Continued water quality monitoring of Deer Creek at the Litzsinger Road Ecology Center to determine seasonal variations in water quality and groundwater contributions

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1. Introduction and project background

Urban land use often exacerbates problems with both water quantity and quality, yet water and pollutant transport processes in urban watersheds are still poorly understood. In watersheds with low levels of development, "older" groundwater (i.e., baseflow) comprises the majority of the water volume transported during flood events, while the "newer" water from recent rainfall (i.e., surface runoff) represents only a small portion of the total flow (Buttle et al., 1995; Genereux and Hooper, 1998; Burns, 2002). In urban environments, large portions of watersheds are covered with impervious surfaces, which can intensify local flooding issues (Rodriguez et al., 2004; Rose, 2003) that are followed by periods of low water retention (Criss and Shock, 2001). The engineering of stream channels (i.e., straightening and lining) can further exacerbate these issues.

Surprisingly, few studies have directly addressed the relative contributions of baseflow and surface runoff to urban streams despite their proximity to humans, risk as flood hazards, and importance as ecological refuges. Buttle et al. (1995), Sidle and Lee (1999), and Gremillion et al. (2000) showed that baseflow can account for large portions of the total discharge volume in urban streams during floods. Indeed, Deer Creek features large contributions of baseflow during summer flood events (up to 92%; Hasenmueller and Shaughnessy, 2016). This result is intriguing given that floods in other Saint Louis area streams, including Deer Creek's tributary Black Creek, are often comprised of <25% baseflow (Hasenmueller et al., 2017). Thus, it is of particular interest to understand why Deer Creek has uniquely high baseflow contributions during floods. It is also important to determine if there are any seasonal variations in baseflow at Deer Creek because previous monitoring efforts focused only on flood events during the summer months (Hasenmueller and Shaughnessy, 2016).

In addition to variations in water quantity during flood events, it is critical to characterize the relative quality of water in urban environments because of the risks associated with human and wildlife exposure to polluted surface waterbodies. Studies that continuously assess multiple water quality parameters in urban streams over seasonal timescales are relatively rare and therefore important contributions to our understanding of urban watersheds. Moreover, there are many potential contaminant sources that may lead to low water quality in urban streams, and the relative contributions of baseflow and surface runoff can affect the type and quantity of pollutants and pathogens that are delivered to urban streams (Wong et al., 2006).

Building on previous work by our group (Hasenmueller and Shaughnessy, 2016) and others (Intuition and Logic, 2005; Lopez, 2009; Haake, 2011; Chott, 2013; Rinne, 2013), this report summarizes the major findings on seasonal variations in water quality and groundwater contributions during flooding to Deer Creek at the Litzsinger Road Ecology Center. Deer Creek at the Litzsinger Road Ecology Center is an ideal site to test urban stream response to flooding events because of extensive monitoring already conducted at the site (Intuition and Logic, 2005; Lopez, 2009; Haake, 2011; Chott, 2013; Rinne, 2013; Hasenmueller and Shaughnessy, 2016), the presences of rapid perturbations in stream flow (USGS, 2017), and the education mission of the Litzsinger Road Ecology Center.

2. Methods

2.1. Field methods

To understand seasonal effects on water quantity and quality at Deer Creek, we combined weekly field sampling, high frequency sampling during storm perturbations, and continuous *in situ* monitoring of water quality parameters. The Litzsinger Road Ecology Center site was visited on an approximately weekly basis from September 2, 2016 to May 12, 2017 to measure temperature, conductivity (measured as specific conductance), chloride (Cl^-), turbidity, dissolved oxygen (DO), and pH with handheld meters. During site visits from September 2 to December 31, 2016, we also collected physical samples of the stream water for lab analyses of *Escherichia coli* (*E. coli*), total coliforms, and stable isotopes. Additional physical samples were also collected using an automatic sampling device (i.e., ISCO model 6712) to characterize stream response during flooding; generally 10-50 samples were obtained to characterize these events. An *in situ* continuous monitoring device (i.e., YSI 6600 V2 sonde), which continuously measured (5-minute data intervals) a suite of water quality parameters, including temperature, conductivity, Cl^-, turbidity, DO, and pH, was deployed from September 2, 2016 to May 12, 2017.

In addition to chemical data collected for the stream, we also archived discharge data measured by USGS gaging station 07010075, which is located only 300 m downstream of our monitoring site (USGS, 2017). Precipitation samples were collected for chemical and isotopic analyses to determine the proportion of “new” water contributed to stream flow during floods using the same methods reported by Hasenmueller and Shaughnessy (2016).

2.2. Lab methods

Grab samples for *E. coli* and total coliforms were collected in pre-cleaned, autoclaved HDPE bottles. We used the IDEXX Colilert reagent and 51-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 cfu/100 mL. If we expected high bacteria levels, we diluted the samples with autoclaved, deionized water. We also analyzed a separate subset of stream samples and the precipitation samples for stable isotopes using the same methods as Hasenmueller and Shaughnessy (2016). Briefly, 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‰.

2.3. Hydrograph separations

We used our conductivity and isotope data from flood responses to quantify the changes in 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) over seasonal timescales. The relationship for two end-member mixing takes the form of equation (1),

$$Q_t C_t = Q_b C_b + Q_e C_e \tag{1}$$

where Q is the discharge, C is the tracer value, 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):

$$X_b = \frac{C_t - C_e}{C_b - C_e} \tag{2}$$

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. Our fall and winter hydrograph separation datasets were compared to summer flood responses at Deer Creek collected by Hasenmueller and Shaughnessy (2016) in the summer of 2015.

3. Results and discussion

3.1. Seasonal variations in water quality at Deer Creek

Our monitoring results are outlined in the following sections and summarized in Fig. 1 and Table 1. These efforts capture Deer Creek's physical and geochemical responses from September 2, 2016 through May 12, 2017 (i.e., fall, winter, and spring), which we compared to results from Hasenmueller and Shaughnessy (2016) collected during the summer of 2015. We compared these time periods in an effort to understand seasonal variations in water quality and flowpaths at Deer Creek.

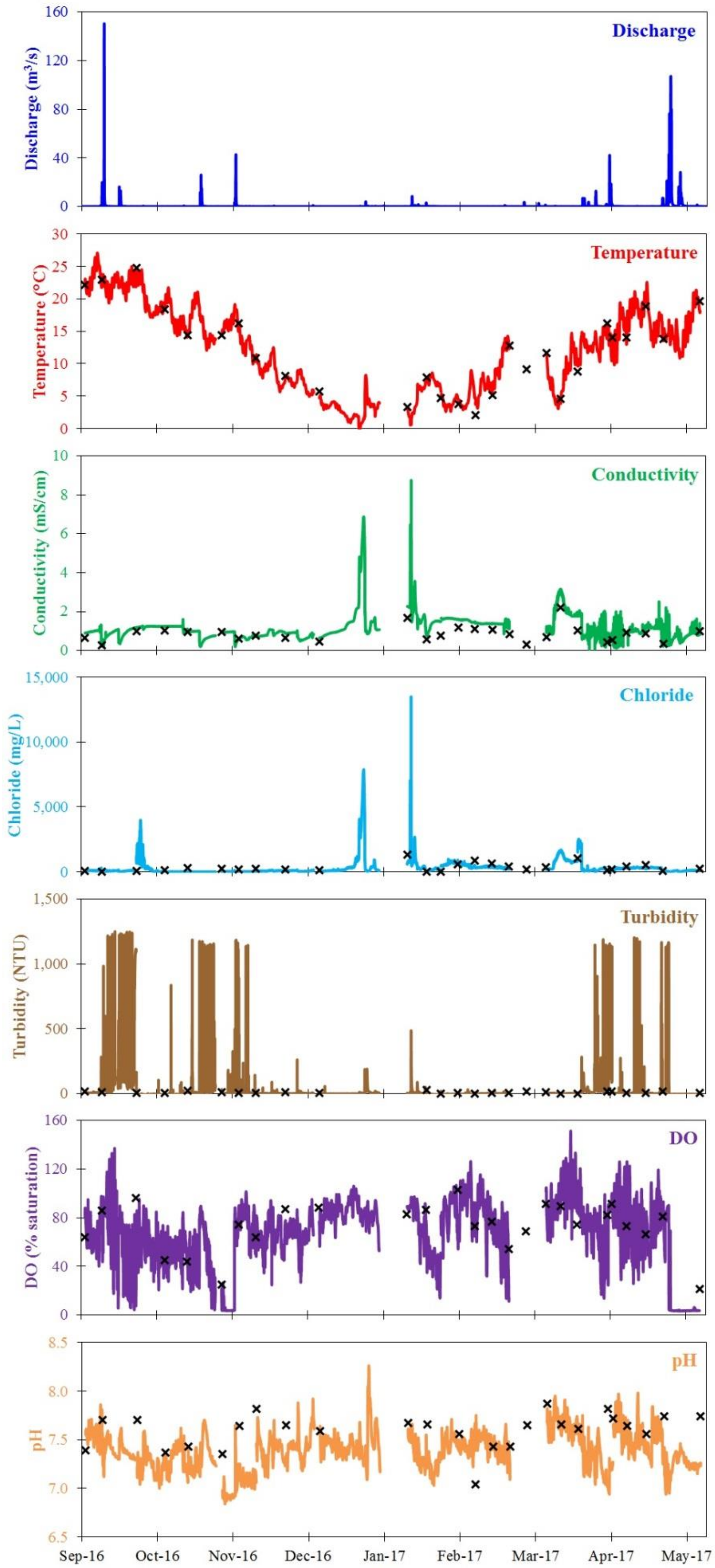

Figure 1. Deer Creek discharge (USGS, 2017) and water quality data from September 2, 2016 through May 12, 2017. Measured water quality parameters include temperature (ºC), conductivity (mS/cm), Cl^- (mg/L), turbidity (NTU), DO (% saturation), and pH. Crosses indicate point measurements of water quality parameters collected during field visits. These point data were used to correct any drift in the monitoring sensors.

3.1.1. Temperature

Expectedly, water temperature at Deer Creek was lower during the of fall of 2016 through the spring of 2017 (range = -0.2-27.1ºC; average = 12.0ºC; Fig. 1) compared to the summer of 2015 (range = 17.7-31.4 ºC; average = 23.8ºC; Hasenmueller and Shaughnessy, 2016). Similar to the summer of 2015, we observed both diurnal and flood-induced fluctuations in temperature, with flood response being a stronger control on stream temperature than daily oscillations in air temperature. In detail, daily oscillations were attenuated during flood events, and 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 and Cl^-

The conductivity at Deer Creek was highly variable and depended on flow conditions and land use practices. The conductivity ranged from a minimum of 0.04 mS/cm during peak flooding to a maximum of 8.74 mS/cm during the winter road salting season (Fig. 1). During low flow periods in the non-road salting months, the average conductivity (1.16 mS/cm) observed at Deer Creek was well above background levels for rural stream systems in the region (i.e., 0.2-0.5 mS/cm; Winston and Criss, 2002; Hasenmueller et al., 2017). This indicates that there is likely substantial contamination of the shallow groundwater in the watershed due incomplete flushing of winter road salt after application.

Continuous monitoring data show that periods of high conductivity following road salt applications were predictably associated with high Cl^- levels (range = 0.0-13,485.8 mg/L; average = 318.5 mg/L; Fig. 1). Moreover, these spikes in Cl^- concentration during the winter were consistently higher than the USEPA limits (Fig. 2; USEPA, 2017) for chronic Cl^- contamination (230 mg/L) and, on several occasions, exceeded the acute contamination level (860 mg/L). Following one road salting event in January 2017, the Cl^- concentrations were extraordinarily high at 13,485.8 mg/L; close to the concentration observed in salt-laden snowmelt runoff from roads in the area (Hasenmueller and Criss, 2013). Cl^-, like conductivity, was also elevated during the summer months (Hasenmueller and Shaughnessy, 2016). Nevertheless, the average Cl^- concentration observed during this study was nearly an order of magnitude higher than the average Cl^- concentration observed in the summer of 2015. Thus, large amounts of the salt applied during the winter are eventually flushed from the watershed in the late summer.

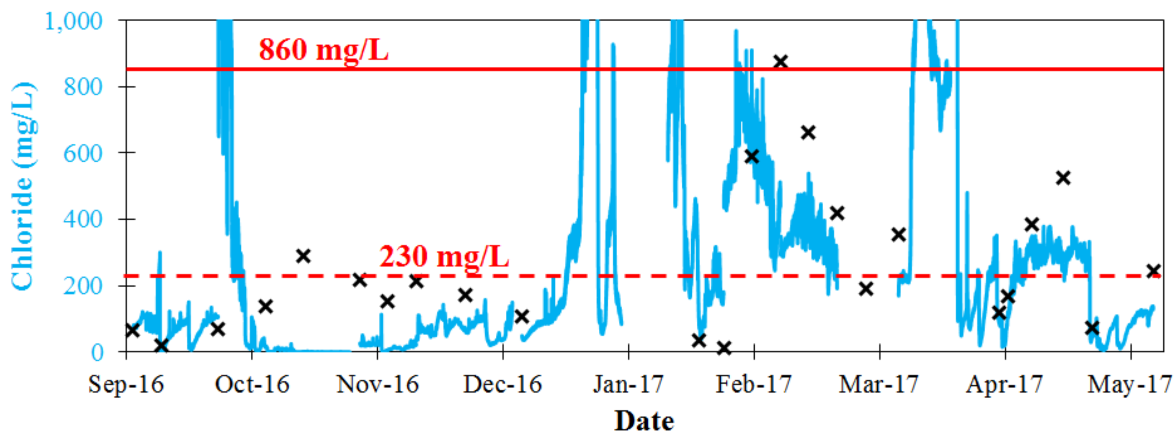

Figure 2. Deer Creek Cl^- (mg/L) concentrations from September 2, 2016 through May 12, 2017. Only data <1,000 mg/L from Fig. 1 are shown. Crosses indicate point measurements of Cl^-, the dashed red line indicates the USEPA limit for chronic Cl^- contamination (230 mg/L), and the solid red line indicates the USEPA limit for acute Cl^- contamination (860 mg/L). Both regulatory limits are frequently exceeded following winter road salt applications.

3.1.3. Turbidity

Turbidity (a proxy for total suspended solids) ranged from nearly zero to 1,239 NTU during the monitoring period (Fig. 1). Turbidity was generally low (<10 NTU) during low flow conditions, but increased by up to 124-fold during flood events. Interestingly, high turbidity levels in response to flood events at Deer Creek were protracted compared to the flood-induced turbidity responses observed in other local streams (Hasenmueller et al., 2017). For other streams in the area, high turbidity values were typically observed only on the rising limb of the flood hydrograph. In contrast, our monitoring site at the Litzsinger Road Ecology Center exhibited high turbidity throughout the monitored floods, including on the recessional limbs. We suspect this response is due, in part, to the high erosion rates observed at the site where our monitoring device is deployed. The monitoring device is located on a cut bank that has experienced significant erosion. We surmise that even during the lower discharge rates that occur on the recessional limbs of flood hydrographs there is still significant suspension of sediments occurring at this site.

3.1.4. DO

The DO ranged from 0.33 mg/L (3.3% saturation) up to 15.76 mg/L (151.3% saturation), with an average value of 7.49 mg/L (66.7% saturation; Fig. 1). The average daily DO values generally increased during the winter months when temperatures were lower. This is a result of gases like O_2 being more soluble in water at low temperatures. Similar to the summer of 2015 (Hasenmueller and Shaughnessy, 2016), we observed diurnal oscillations in DO 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 (i.e., >100% saturation). The largest variations in DO tended to occur during low flow periods. The oscillations in DO also increased with the higher temperatures observed during the early fall and late spring (Fig. 3), likely because aquatic photosynthesizes are more active when stream temperatures are higher. 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), enhanced 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. Additionally, we observed extremely low DO levels for short periods in October 2016 and late April and May 2017 (Fig. 1). We suspect that these low values are due to sediment accumulation (from the high erosion rates) around the housing unit for our instrumentation rather than chronically low DO levels at Deer Creek. Indeed, the measured DO levels increased after these low DO periods when we removed our monitoring devices for calibration (Fig. 1), thereby clearing the housing unit of sediment.

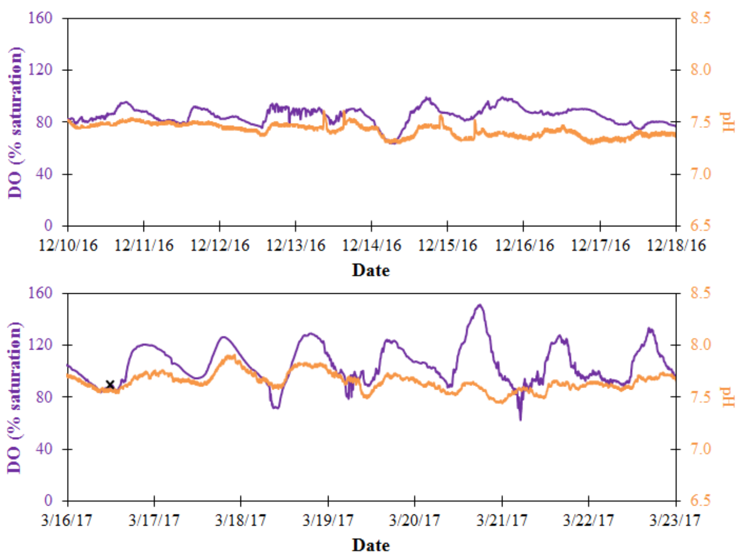

Figure 3. Stream DO (% saturation) and pH response during low flow conditions at Deer Creek during the winter (top; average water temperature was ~2°C) and during the early spring (bottom; average water temperature was ~10°C). Diurnal oscillations in DO and pH decreased with decreasing temperature as biological activity decreased.

3.1.5. pH

Stream pH was circum-neutral during the monitoring period, ranging from 6.8 to 8.3 (average = 7.4). The pH values observed during this study were slightly lower than those observed by Hasenmueller and Shaughnessy (2016) in the summer of 2015, when stream pH ranged from 7.2 to 8.5. We suspect that the lower pH levels observed during this study were the result of lower biological activity. In detail, photosynthetic organisms remove dissolve CO_2 from the water during the warmer months. In the cooler months, when these organisms are less active, stream CO_2 levels can increase thereby decreasing the pH.

Biological activity in Deer Creek also caused diurnal variations in pH similar to those observed in the DO signature (Fig. 3). 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 were less active. Similar to the DO response, these oscillation decreased in amplitude during the coolest months.

3.1.6. Bacteria loads

Water samples were analyzed for bacteria levels (i.e., *E. coli* and total coliform) during baseflow conditions for the fall and winter of 2016 (Table 1). The bacteria levels at Deer Creek were frequently elevated during the monitoring period. Indeed, *E. coli* levels often exceeded the USEPA regulatory limit of 206 cfu/100 mL (MoDNR, 2009), with 3 of our 6 measurements above the USEPA limit. Total coliform levels always exceeded the maximum detection limit for our analytical technique, even when samples were diluted.

Table 1. *E. coli* and total coliform level in Deer Creek.

Date and Time	*E. coli* (cfu/100 mL)	Total coliform (cfu/100 mL)
09/23/2016 15:05	212.4	>802.0
10/05/2016 08:00	34.8	>802.0
10/14/2016 13:35	171.6	>802.0
10/28/2016 13:30	519.2	>802.0
11/04/2016 13:47	802.0	>802.0
12/07/2016 13:30	34.8	>802.0

Using both the 2015 (Hasenmueller and Shaughnessy, 2016) and 2016 (this study) bacteria data, we observed that the strongest controls on bacteria loads were stream discharge and temperature (Fig. 4). Both *E. coli* and total coliform bacteria colony numbers were positively correlated with discharge, where the highest bacteria levels were observed during flooding events. Additionally, *E. coli* levels were nearly 80% lower in fall and winter of 2016 compared to the summer of 2015 during low flow conditions. This result is unsurprising given that bacterial growth decreases with decreasing temperature.

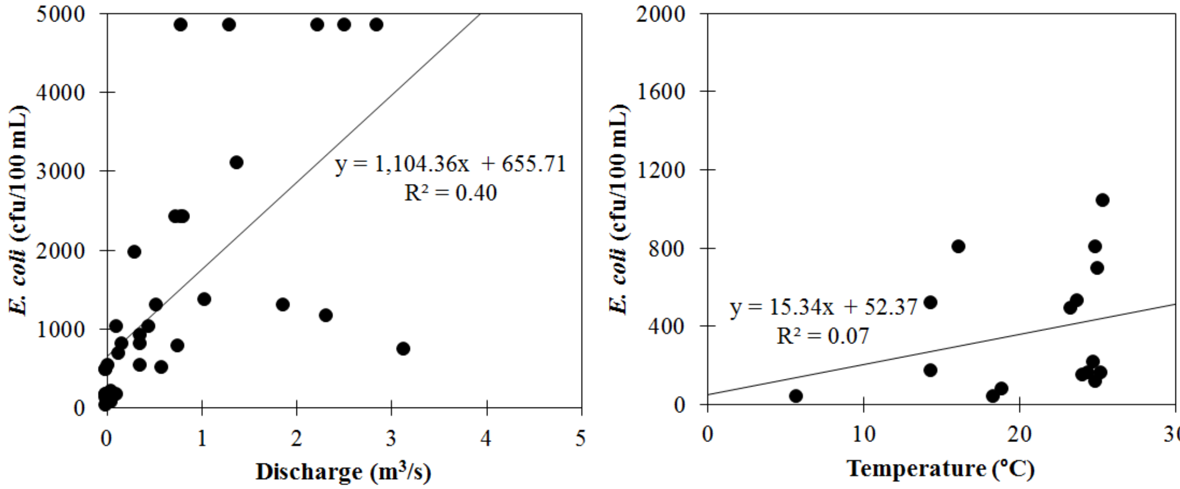

Figure 4. *E.coli* (cfu/100 mL) levels plotted as a function of stream discharge (left) and temperature (right). There is a positive correlation between *E. coli* and both parameters. Note that the *E. coli* data for both this study and the Hasenmueller and Shaughnessy (2016) study are plotted. Additionally, only the *E. coli* and temperature data during low flow conditions are plotted. This is because flood events strongly control stream temperature and are independent of seasonal changes.

3.2. Seasonal variations in baseflow contributions to flood events at Deer Creek

During the monitoring period, we captured multiple flood events for Deer Creek at the Litzsinger Road Ecology Center with our monitoring equipment, including four extreme floods with discharges above 40 m^3/s during peak flow (Fig. 1). We used a combination of H and O isotopes and conductivity to conduct hydrograph separations for the Deer Creek floods to determine the relative contributions of “older” groundwater and “newer” rainfall to the stream using the methods of Pellerin et al. (2008), Hasenmueller and Shaughnessy (2016), and Hasenmueller et al. (2017). There was good agreement between the two hydrograph separation methods (i.e., <5% difference) prior to the road salting events in the winter (during this time, conductivity in the stream was significantly affected by road salt applications; thus, conductivity hydrograph separation were not reliable). We used conductivity hydrograph separations for seven flood events that occurred from September to December 2016 (Table 2).

Table 2. Baseflow contributions during flooding events.

Date and Time	**Peak discharge (m^3/s)**	**Baseflow (% of total discharge)**
9/8/2016 7:00	162.5	23%
9/16/2016 5:51	36.2	26%
9/25/2016 21:25	0.3	100%
10/19/2016 9:51	39.4	24%
11/2/2016 18:51	75.3	27%
11/23/2016 8:29	45.2	92%
11/27/2016 18:51	2.5	76%

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 high contribution of baseflow to Deer Creek during flood events. These high baseflow inputs were also observed in Hasenmueller and Shaughnessy's (2016) previous study of Deer Creek. Our analyses showed that, on average, flood events were comprised mostly of baseflow (an average of 53% of the total stream flow during the flood for all seven flood events). Generally baseflow contributions decreased with increasing discharge volumes, and the largest floods had the lowest baseflow contributions. In contrast to the summer of 2015 hydrograph separation results (Hasenmueller and Shaughnessy, 2016), we found a slightly higher prevalence of event water-dominated floods (>50% of the total discharge) at Deer Creek in the fall and winter of 2016 (57% of all floods) compared to the summer of 2015 (42% of all floods; Hasenmueller and Shaughnessy, 2016). We hypothesize that the slightly lower total baseflow contributions during the fall and winter months are the result of decreased vegetative cover from leaf drop in the fall. Leafy vegetation can decrease surface runoff during the summer months, so we suspect the higher surface runoff component in the fall and winter months is related to this change in leafy cover in the Deer Creek watershed.

4. Conclusions and need for future work

Our monitoring efforts from September 2, 2016 through May 12, 2017 yielded an extensive suite of water quality data for Deer Creek at the Litzsinger Road Ecology Center. Our datasets include continuous water quality records (i.e., temperature, conductivity, Cl^-, turbidity, DO, and pH), bacteria levels (i.e., *E. coli* and total coliforms), and the relative contributions of "older" groundwater (i.e., baseflow) versus "newer" event water (i.e., recent rainfall) to the stream during floods. We observed extremely high conductivity and Cl^- values during the winter months, which coincided with winter road salting. Importantly, Cl^- values commonly exceeded USEPA regulatory limits for aquatic life. These deicing chemicals were incompletely flushed from the watershed after road salt applications, leading to elevated conductivity and Cl^- values during the non-salting seasons, including during the previous monitoring efforts in the summer of 2015. During flooding events, conductivity and Cl^- levels decreased as a result of the influx of dilute rainwater. Additionally, we observed high turbidity levels during these flood events. We also observed large fluctuations in DO and pH (as was also observed in the summer of 2015) that are likely the result of biological activity in the stream. These fluctuations decreased in amplitude during the winter when aquatic organisms were less active. Likewise, we observed lower *E. coli* and total coliform levels during the cooler months of the fall and winter of 2016, though *E. coli* levels still periodically exceeded USEPA regulatory limits.

In addition to our water quality monitoring efforts, we confirmed the previous observations from the summer of 2015 that Deer Creek is generally dominated by baseflow contributions during flood events. Nevertheless, baseflow contributions decreased in the fall and winter months compared to the summer. We suspect that lower baseflow contributions in the fall and winter months are due, in part, to leaf drop in the fall. Decreased leaf cover in the watershed following leaf drop leads to more surface runoff during rainfall events. We hope to continue our monitoring of Deer Creek at the Litzsinger Road Ecology Center. We would like to obtain a full year of monitoring data to further assess the seasonal water quality and baseflow responses in the stream. Once we have obtained these data, we plan to publish our findings in an academic journal.

5. Acknowledgements

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