

The influence of urban hydrology on water quality in the South Platte River, Denver, Colorado, USA

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Abstract

As the global population continues to shift into cities, urban hydrologic systems are becoming increasingly important drivers of overall water quality. Engineered waterways and impervious surfaces strongly influence baseline flow, peak flow, and the transport of pollutants in the urban environment. Between May 2016 – May 2019, we systematically measured water temperature, pH, dissolved oxygen, biochemical oxygen demand, and the concentrations of nitrate-N, ammonia-N, and orthophosphate in the South Platte River in the Denver metropolitan area, Colorado, USA. We found that the overall water quality of the river decreased through the study area. In addition, there appear to be several hotspots with consistently poor water quality. While it is beyond the scope of this paper to determine the specific sources of the hotspots, it seems likely that wastewater treatment facilities contribute to elevated pollution levels. We also found that water quality was strongly influenced by season. Decreased natural flows during the late fall and winter lead to higher concentrations of nutrients and lower dissolved oxygen levels. Most of the samples collected in this study had nutrient levels that were out of compliance with state regulations for nitrogen and phosphorus concentrations while dissolved oxygen and temperature levels were better than threshold values. Urban hydrologic systems are complex and improving water-quality may be difficult. However, tightening of water-quality standards could result in positive changes to this system.

Keywords

urban hydrology, impervious surface, water quality, engineered waterways, nutrient pollution, environmental compliance, seasonal hydrology, biochemical oxygen demand

Introduction

As of 2018, over 55% of the global population lives in cities, with nearly 25% living in a city over 1 million people. By 2030, the United Nations predicts that over 60% of the global population will be urban and this number will likely continue to rise for the foreseeable future (United Nations, 2018). Consequently, to understand ecological systems in our anthropogenic world, it is critical to consider the influence of densely populated areas on these systems. Humans fundamentally change natural systems in a variety of ways including physical alterations, changes in energy flow, and disruption of biogeochemical cycles. Due to the overwhelming size of modern cities and the increasing demand for resources, hydrologic systems are severely impacted (Millennium Ecosystem Assessment, 2005).

Within a waterway, the flow regime is a measure of the pattern and variation in streamflow over time and includes the magnitude, frequency, duration, timing, and rate of change of hydrologic conditions in a river. In a natural system, the flow regime is controlled by a range of parameters including climate, geomorphology, soils, biota, watershed size, and stream pattern (Poff et al., 1997). In the urban environment, physical modifications including dam construction and impervious surface can fundamentally alter the natural flow regime (Baker, Richards, Loftus, & Kramer, 2004).

Dams serve a variety of purposes, but two of the most common are flood control and water storage (Graf, 2001). By regulating discharge from the reservoir, managers can reduce the magnitude of high flow events and minimize the risk of downstream flooding. Often, water is removed directly from the reservoir for use, thus reducing flow in the downstream river. Low flow from dam restriction can partially explain some of the water degradation in urban areas; with reduced flow, pollutant concentrations may be elevated due to a lack of dilution (Mosley, 2015; Olatunde et al., 2015; Rolls, Leigh, & Sheldon, 2012).

Perhaps the most significant aspect of the urban landscape that affects waterways is increased impervious land cover. Urban catchments are dominated by large, impervious surface areas that reduce infiltration and funnel water into engineered systems designed to convey water quickly and efficiently (Booth & Jackson, 1997). These engineered drainage areas tend to result in flashy flows, with flowrates dramatically affected by even small precipitation events. In addition, rapid sheet flow leads to the accumulation of nutrients, heavy metals, sediment, and other pollutants and transports them to the river (Paul & Meyer, 2001; Rolls et al., 2012; Walsh et al., 2005).

In many urban areas, altered hydrology contributes significantly to the overall water quality in urban rivers. Elevated concentrations of nitrogen, especially ammonia (NH_3), nitrate (NO_3^-), and nitrite (NO_2^-) (Groffman, Law, Belt, Band, & Fisher, 2004; Larned, Snelder, Unwin, & McBride, 2016; Schoonover, Lockaby, & Pan, 2005); and phosphorus, including total phosphorus (TP) and orthophosphate (PO_4^{3-}) (Carpenter et al., 1998; Nagy, Lockaby, Kalin, & Anderson, 2012; Zhang, Shao, Liu, Xu, & Fan, 2015) have been observed in many urban areas. In addition to surface runoff, wastewater treatment plant effluent, raw sewage, fertilizer, and fossil fuel combustion (atmospheric deposition) are common sources of nitrogen and phosphorus (Bernhardt, Band, Walsh, & Berke, 2008; Brown et al., 2009; Gregory & Calhoun, 2007; Son, Goodwin, & Carlson, 2015).

Biochemical oxygen demand (BOD) is often used to assess the amount of organic pollution in a body of water. In urban areas, elevated BOD can be attributed to a variety of causes including discharge from wastewater treatment facilities, effluent from pulp and paper mills and food processing plants, dead plants and animals, and raw sewage (Magdaleno et al., 2001; Olatunde et al., 2015; Rice & Bridgewater, 2012). When BOD is high, dissolved oxygen (DO) is often low, although DO can also be affected by temperature, the presence of ammonia, and the degree of mixing due to water movement (Rice & Bridgewater, 2012). Low DO concentrations are common in urban waterways and can significantly affect the health of aquatic biota (Glinska-Lewczuk et al., 2016; Olatunde et al., 2015; Ouyang, Zhu, & Kuang, 2006).

Urban areas in general tend to have higher air temperatures due to the urban heat island effect. This phenomenon, in addition to stormwater runoff, effluent from electricity generation, and effluent from industrial processes can contribute to elevated temperatures in urban streams (Abdi & Endreny, 2019; Herb, Janke, Mohseni, & Stefan, 2008; Somers et al., 2013). Water temperature is one of the most important factors influencing the aquatic biotic community. Restoring native biota to an urban river is often challenging due to the thermal characteristics of the system (Cockerill & Anderson, 2014; Wang, Lyons, & Kanehl, 2003).

Water in urban systems often departs from neutral and, in some cases, it can be strongly acidic or basic (Pasquini, Formica, & Sacchi, 2012; Peters, 2009; Szita et al., 2019). Industrial pollutants, atmospheric pollution (deposition), and underlying geology (carbonate minerals) can affect pH in the urban environment (Malmqvist & Rundle, 2002; Peters, 2009). Acidification of urban rivers is directly detrimental to biota and is also correlated with increased concentrations of heavy metals (Das, Nordin, & Mazumder, 2009).

While it seems clear that urban hydrology tends to affect water quality in a negative way, it is less clear how these effects are impacted over space and time. In this study, we measured a range of water quality parameters in the South Platte River, which flows approximately 60 km through the Denver metropolitan area, Colorado, USA. We had two goals: 1) To measure water quality over several years to determine whether seasonal hydrologic patterns influence water quality and 2) To evaluate how the urban drainage system and the amount of impervious surface area affected water quality in this system.

Methods

Study Area

The South Platte River presents a unique opportunity to investigate the influence of urbanization on water quality. It emerges from the Rocky Mountains in the southwest corner of the Denver metropolitan area and travels more than 60 km northeast through the length of the city (Figure 1). There is little development upstream of the emergence point, although abandoned mines may affect water pH and contribute some heavy metals and sediment. As the river flows through the metro area, it moves through several different levels of urbanization. It begins by moving through suburban areas for approximately 30 kilometers, then goes directly through the highly urbanized core of the downtown area for approximately 10 km before moving again into suburban areas for approximately 10 km and finally through exurban, agricultural, and natural grassland areas for another 10 km.

The South Platte Watershed has an area of approximately 62,937 km² and is located in three states: Colorado (79% of the watershed), Nebraska (15%), and Wyoming (6%) (Figure 2). The South Platte River originates in the Rocky Mountains in central Colorado, at an elevation over 4,300 m and travels approximately 725 km to its confluence with the North Platte River. The Platte River is a part of the Mississippi River watershed which ends in the Gulf of Mexico (Dennehy, Litke, McMahon, Heiny, & Tate, 1995). Once the South Platte River enters the Denver metro area, it is designated as a warm water stream, meaning warm-water aquatic species are most commonly found in the river (Colorado Department of Public Health and Environment, 2017).

The basin includes two physiographic provinces, the Front Range Section of the Southern Rocky Mountain Province and the Colorado Piedmont Section of the Great Plains Province. Much of the geology underlying the Denver region consists of unconsolidated surficial eolian and fluvial deposits and sedimentary rock formations (Trimble, Machette, Moore, & Murry, 2003). Denver's climate is semi-arid, with an average annual precipitation of 36.3 cm and an average annual temperature of 10.3°C. Most of Denver's precipitation arrives between May and August, in the form of rain. (National Weather Service, 2020). Headwater areas to the west of Denver average 75 cm or more of precipitation, with most of it coming as snow (Dennehy et al., 1995).

Although urban land makes up less than 10% of the area in the basin, cities along Colorado's Front Range are growing rapidly, putting strain on the South Platte River. Over 70% of Colorado's 5.7 million people live in the basin, including approximately 3.2 million people that live in the Denver metropolitan area alone (Colorado Department of Public Health & Environment, 2018; United States Census, 2020). The Colorado State Demography Office (2020) projects the Denver metro population will surpass 4 million people by 2050.

The South Platte River is a major source of water for the Front Range, providing more than 50% of the water used by Denver metropolitan municipalities (Denver Water, 2020). Within the Denver metro area, most of the river flow is diverted for domestic and industrial use and is returned to the river through wastewater effluent, which makes up the majority of the flow downstream of the city through much of the year (Metro Wastewater Reclamation District, 2020; Strange, Fausch, & Covich, 1999; Waskom, 2013). Before entering the Denver metropolitan area, the South Platte River travels through numerous dams, including the dam at Chatfield Reservoir on the southwestern edge of the city. Consequently, the magnitude of spring high flows have been somewhat minimized, although flow still peaks in late spring, diminishes through the summer and autumn and remains low through the winter. In addition, main channel flow is relatively consistent year-to-year making the impacts of urban runoff even more important (Figure 3) (Dennehy et al., 1998; United States Geological Survey, 2020; Waskom, 2013).

Elevated nutrient concentrations, pesticide residue, heavy metals contamination, elevated levels of *E. coli*, elevated temperature, low dissolved oxygen, and excessive sediment loading have been observed in the South Platte River. (Dennehy et al., 1998; Denver Environmental Health, 2016). In 2018, the South Platte River and all of its metro area tributaries appeared on the state of Colorado 303d list of impaired or threatened waters due to diminished water quality (Colorado Department of Public Health & Environment, 2018).

Sample collection and analysis

In May 2016, we identified 14 sampling sites along the South Platte River, spanning the length of the Denver metropolitan area (Figure 1). The first point was located at the mouth of Waterton Canyon, where the South Platte River emerges from the foothills. From preliminary work, we knew that water quality at this location was similar to points higher in the watershed and for this reason, we used it as our upstream control point (Heilman & Schliemann, 2015). From Waterton Canyon, water flows into Chatfield Reservoir. We placed our second sampling point immediately downstream of the reservoir, 14 km from the first point. The remaining points were spaced approximately 4.8 km (3 mi) apart with negligible variation due to sampling accessibility. Additional sampling sites were included above and below two of the main tributaries to the South Platte River: Cherry Creek and Clear Creek (Figure 1).

From May 2016 – May 2019, every two weeks (March – November) and every four weeks (December – February), we assessed a range of water quality parameters at every site. We measured water temperature, pH, dissolved oxygen (DO) in situ; and collected grab samples to measure the concentrations of nitrate-N ($\text{NO}_3\text{-N}$), ammonia-N ($\text{NH}_3\text{-N}$), and orthophosphate (PO_4^{3-}) in the lab within 3 hours of collection. In addition, we performed a BOD₅ test using a DO probe and standard methods (Eaton, Clesceri, Rice, Greenberg, & Franson, 2005). Temperature, pH, DO, BOD, and the concentration of $\text{NO}_3\text{-N}$ were measured using Hach probes and a Hach HQ40d meter (Hach CO, Longmont, Colorado, USA). The concentrations of $\text{NH}_3\text{-N}$ and orthophosphate were measured colorimetrically using a Hach DR900 colorimeter (Hach CO, 2020).

From November 2017 – February 2018, we systematically inventoried all visible storm drains, effluent points, and natural tributaries that join the South Platte River from the 14 km site to the 63 km site. We did not sample between the 0 km and 14 km sites due to access limitations. Furthermore, this area is a state park, with a little urban development. Daily, we walked segments of the river, marking each point using a handheld Garmin etrex 20x GPS unit (Garmin Ltd., Olathe, Kansas, USA). We also recorded whether the outfall point had flowing water, the type of outfall (storm drain, effluent point, or natural), the outfall structure (i.e., pipe or culvert), and the relative size of the outfall.

After collecting 18 months of data, we noticed that two of the areas we were sampling (28 km – 37 km and 47 – 48 km) seemed to have consistently high concentrations of nutrients. Consequently, in November 2017, we initiated an intensive study of these two “hotspot” areas. Over six months (November 2017 – April 2018), we sampled each flowing outfall from the beginning of the hotspot (i.e. 28 km and 47 km, respectively) to 5 km upstream (i.e. 23 km and 42 km, respectively). In addition, we sampled the river in this same section intensively, taking samples every 100 m. At each sampling point, we measured the parameters discussed above.

Statistical methods

For each water quality variable, we fitted the multiple regression model

$$Y = \text{Control Site} + \text{Distance} + \text{Month} + \text{Year},$$

where Y is BOD, nitrate-N, orthophosphate, ammonia-N, DO, pH, or temperature. Control Site is an indicator (1 = control site, 0 = every other site) that allows for an upward or downward shift in the mean of Y at the control site relative to the other sites. It will be positive or negative, respectively, depending on whether the control site had elevated or lowered levels of Y compared to the other sites. Distance is the number of kilometers downstream from the control site (0.0-63.1 kilometers) and is used to test for an upstream-to-downstream trend in Y. Month is a categorical variable that allows for seasonal fluctuations in Y, and Year (2016-2019) allows for long-term changes in Y.

Observations made close together in space and time are correlated, so we fitted the models using generalized least squares, which allows for correlated observations, with a Gaussian spatio-temporal correlation structure (Wikle, Zammit-Mangion, & Cressie, 2019). This says the correlation between two observations Y_i and Y_j a

distance d^{st} apart in space and time is

$$\text{cor}(Y_i, Y_j) = e^{-(d^{\text{st}}/r)^2},$$

where the range parameter r controls the spatio-temporal extent of the correlation. Following Liu et al. (2017), we defined the spatio-temporal distance d^{st} between a location s_i on the river on day t_i and another location s_j on day t_j as a combination of the spatial distance $|s_i - s_j|$ (kilometers) and temporal distance $|t_i - t_j|$ (days),

$$(d^{\text{st}})^2 = (s_i - s_j)^2 + \tau^2 \times (t_i - t_j)^2,$$

where τ is a time scaling factor that balances the different scales of spatial and temporal distances. We selected the values of r and τ using 10-fold cross validation, and fitted the models to the data in R using the "nlme" package (Pinheiro, Bates, DebRoy, & Sarkar, 2019). Statistical significance of model terms was assessed at the 0.05 level.

We identified spatio-temporal hot (or cold) spots in each of the seven water quality variables using a Getis-Ord local G procedure (Ord & Getis, 1995). More specifically, the statistic G_i^* was computed for each spatio-temporal observation point, giving roughly $n = 875$ values of G_i^* for each variable (but only $n = 559$ for BOD and $n = 686$ for ammonia-N). G_i^* is a standardized ratio of a local mean to the global mean. It identifies spatio-temporal clusters of relatively high or low values of the water quality variable. Hot spots are observation points for which G_i^* is higher than a Bonferonni-corrected 95th percentile cutoff, and cold spots points for which it is lower than the 5th percentile cutoff. Local means were computed within distance $d^{\text{st}} = 4.8$ of each observation point, and we carried out the procedure in R using the "spdep" package (Bivand & Wong, 2018).

Results

Figures 4-10 show the patterns of change in each water quality variable over space and time. For the regression models, the Gaussian correlation range parameter was estimated to be $r = 3.4$. The time scaling factor in d^{st} was estimated to be $\tau = 0.21$, indicating that a distance of one kilometer is equivalent to a time span of about 5 days (0.21×5 days [?] 1 km). In other words, two observations made one kilometer apart (on the same day) are as correlated with each other as two made five days apart (at the same site).

The estimated coefficient for the distance term in the regression models indicates the direction and magnitude of the change in the water quality variable per kilometer, and the corresponding t test indicates whether the change was statistically significant. Table 1 shows the estimated coefficient and t test result for each water quality variable.

Thus BOD, orthophosphate, and ammonia-N, all increased statistically significantly, by 0.049, 0.023, and 0.005 mg/L per kilometer, respectively, and temperature increased by 0.077 °C per kilometer. Nitrate-N and DO both decreased significantly, by 0.022 and 0.035 mg/L per kilometer, respectively. The decrease in nitrate-N was due to the very high nitrate-N values observed at the 14 km and 19 km sites. The pH did not change significantly over the stretch of river studied.

The seasonal (month) effect in the regression model was statistically significant for BOD, nitrate-N, DO, and temperature ($p = 0.000$ in all four cases, using a likelihood-ratio chi square test), but not for orthophosphate, ammonia-N, or pH ($p = 0.253, 0.979, \text{ and } 0.801$, respectively). There was not a significant long term trend (year effect) in any of the variables except temperature, which showed a significant decrease over the three year study period ($p = 0.158, 0.472, 0.419, 0.472, 0.760, \text{ and } 0.118$, respectively for BOD, nitrate-N, orthophosphate, ammonia-N, DO, and pH, and $p = 0.024$ for temperature). The control site shift coefficient b was negative and significant, indicating lower values relative to the other sites, for nitrate-N ($b = -5.94, p = 0.000$), pH ($b = -0.54$ and $p = 0.000$), and temperature ($b = -2.09$ and $p = 0.001$), but not significant for BOD, orthophosphate, ammonia-N, or DO ($p = 0.833, 0.225, 0.767, \text{ and } 0.985$, respectively). Thus,

nitrate-N was 5.94 mg/L lower at the control site relative to the other sites, pH was 0.54 units lower, and temperature was 2.09 °C lower.

Discussion

In general, water quality decreased as the river moved through the Denver metro area, which seems to imply that in this system, urban hydrology, especially impervious surfaces and engineered drainage, may be influencing the river. In addition to a general decrease in water quality through the study area, we also noted several hotspots of severely degraded water quality. The data also shows strong seasonality in water quality, with higher concentrations of nutrients and higher BOD in the winter months.

Water quality generally decreased through the Denver metro area. Specifically, DO decreased (Figure 5); the concentrations of orthophosphate (Figure 8) and ammonia-N (Figure 6) increased; and BOD (Figure 4) and temperature (Figure 9) increased from the 0 km site to the 63 km site ($p < 0.05$). Nitrate-N did not show the same overall trend of increasing concentration (Figure 7), but this is primarily because the 14 km and 19 km sites had excessively high concentrations. However, compared to the 0 km site (the control point), nitrate-N concentrations were elevated at all sites within the city. Compared to the other parameters measured, pH seems to be more variable and does not display a distinct trend (Figure 10). All of the measured pH values were between 6.2 – 8.9, although overall, they tended to be slightly basic.

Hotspots

Although there was a general trend of decreasing water quality through the study area, it is evident that certain locations had a disproportionate influence on the overall water quality. In this study, we identified three hotspots (Figure 11). Nitrate-N reached its highest concentrations at the 14 km site (max 25.8 mg/L) and remained high through the 19 km site (max 20 mg/L) (Figure 7). These elevated nitrate-N values are surprising given that most of the area immediately upstream of the 14 km site is contained within Chatfield State Park (Figure 12). This park has little development and most of the area is natural, consisting of the Chatfield Reservoir, shortgrass prairie ecosystems, and wetland ecosystems. Nitrogen is generally removed from the fluvial system within lakes and reservoirs through denitrification, sediment burial, and uptake by vegetation (Harrison et al., 2009). Given this, we would expect to see nitrogen levels decrease downstream of the reservoir, but in this study, we found the opposite. While it is not possible to conclusively identify the source of this nitrate-N pollution, in urban areas, wastewater treatment facilities often contribute to nutrient pollution (Bernhardt et al., 2008; Brown et al., 2009). Approximately 2.3 km upstream of the 14 km site is the discharge point for Marcy Gulch, which drains the Marcy Gulch Wastewater Treatment Plant (Figure 12).

There was a second, large hotspot located between 28 km and 37 km (Figure 13). This area had high BOD (max 10.5 mg/L) (Figure 4) as well as elevated concentrations of ammonia-N (max 3.4 mg/L) (Figure 6), nitrate-N (max 11.9 mg/L) (Figure 7), and orthophosphate (max 9.9 mg/L) (Figure 8). Additional testing in 2017-2018 upstream of this area revealed several potential point sources of this pollution (Figure 13). Two small tributaries: Little Dry Creek (24.3 km) and West Harvard Gulch (25.2 km) had elevated concentrations of nitrate-N (mean 2.9 mg/L and 8.1 mg/L, respectively). In addition, the effluent from the South Platte Water Renewal Partners Facility, a wastewater treatment plant (25.5 km), had elevated concentrations of nitrate-N (mean 6.2 mg/L), ammonia-N (mean 3.1 mg/L), and orthophosphate (mean 10.5 mg/L).

This hotspot is also located in the most urbanized part of the city, with considerable areas of impervious surface. Over 90 storm drains flow into the river over this stretch, which amounts to 11.11 storm drains/km and accounts for more than 35% of all drains identified. It is likely that discharges from the storm drains contribute to the high levels of pollutants detected. All measured parameters improved at the next site (38 km). Cherry Creek, one of the river's main tributaries, joins the South Platte just upstream of this point, at 37.2 km. It is likely that added flow from the confluence at Cherry Creek improved water quality by dilution.

There was a third hotspot between 47 km to 48 km (Figure 14). This area had elevated BOD (max 15.0

mg/L) (Figure 4), elevated ammonia-N (max 1.8 mg/L) (Figure 6), elevated orthophosphate (max 14.3 mg/L) (Figure 8), and reduced DO (min 3.11 mg/L) (Figure 5). This area has more pervious land cover and fewer outfalls (0.43 outfalls/km) than the other hotspots. In addition, two large tributaries join the South Platte River in this area: Sand Creek at 45.5 km and Clear Creek at 47.2 km. However, the city around this hotspot is highly industrialized, which could be contributing to the diminished water quality. Two potential sources of pollution in this area are the Robert W. Hite Treatment Facility, the largest wastewater treatment facility in the metro area, and the Suncor Commerce City oil refinery.

The Robert W. Hite Treatment Facility discharges approximately 130 MGD of treated wastewater into the river at 45 km. Through much of the year, this effluent makes up a significant portion of the downstream flow in the South Platte River (Metro Wastewater Reclamation District, 2020). However, additional testing in 2017-2018, revealed that the wastewater treatment effluent had relatively low concentrations of nitrate-N (mean 3.1 mg/L), ammonia-N (mean 0.16 mg/L) and orthophosphate (0.3 mg/L). From this data, we can presume that while the wastewater treatment facility is contributing to the diminished water quality, it is not the main source of the pollution we see in this area.

The Suncor Commerce City oil refinery is located on Sand Creek, approximately 1 km east of the South Platte River. Through its normal operations, Suncor discharges wastewater effluent into Sand Creek. Oil refinery discharge can contain a range of pollutants including hydrocarbons, sulphides, ammonia, suspended solids, nitrogen compounds, and heavy metals (Diya'uddeen, Daud, & Aziz, 2011; Wake, 2005). While we did not directly sample the Suncor effluent, we did sample Sand Creek, about 0.75 km downstream from Suncor. This area had elevated concentrations of nitrate-N (mean 4.9 mg/L), ammonia-N (mean 0.17 mg/L), and orthophosphate (mean 3.8 mg/L). Without more intensive sampling, it is not possible to conclude that Suncor is the source of elevated nutrient concentrations. Given the other industries in the area, there could be other sources of pollution. During our intensive sampling, we found elevated nitrate-N levels at three additional points along the South Platte River in this area: two outfalls at 43.4 km and 43.6 km (mean 8 mg/L and 11.1 mg/L, respectively) and one industrial effluent point at 44.2 km (mean 13.1 mg/L).

Seasonality

Water quality in this study showed strong seasonality. BOD and the concentrations of ammonia-N, nitrate-N, and orthophosphate were highest in the fall and winter (Figures 4, 6, 7, 8, respectively). These times coincide with the lowest flows in the river (Figure 3). Low flow can result in higher concentrations of nutrients as there is less water for dilution. In addition, biological uptake of nutrients is lower during the cold months of the year (Olatunde et al., 2015; Rolls et al., 2012). Not surprisingly, water temperature also showed strong seasonality, with temperatures reaching their maximum values in July (max 25.9°C) (Figure 9). DO saturation is inversely related to temperature but is also influenced by hydrology, BOD, and pH. In this study, we measured the lowest DO values in early fall when temperatures were still relatively high and flow in the river was low (Figure 5).

Environmental Compliance

In the United States, the Clean Water Act (CWA) is the Federal statute that governs water quality. Under the CWA, each state is permitted to set their own standards, provided that they are at least as stringent as the standards set in the CWA (Federal Water Pollution Control Act, 1972). In Colorado, the state has adopted Regulation 31, which establishes standards for classifying surface waters within the state of Colorado using a range of parameters. For warm-water streams, such as the South Platte River in the Denver metro area, the interim total phosphorus maximum allowable concentration is 0.170 mg/L and the interim total nitrogen maximum allowable concentration is 2.01 mg/L (Colorado Department of Public Health and Environment, 2017).

Over most of the Denver metropolitan area, nitrogen and phosphorus concentrations measured in this study were above the limits set by Regulation 31. Nitrate-N concentrations in the South Platte ranged from a low of 0 mg/L at the 0 km control site in August of 2016 to a high of 25.8 mg/L at the 14 km site in February of 2018. Ammonia-N concentrations in the South Platte ranged from a low of 0 mg/L at nearly every site

at some point during the study to a high of 3.4 mg/L at the 33 km site in February of 2018. The nitrate-N concentrations were higher than the ammonia-N concentrations in 99.9% of the samples. In many cases, nitrate-N was an order of magnitude higher than ammonia-N. When considered together (ammonia-N + nitrate-N), the concentration exceeded the maximum allowable level of total nitrogen in more than 76% of the samples.

Orthophosphate concentrations in the South Platte ranged from a low of 0 mg/L at the 0 km site on 14 different sampling dates, representing all months of the year, to a high of 14.3 mg/L at 47 km site in October of 2017. Over 85% of the samples tested had concentrations of orthophosphate that exceeded the maximum allowable total phosphate concentration of 0.170 mg/L.

In addition to Regulation 31, the South Platte River and several of its tributaries in the eastern plains of Colorado are managed according to state Regulation 38 (Colorado Department of Public Health & Environment, 2012). According to Regulation 38, a Tier I Warm Stream, such as the South Platte River, has a maximum daily temperature limit of 29.0°C for March – November and 14.5 °C for December – February. All of the temperature readings collected were below these limits; however, while the summer temperatures are within the Regulation 38 limits, they are often too high to support healthy populations of several species of desirable cold-water fish including *Oncorhynchus mykiss* (rainbow trout) and *Salmo trutta* (brown trout). The optimal summer temperature for growth and reproduction of *O. mykiss* is generally reported to be between 17 and 19 °C (Hokanson, Kleiner, & Thorslund, 1977). Almost 29% of our samples from March – November exceeded 19°C. Trout Unlimited, an American non-profit has been working with local municipalities to restore trout populations to the South Platte in the Denver metro area. By building cold water refugia, with deep pools and riparian vegetation for shade, the group has created cooler conditions that support small pockets of trout (Trout Unlimited, 2020). However, it is unclear whether these isolated populations will be self-sustaining in the long-term due to their limited population size and low genetic diversity.

Regulation 38 also establishes a minimum DO of 5.0 mg/L May 1 – July 15 and 4.5 mg/L for the rest of the year. The reasoning is that higher DO concentrations are necessary for spawning, which generally occurs May 1 – July 15. The South Platte River is generally in compliance with only 0.32% of our measurements below this threshold.

Conclusions

Urban hydrology seems to be influencing water quality in the South Platte River in the Denver metropolitan area. Water quality generally decreased as the river moved through the Denver metro area. In addition, the second hotspot location (28 km – 37 km) is in the urban heart of the city with the highest concentration of storm drains and the highest degree of impervious surface. In the fall and winter when natural flow is lowest, water quality reached its lowest levels. During these times of the year, the majority of flow is from treated wastewater, which suggests that it may be strongly influencing water quality in the South Platte River.

While it is beyond the scope of this paper to identify specific sources of water pollution in this system, we were able to make some reasonable conjectures. It appears that wastewater treatment facilities may be one of the main sources of nitrogen and phosphorus pollution in this system. However, not all facilities are releasing similar concentrations of these pollutants. Some facilities, such as Robert W. Hite Treatment Facility seem to be treating their effluent to fairly low levels prior to discharge. It also seems likely that industrial activity may be an important source of pollution in isolated areas. For example, at the third hotspot area (47 km – 48 km), there are a number of industrial properties including the Suncor Commerce City oil refinery.

Most of the samples collected in this study exceeded state limits for nitrogen and/ or phosphorus concentrations. These elevated levels may be leading to other undesirable downstream effects, such as eutrophication. The river was mostly in compliance with state regulations in terms of DO and temperature, although the temperature standard is for a warm-water stream and many desirable fish, including *Oncorhynchus mykiss* (rainbow trout) and *Salmo trutta* (brown trout) are unlikely to survive long-term in this system unaided. Urban hydrologic systems are complex and improving water-quality may be difficult. However, tightening of water-quality standards, especially for wastewater treatment facilities, could result in positive changes to

this system.

Data availability statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

References

- Abdi, R., & Endreny, T. (2019). A River Temperature Model to Assist Managers in Identifying Thermal Pollution Causes and Solutions. *Water*, 11 (5), 17. doi:10.3390/w11051060
- Baker, D. B., Richards, R. P., Loftus, T. T., & Kramer, J. W. (2004). A new flashiness index: Characteristics and applications to midwestern rivers and streams. *Journal of the American Water Resources Association*, 40 (2), 503-522. doi:10.1111/j.1752-1688.2004.tb01046.x
- Bernhardt, E. S., Band, L. E., Walsh, C. J., & Berke, P. E. (2008). Understanding, managing, and minimizing urban impacts on surface water nitrogen loading. In R. S. Ostfeld & W. H. Schlesinger (Eds.), *Year in Ecology and Conservation Biology 2008* (Vol. 1134, pp. 61-96). Malden: Wiley-Blackwell.
- Bivand, R. S., & Wong, D. W. S. (2018). Comparing implementations of global and local indicators of spatial association. *Test*, 27 (3), 716-748. doi:10.1007/s11749-018-0599-x
- Booth, D. B., & Jackson, C. R. (1997). Urbanization of aquatic systems: Degradation thresholds, stormwater detection, and the limits of mitigation. *Journal of the American Water Resources Association*, 33 (5), 1077-1090. doi:10.1111/j.1752-1688.1997.tb04126.x
- Brown, L. R., Cuffney, T. F., Coles, J. F., Fitzpatrick, F., McMahon, G., Steuer, J., . . . May, J. T. (2009). Urban streams across the USA: lessons learned from studies in 9 metropolitan areas. *Journal of the North American Benthological Society*, 28 (4), 1051-1069. doi:10.1899/08-153.1
- Carpenter, S. R., Caraco, N. F., Correll, D. L., Howarth, R. W., Sharpley, A. N., & Smith, V. H. (1998). Nonpoint pollution of surface waters with phosphorus and nitrogen. *Ecological Applications*, 8 (3), 559-568. doi:10.1890/1051-0761(1998)008[0559:nposww]2.0.co;2
- Cockerill, K., & Anderson, W. P. (2014). Creating False Images: Stream Restoration in an Urban Setting. *Journal of the American Water Resources Association*, 50 (2), 468-482. doi:10.1111/jawr.12131
- Colorado Department of Public Health & Environment. Regulation 85 Nutrients management control regulation, CO Admin. Rules, 5 CCR 1002-85 (2012)
- Colorado Department of Public Health & Environment. (2018). *Integrated Water Quality Monitoring and Assessment Report*. State of Colorado
- Colorado Department of Public Health and Environment. Regulation 31 The basic standards and methodologies for surface water, CO Admin. Rules, 5 CCR 1002-31 (2017)
- Colorado State Demography Office. (2020). Preliminary Population Forecasts by Region, 2010-2050. Retrieved from <https://demography.dola.colorado.gov/population/>
- Das, B., Nordin, R., & Mazumder, A. (2009). Watershed land use as a determinant of metal concentrations in freshwater systems. *Environmental Geochemistry and Health*, 31 (6), 595-607. doi:10.1007/s10653-008-9244-z
- Dennehy, K. F., Litke, D. W., McMahon, P. B., Heiny, J. S., & Tate, C. M. (1995). *Water-Quality Assessment of the South Platte River Basin, Colorado, Nebraska, and Wyoming- Analysis of Available Nutrient, Suspended- Sediment, and Pesticide Data, Water Years 1980-92*. United States Department of the Interior
- Dennehy, K. F., Litke, D. W., Tate, C. M., Qi, S. L., McMahon, P. B., Bruce, B. W., . . . Heiny, J. S. (1998). *Water Quality in the South Platte River Basin*.

Denver Environmental Health. (2016). *Water Quality Update: An overview of water quality in Denver's streams* .

Denver Water. (2020). Collection System. Retrieved from <https://www.denverwater.org/your-water/water-supply-and-planning/collection-system>

Diya'uddeen, B. H., Daud, W., & Aziz, A. R. A. (2011). Treatment technologies for petroleum refinery effluents: A review. *Process Safety and Environmental Protection*, *89* (2), 95-105. doi:10.1016/j.psep.2010.11.003

Eaton, A. D., Clesceri, L. S., Rice, E. W., Greenberg, A. E., & Franson, M. H. (Eds.). (2005). *Standard Methods for the Examination of Water & Wastewater* (21 ed.). Baltimore: United Book Press, Inc.

Federal Water Pollution Control Act, (1972).

Garmin Ltd. (2020). Retrieved from garmin.com

Glinska-Lewczuk, K., Golas, I., Koc, J., Gotkowska-Plachta, A., Harnisz, M., & Rochwerger, A. (2016). The impact of urban areas on the water quality gradient along a lowland river. *Environmental Monitoring and Assessment*, *188* (11), 15. doi:10.1007/s10661-016-5638-z

Graf, W. L. (2001). Damage control: Restoring the physical integrity of America's rivers. *Annals of the Association of American Geographers*, *91* (1), 1-27. doi:10.1111/0004-5608.00231

Gregory, M. B., & Calhoun, D. L. (2007). *Physical, chemical, and biological responses of streams to increasing watershed urbanization in the Piedmont Ecoregion of Georgia and Alabama, Chapter B of Effects of urbanization on stream ecosystems in six metropolitan areas of the United States: U.S. Geological Survey Scientific Investigations Report 2006-5101-B* .

Groffman, P. M., Law, N. L., Belt, K. T., Band, L. E., & Fisher, G. T. (2004). Nitrogen fluxes and retention in urban watershed ecosystems. *Ecosystems*, *7* (4), 393-403. doi:10.1007/s10021-003-0039-x

Hach CO. (2020). Retrieved from Hach.com

Harrison, J. A., Maranger, R. J., Alexander, R. B., Giblin, A. E., Jacinthe, P. A., Mayorga, E., . . . Wollheim, W. M. (2009). The regional and global significance of nitrogen removal in lakes and reservoirs. *Biogeochemistry*, *93* (1-2), 143-157. doi:10.1007/s10533-008-9272-x

Heilman, K., & Schliemann, S. A. (2015). *[Characterizing Water Quality of the South Platte River from Cheesman Canyon to Brighton, CO]. Unpublished raw data.*

Herb, W. R., Janke, B., Mohseni, O., & Stefan, H. G. (2008). Thermal pollution of streams by runoff from paved surfaces. *Hydrological Processes*, *22* (7), 987-999. doi:10.1002/hyp.6986

Hokanson, K. E. F., Kleiner, C. F., & Thorslund, T. W. (1977). Effects of Constant Temperatures and Diel Temperature-Fluctuations on Specific Growth and Mortality-Rates and Yield of Juvenile Rainbow-Trout, *Salmo-Gairdneri*. *Journal of the Fisheries Research Board of Canada*, *34* (5), 639-648. doi:10.1139/f77-100

Larned, S. T., Snelder, T., Unwin, M. J., & McBride, G. B. (2016). Water quality in New Zealand rivers: current state and trends. *New Zealand Journal of Marine and Freshwater Research*, *50* (3), 389-417. doi:10.1080/00288330.2016.1150309

Liu, J. P., Zhao, Y. Y., Yang, Y., Xu, S. H., Zhang, F. H., Zhang, X. L., . . . Qiu, A. G. (2017). A Mixed Geographically and Temporally Weighted Regression: Exploring Spatial-Temporal Variations from Global and Local Perspectives. *Entropy*, *19* (2), 20. doi:10.3390/e19020053

Magdaleno, A., Puig, A., de Cabo, L., Salinas, C., Arreghini, S., Korol, S., . . . Moretton, J. (2001). Water pollution in an urban Argentine river. *Bulletin of Environmental Contamination and Toxicology*, *67* (3), 408-415. Retrieved from <Go to ISI>://WOS:000170374100014

Malmqvist, B., & Rundle, S. (2002). Threats to the running water ecosystems of the world. *Environmental Conservation*, 29 (2), 134-153. doi:10.1017/s0376892902000097

Metro Wastewater Reclamation District. (2020). About Us. Retrieved from <http://www.metrowastewater.com/aboutus/Page>

Millennium Ecosystem Assessment. (2005). *Ecosystems and Human Well-being: Synthesis*. Washington DC: Island Press.

Mosley, L. M. (2015). Drought impacts on the water quality of freshwater systems; review and integration. *Earth-Science Reviews*, 140, 203-214. doi:10.1016/j.earscirev.2014.11.010

Nagy, R. C., Lockaby, B. G., Kalin, L., & Anderson, C. (2012). Effects of urbanization on stream hydrology and water quality: the Florida Gulf Coast. *Hydrological Processes*, 26 (13), 2019-2030. doi:10.1002/hyp.8336

National Weather Service. (2020). Denver's 2018 Annual Climate Summary. Retrieved from https://www.weather.gov/bou/D2018_climate_summary

Olatunde, O. S., Olalekan, F. S., Beatrice, O. O., Bhekumusa, X. J., Zacheaus, O. O., & Kehinde, A. N. (2015). Nutrient Enrichment and Hypoxia Threat in Urban Surface Water. *Clean-Soil Air Water*, 43 (2), 205-209. doi:10.1002/clen.201300292

Ord, J. K., & Getis, A. (1995). Local Spatial Autocorrelation Statistics - Distributional Issues and an Application. *Geographical Analysis*, 27 (4), 286-306. doi:10.1111/j.1538-4632.1995.tb00912.x

Ouyang, T. P., Zhu, Z. Y., & Kuang, Y. Q. (2006). Assessing impact of urbanization on river water quality in the Pearl River Delta Economic Zone, China. *Environmental Monitoring and Assessment*, 120 (1-3), 313-325. doi:10.1007/s10661-005-9064-x

Pasquini, A. I., Formica, S. M., & Sacchi, G. A. (2012). Hydrochemistry and nutrients dynamic in the Suquia River urban catchment's, Crdoba, Argentina. *Environmental Earth Sciences*, 65 (2), 453-467. doi:10.1007/s12665-011-0978-z

Paul, M. J., & Meyer, J. L. (2001). Streams in the urban landscape. *Annual Review of Ecology and Systematics*, 32, 333-365. doi:10.1146/annurev.ecolsys.32.081501.114040

Peters, N. E. (2009). Effects of urbanization on stream water quality in the city of Atlanta, Georgia, USA. *Hydrological Processes*, 23 (20), 2860-2878. doi:10.1002/hyp.7373

Pinheiro, J., Bates, D., DebRoy, S., & Sarkar, D., & R Core Team. (2019). nlme: Linear and Nonlinear Mixed Effects Models. R package version 3.1-140. Retrieved from <https://CRAN.R-project.org/package=nlme>

Poff, N. L., Allan, J. D., Bain, M. B., Karr, J. R., Prestegard, K. L., Richter, B. D., . . . Stromberg, J. C. (1997). The natural flow regime. *Bioscience*, 47 (11), 769-784. doi:10.2307/1313099

Rice, E. W., & Bridgewater, L. (Eds.). (2012). *Standard Methods for the Examination of Water and Wastewater* (Vol. 22). Washington, DC: American Public Health Association.

Rolls, R. J., Leigh, C., & Sheldon, F. (2012). Mechanistic effects of low-flow hydrology on riverine ecosystems: ecological principles and consequences of alteration. *Freshwater Science*, 31 (4), 1163-1186. doi:10.1899/12-002.1

Schoonover, J. E., Lockaby, B. G., & Pan, S. (2005). Changes in chemical and physical properties of stream water across an urban-rural gradient in western Georgia. *Urban Ecosystems*, 8 (1), 107-124. doi:10.1007/s11252-005-1422-5

Somers, K. A., Bernhardt, E. S., Grace, J. B., Hassett, B. A., Sudduth, E. B., Wang, S. Y., & Urban, D. L. (2013). Streams in the urban heat island: spatial and temporal variability in temperature. *Freshwater Science*, 32 (1), 309-326. doi:10.1899/12-046.1

Son, J. H., Goodwin, S., & Carlson, K. (2015). Total Phosphorus Input to the Cache la Poudre River in Northern Colorado. *Water Environment Research*, 87 (2), 169-178. doi:10.2175/106143014x14062131179393

Strange, E. M., Fausch, K. D., & Covich, A. P. (1999). Sustaining ecosystem services in human-dominated watersheds: Biohydrology and ecosystem processes in the South Platte River Basin. *Environmental Management*, 24 (1), 39-54. Retrieved from <Go to ISI>://WOS:000080692300004

Szita, R., Horvath, A., Winkler, D., Kalicz, P., Gribovszki, Z., & Csaki, P. (2019). A complex urban ecological investigation in a mid-sized Hungarian city - SITE assessment and monitoring of a liveable urban area, PART 1: Water quality measurement. *Journal of Environmental Management*, 247 , 78-87. doi:10.1016/j.jenvman.2019.06.063

Trimble, D. E., Machette, M. N., Moore, D. W., & Murry, K. E. (Cartographer). (2003). Geologic Map of the Greater Denver Area, Front Range Urban Corridor, Colorado

Trout Unlimited. (2020). Retrieved from tu.org

United Nations. (2018). *World Urbanization Prospects: The 2018 Revision* . New York: United Nations

United States Census. (2020). United States Census. Retrieved from census.gov

United States Geological Survey. (2020). National Water Information System: Web Interface. Retrieved from https://waterdata.usgs.gov/co/nwis/uv?site_no=06711565

Wake, H. (2005). Oil refineries: a review of their ecological impacts on the aquatic environment. *Estuarine Coastal and Shelf Science*, 62 (1-2), 131-140. doi:10.1016/j.ecss.2004.08.013

Walsh, C. J., Roy, A. H., Feminella, J. W., Cottingham, P. D., Groffman, P. M., & Morgan, R. P. (2005). The urban stream syndrome: current knowledge and the search for a cure. *Journal of the North American Benthological Society*, 24 (3), 706-723. doi:10.1899/04-020.1

Wang, L. Z., Lyons, J., & Kanehl, P. (2003). Impacts of urban land cover on trout streams in Wisconsin and Minnesota. *Transactions of the American Fisheries Society*, 132 (5), 825-839. doi:10.1577/t02-099

Waskom, R. M. (2013). *Report to the Colorado Legislature HB12-1278 Study of the South Platte River Alluvial Aquifer* . Retrieved from

Wikle, C. K., Zammit-Mangion, A., & Cressie, N. (2019). *Spatio-Temporal Statistics with R* . Boca Raton, FL: Chapman & Hall/CRC.

Zhang, L., Shao, S. H., Liu, C., Xu, T. T., & Fan, C. X. (2015). Forms of Nutrients in Rivers Flowing into Lake Chaohu: A Comparison between Urban and Rural Rivers. *Water*, 7 (8), 4523-4536. doi:10.3390/w7084523

Table

Changes in Water Quality Through the Denver Metropolitan Area	Changes in Water Quality Through the Denver Metropolitan Area	Changes in Water Quality Through the Denver Metropolitan Area	Changes in Water Quality Through the Denver Metropolitan Area	Changes in Water Quality Through the Denver Metropolitan Area
Water quality variable	Estimated change per km (regression coefficient)	Standard error of the estimate	t	p-value
BOD	0.049	0.007	7.35	0.000*
Nitrate-N	-0.022	0.010	-2.18	0.029*
Orthophosphate	0.023	0.008	2.95	0.003*
Ammonia-N	0.005	0.002	2.09	0.037*

Changes in Water Quality Through the Denver Metropolitan Area	Changes in Water Quality Through the Denver Metropolitan Area	Changes in Water Quality Through the Denver Metropolitan Area	Changes in Water Quality Through the Denver Metropolitan Area	Changes in Water Quality Through the Denver Metropolitan Area
DO	-0.035	0.008	-4.60	0.000*
pH	-0.003	0.002	-1.41	0.158
Temperature	0.077	0.010	7.46	0.000*

Table 1: Estimated coefficient of the distance term in the multiple regression models and results of the t tests. Asterisks denote statistically significant results at the 0.05 level, and the sign of the coefficient indicates whether the variable increased or decreased with downstream distance.

Figure Legends

Figure 1: Site locations along the South Platte River in the Denver metropolitan area.

Figure 2: South Platte Watershed

Figure 3: South Platte River mean daily discharge (1995-2019), Denver, CO.

Figure 4: Biochemical oxygen demand (BOD)- Scatterplot vs distance downstream from site 1 (at 0 km), with a loess curve for each month and (black) for all months (top). Hovmöller plots showing a spatio-temporal (weighted) moving average of BOD with hot spots shown as ellipses (bottom).

Figure 5: Dissolved oxygen (DO)- Scatterplot vs distance downstream from site 1 (at 0 km), with a loess curve for each month and (black) for all months (top). Hovmöller plots showing a spatio-temporal (weighted) moving average of DO with cold spots shown as ellipses (bottom).

Figure 6: Ammonia-N- Scatterplot vs distance downstream from site 1 (at 0 km), with a loess curve for each month and (black) for all months (top). Hovmöller plots showing a spatio-temporal (weighted) moving average of $\text{NH}_3\text{-N}$ with hot spots shown as ellipses (bottom).

Figure 7: Nitrate-N- Scatterplot vs distance downstream from site 1 (at 0 km), with a loess curve for each month and (black) for all months (top). Hovmöller plots showing a spatio-temporal (weighted) moving average of $\text{NO}_3\text{-N}$ with hot spots shown as ellipses (bottom).

Figure 8: Orthophosphate- Scatterplot vs distance downstream from site 1 (at 0 km), with a loess curve for each month and (black) for all months (top). Hovmöller plots showing a spatio-temporal (weighted) moving average of orthophosphate with hot spots shown as ellipses (bottom).

Figure 9: Water Temperature- Scatterplot vs distance downstream from site 1 (at 0 km), with a loess curve for each month and (black) for all months (top). Hovmöller plots showing a spatio-temporal (weighted) moving average of temperature with hot spots shown as ellipses (bottom).

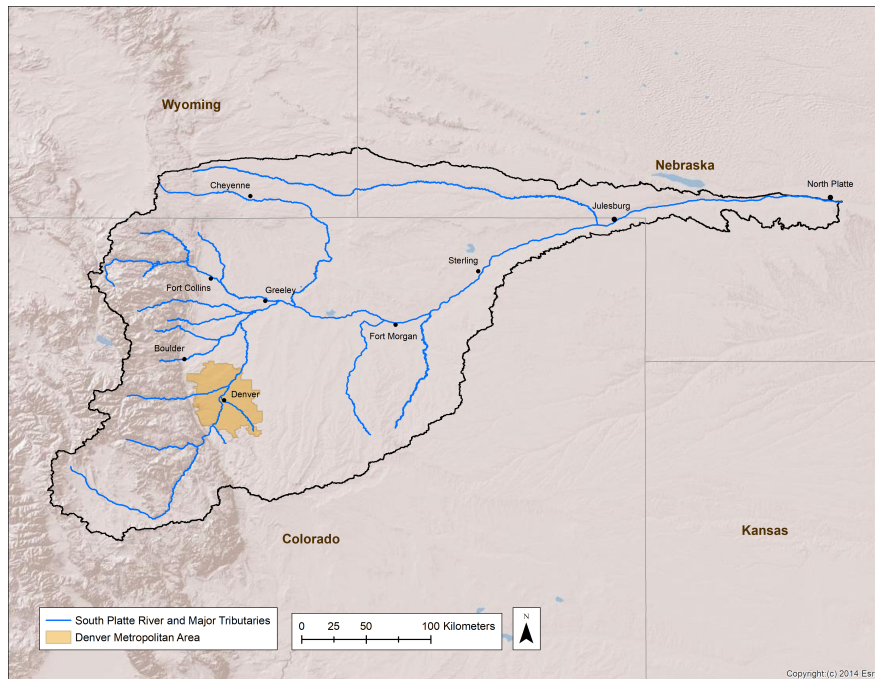
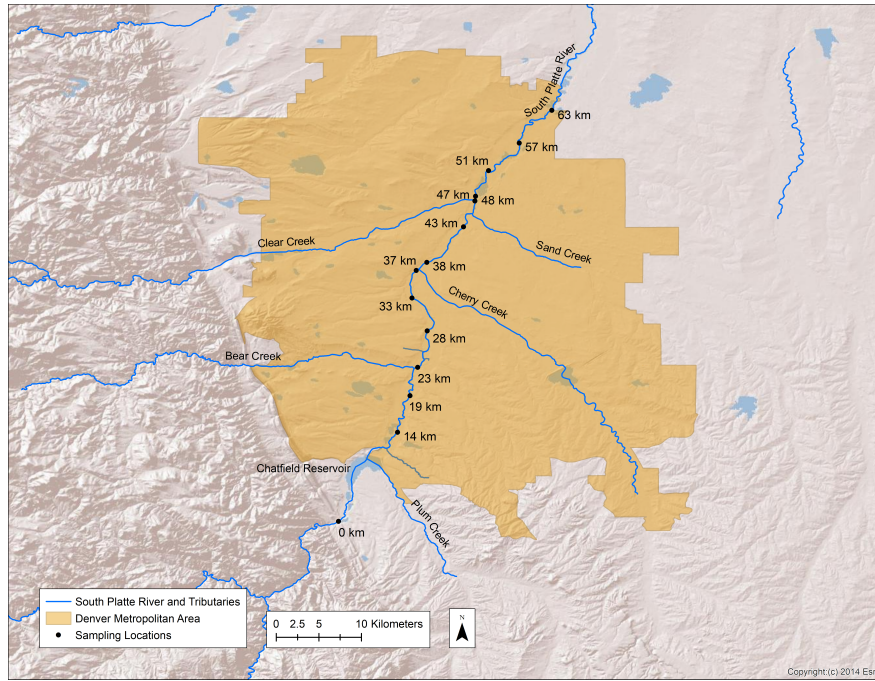
Figure 10: pH- Scatterplot vs distance downstream from site 1 (at 0 km), with a loess curve for each month and (black) for all months (top). Hovmöller plots showing a spatio-temporal (weighted) moving average of pH. No hot spots were detected.

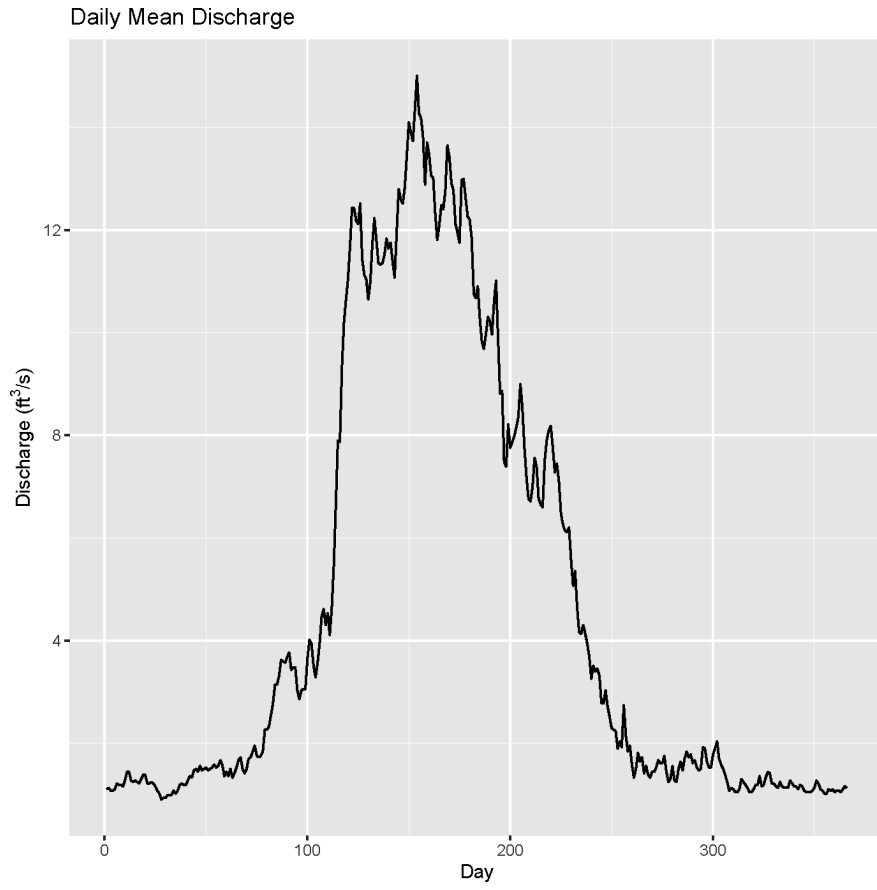
Figure 11: Three hotspot areas

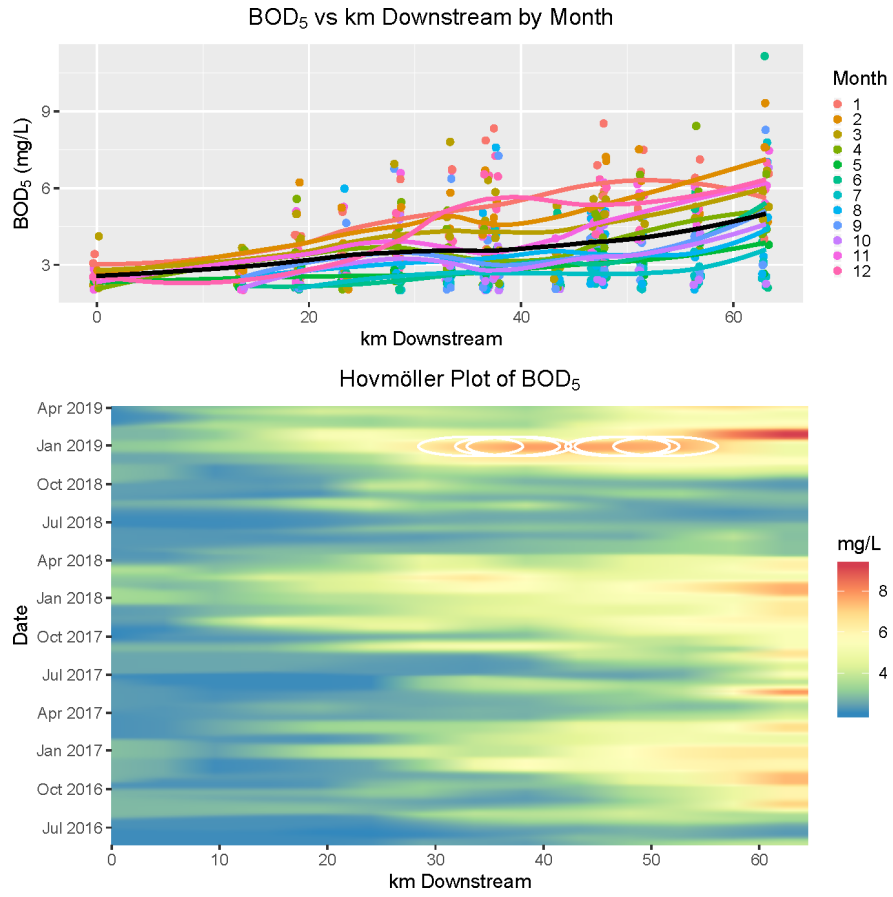
Figure 12: Hotspot 1. Nitrate-N reached its highest concentrations at the 14 km site and remained high through the 19 km site.

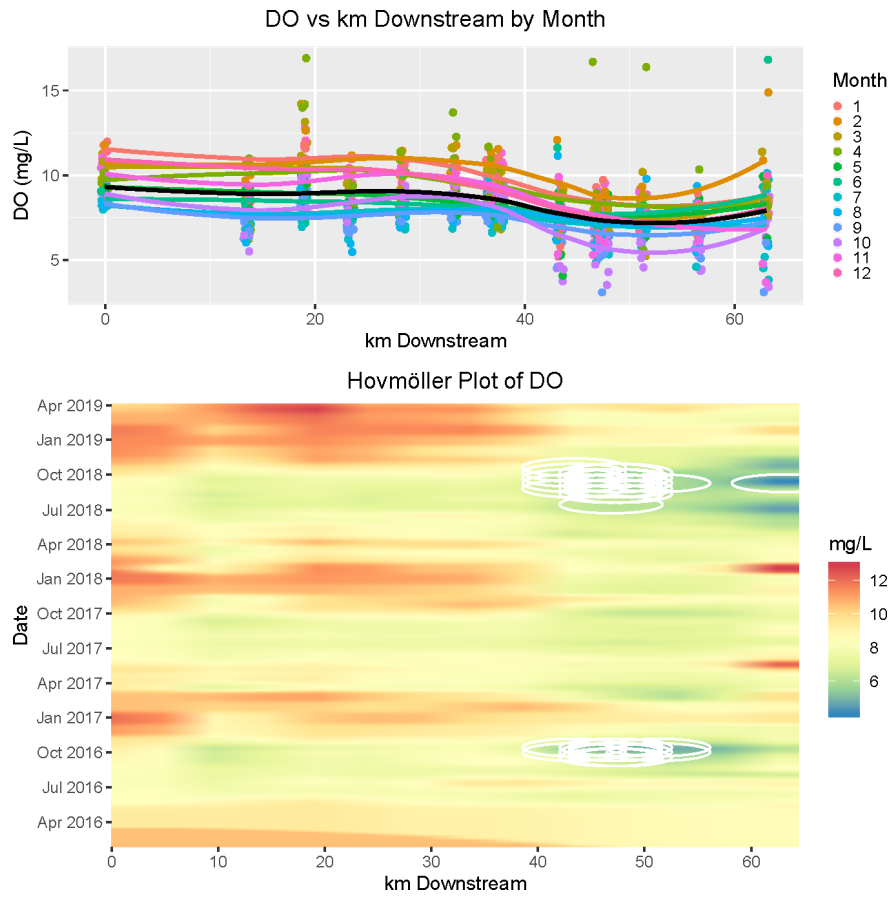
Figure 13: Hotspot 2. The area from 28 km – 37 km had high BOD as well as elevated concentrations of ammonia-N, nitrate-N, and orthophosphate.

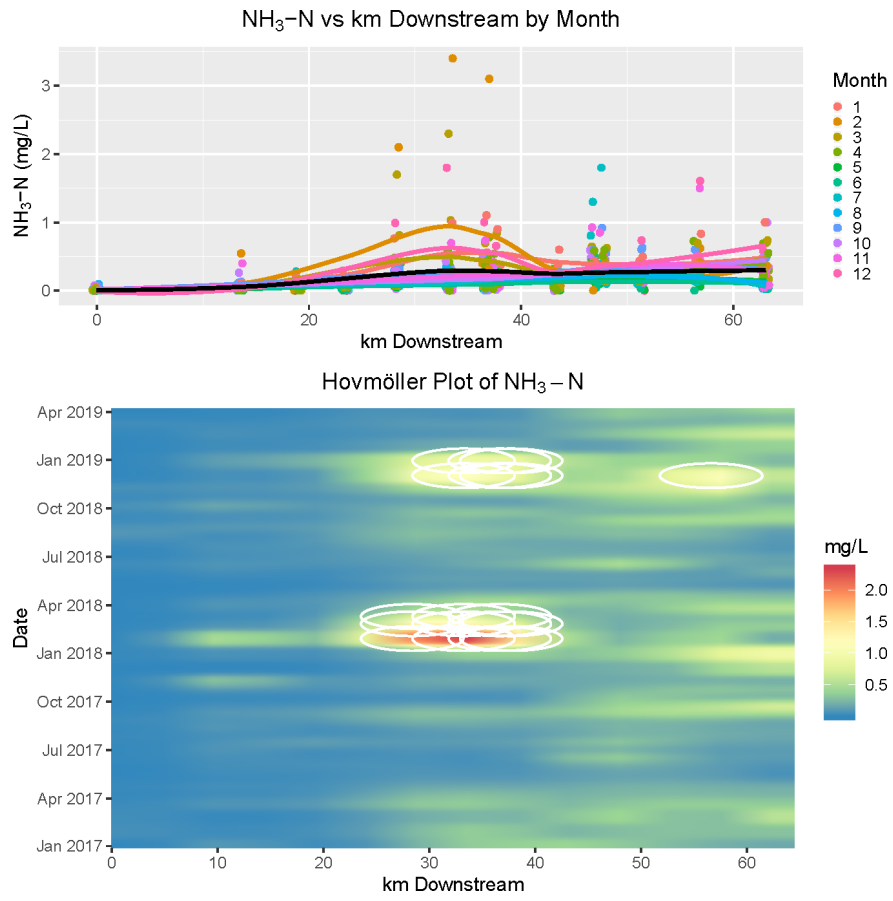
Figure 14- Hotspot 3. The area from 47 km – 48 km had elevated BOD, elevated ammonia-N, elevated orthophosphate, and reduced DO.



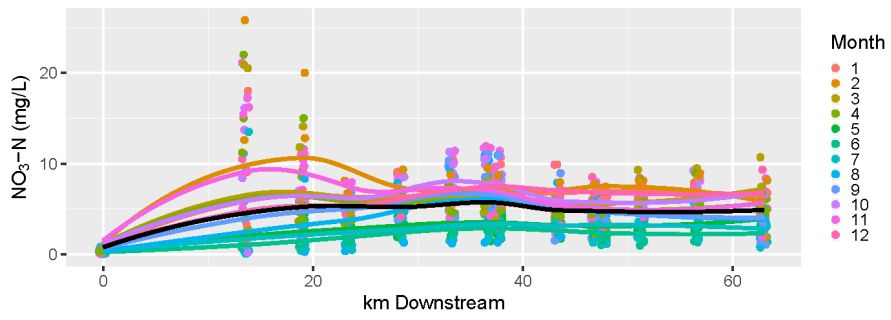




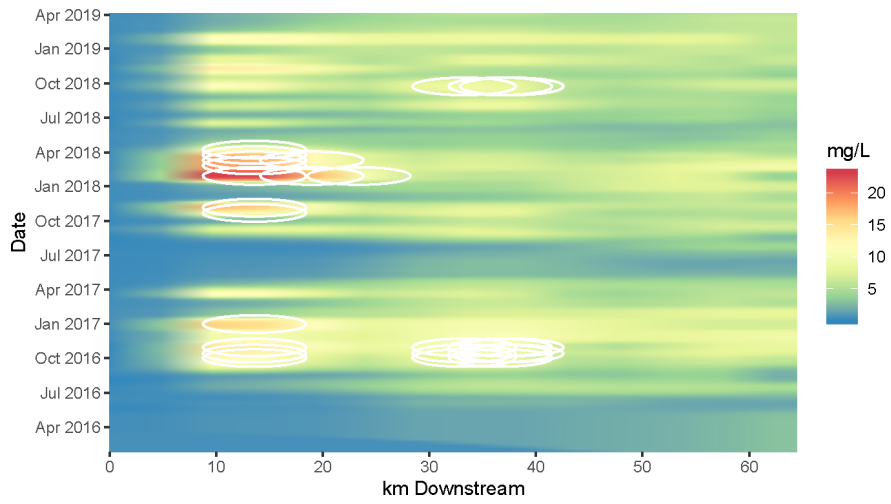




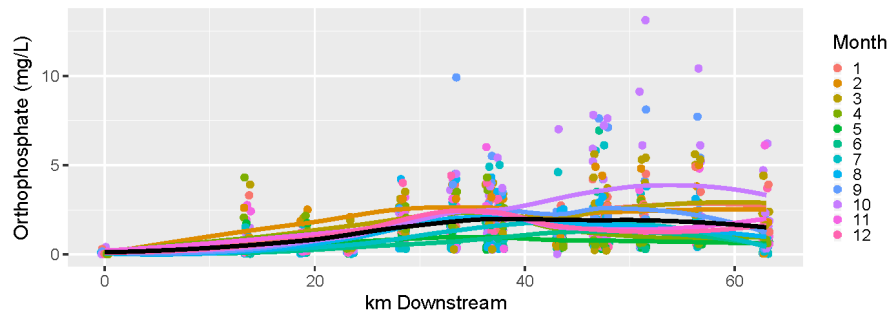
NO₃-N vs km Downstream by Month



Hovmöller Plot of NO₃-N



Orthophosphate vs km Downstream by Month



Hovmöller Plot of Orthophosphate

