Fig. 1), displayed evidence of first flush behavior (Fig. 4), and were diluted during flooding events by incoming dilute rainfall (Fig. 4).

The Ca (average = 36 mg/L; range = 23 to 84 mg/L), Mg (average = 7.5 mg/L; range = 4.6 to 15.1 mg/L), and K (average = 1.6 mg/L; range = 0.7 to 2.9 mg/L) were similar to natural surface water and groundwater concentrations in the area (USGS, 2016).

However, Na (average = 25 mg/L; range = 11 to 70 mg/L) and Cl (average = 36 mg/L; range = 23 to 84 mg/L) were elevated above background levels typical of east-central Missouri (USGS, 2016). Elevated Na and Cl in Deer Creek are the result of road salt application during the winter months. High levels of these Na and Cl are stored in the shallow groundwater (Hasenmueller and Robinson, 2016) and slowly released as baseflow to Deer Creek, even during the summer months, as observed in this study.

In addition to regular grab samples for major elements, we also collected high frequency samples for two flooding events on July 2 and July 20, 2015 (Fig. 4). During the July 2 event, all the major elements increased slightly on the rising limb of the hydrograph, probably due to salts being flushed from soils, then decreased at the onset of peak flow and during the recessional limb of the hydrograph. The July 2 chemograph responses at Deer Creek are typical of major element behavior during floods, but it is important to note that the initial concentrations of the major elements may be lower than typical baseflow conditions because the July 2 event was preceded by a small flood (see Fig. 1 for low flow major element concentrations). In contrast, during the July 20 event, major element concentrations decreased during peak flow then increased dramatically (up to 250%) after peak flow. Approximately 2 hours after peak flow, the concentrations of major elements began to decline. This behavior is not common in flood chemographs, but may be the result of the flood event being relatively small (i.e., only 4.3 cms at peak flow) and the fact that the event was proceeded by a much larger flood (i.e., 30 cms at peak flow).

3.1.6. Bacterial loads

Table 1. Bacteria levels in Deer Creek.

Date and time	*E. coli* (col/100 mL)	Total coliform (col/100 mL)
6/2/15 10:30	77.6	>2419.6
6/22/15 12:00	524.7	>2419.6
6/25/15 9:30	488.4	>2419.6
7/1/15 15:00	686.7	>2419.6
7/2/15 8:00	2406.6	>4839.2
7/2/15 8:30	2406.6	>4839.2
7/2/15 9:00	2406.6	>4839.2
7/2/15 9:30	3106.2	>4839.2
7/2/15 10:00	4839.2	>4839.2
7/2/15 10:30	>4839.2	>4839.2
7/2/15 11:00	>4839.2	>4839.2
7/2/15 13:30	>4839.2	>4839.2
7/2/15 16:30	>4839.2	>4839.2
7/15/15 18:58	471.8	>4839.2
7/20/15 10:45	922.2	>4839.2
7/20/15 11:15	1034.4	>4839.2
7/20/15 11:45	496.2	>4839.2
7/20/15 12:15	774.6	>4839.2
7/20/15 13:15	730.8	>4839.2
7/20/15 13:45	1158.8	>4839.2
7/20/15 14:15	1297.6	>4839.2
7/20/15 16:15	1373.4	>4839.2
7/20/15 18:45	1297.6	>4839.2
7/20/15 22:15	1960.8	>4839.2
7/21/15 13:23	1034.4	>4839.2
7/31/15 10:18	162.2	>802
8/4/15 10:58	115.2	>802
8/10/15 12:15	802	>802
8/11/15 12:40	153.6	>802
8/17/15 12:50	145.6	>802

Bacteria (i.e., *E. coli* and total coliform bacteria) samples were analyzed for both baseflow and flooding conditions (Table 1). Both *E. coli* and total coliform bacteria levels were elevated in Deer Creek and often exceeded the maximum detection limit for our analytical technique, even with dilution. Both *E. coli* and total coliform bacteria colony numbers were positively correlated with discharge in Deer Creek, with the highest levels observed during flooding events. The *E. coli* levels at the Deer Creek monitoring site were frequently higher than EPA regulatory limits (i.e., 206 cfu/100 mL; MoDNR, 2009), with 25 of our 30 measurements above regulatory limits.

3.2. Components of stream flow in Deer Creek during flooding

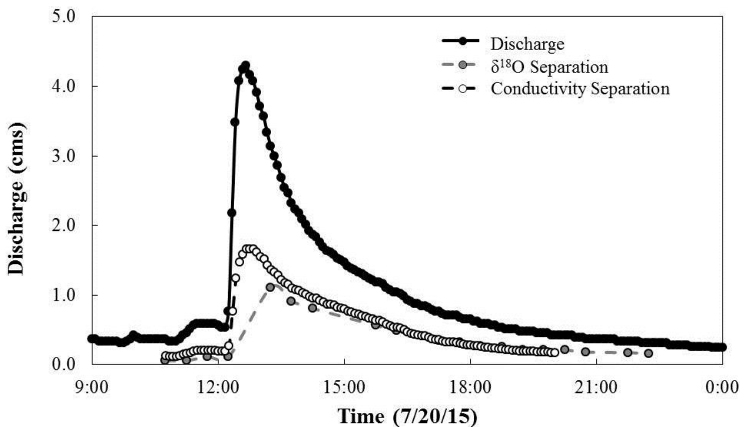

Figure 5. Hydrograph separations for a July 20, 2015 flood event using O isotopes and conductivity. Both methods yield similar results.

During the monitoring period, we captured a total of 14 flooding events with discharges above 2.5 cms during peak flow (Table 2). We used a combination of O isotopes and conductivity to conduct hydrograph separations for the Deer Creek floods. Given that measuring the isotopic composition of flood waters requires physical samples, we tested whether conductivity could be used as a good proxy for the stream isotopic response because we had a continuous, *in situ* record of conductivity changes. Hydrograph separations using conductivity have been used successfully in other studies of urban streams (i.e., Pellerin et al., 2008). For both types of hydrograph separation, we used either the isotopic composition or conductivity of local rainfall, baseflow (i.e., low flow stream conditions in a 1- to 5-day period prior to the flood event), and flood waters. Comparison of the two hydrograph separation methods for a July 20, 2015 flood event showed good agreement between the methods: the isotope hydrograph separation indicated that 44.5% of the total stream flow came from baseflow, while the conductivity hydrograph separation indicated that 43.3% of the total stream flow came from baseflow (Fig. 5).

Conductivity hydrograph separations for all 14 events showed variability in the baseflow component during flooding (Table 2). Despite the prevailing wisdom that urbanization and increased impervious surface area dramatically decrease baseflow to streams (Buttle et al., 1995; Genereux and Hooper, 1998; Burns, 2002; Rose, 2003; Rodriguez et al., 2004), we observed a surprisingly high contribution of baseflow during flood events to Deer Creek (Table 2). Indeed, our analyses showed that, on average, flood events were comprised mostly of baseflow (an average of 56% of the total stream flow during the flood for all 14 flood events). Only 42% of the floods were dominated by event water (i.e., > 50% of the total water). Furthermore, at peak discharge, 64% of the storms had water composed mostly of groundwater (i.e., > 50% of the peak flow). There was a negative correlation (R^2 = 0.45) between the percentage of baseflow during the flood and peak discharge.

Table 2. Baseflow contributions to peak flow and total discharge.

Date and time of peak flow	Q_{Peak} (cms)	Peak flow baseflow (%)	Total baseflow for the entire flood event (%)
6/26/2015 8:00	143.3	10	20
6/28/2015 22:15	16.3	65	74
7/2/2015 9:55	2.9	59	74
7/6/2015 13:30	15.6	100	92
7/8/2015 11:55	47.6	65	46
7/10/2015 6:15	83.8	24	35
7/19/2015 22:25	25.8	46	55
7/27/2015 19:05	29.5	29	36
8/5/2015 23:00	34.6	58	36
8/9/2015 21:55	45.6	78	62
8/19/2015 3:35	32.3	85	75
8/22/2015 17:50	8.0	70	59
9/9/2015 1:55	28.9	38	36
9/11/2015 6:45	2.5	99	83

4. Conclusions and need for future work

Our monitoring efforts over the summer of 2015 yielded an extensive suite of water quality data for Deer Creek at LREC, including continuous water quality records (temperature, conductivity, pH, and DO), major element data (Ca, Mg, K, Na, and Cl), and bacterial levels. We observed elevated salinity levels in the Deer Creek that are the result of excess road salt from the winter months being stored in the shallow groundwater and then being released as baseflow to the stream, large fluctuations in pH and DO that are probably the result of high nutrient loads in the stream enhancing biological activity, and highly elevated *E. coli* and total coliform bacteria levels.

In addition to our monitoring efforts, we made the important discovery that despite draining an urban area, Deer Creek is actually dominated by baseflow contributions during flooding events. This finding contradicts previous findings that urban streams are dominated by recent event water during floods. We hope to continue our monitoring efforts at Deer Creek at the LREC in the future so that we can further develop our flow component dataset and publish our findings in an academic journal.

5. Acknowledgements

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