Precipitation-Driven Anthropogenic Pollutant Fluctuations Within Standing Water Sources of the Edwards Aquifer Region, Texas

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ABSTRACT: The objective of this study was to assess the contribution of urban runoff in pollutant delivery to standing water pools within the Edwards Aquifer region of Texas. Grab samples of water were collected weekly over 5 months at one urban pool, one undeveloped pool, and one control pond that received minimal runoff. Samples were tested for nitrates, total dissolved phosphorus, *Escherichia coli*, and other coliform bacteria. The urban site had higher nitrate, *E. coli*, and other coliform bacteria concentrations than the undeveloped site. Significant positive linear relationships between weekly antecedent rainfall and both nitrate and *E. coli* were found at the urban site but not the undeveloped site. Water quality parameters at the control site remained stable, suggesting increases in nitrate and *E. coli* at the urban site were caused by runoff. Using publicly available data, relationships between water quality and weekly antecedent discharge were tested at 24 additional sites varying in land use. Positive relationships for *E. coli* were found at several urban sites, supporting runoff as a contributor to bacterial loading. Relationships for nitrate were variable, but all additional sites had flowing water, suggesting a unique response of water quality to urban runoff at the sampled urban pool.

KEYWORDS: Water quality, intermittent streams, nitrate, total dissolved phosphorus, *Escherichia coli*, coliform bacteria

Background

Growing anthropogenic water demands, combined with climate change-driven decreases in precipitation, are decreasing streamflow in many regions throughout the world, creating river systems which frequently dry completely down to isolated, standing water pools (Dodds et al., 2013; Milly et al., 2005). Land-use change, both for agricultural and urban development, can significantly increase anthropogenic pollutant loading into rivers and streams. Isolated pools of standing water are often more susceptible to anthropogenic contaminant loading than perennial flowing water, with these conditions more often allowing for the growth of toxic algae and pathogenic bacteria (Davis et al., 2009; Pandey et al., 2014). Nitrogen and phosphorus loading into standing waters by urban effluent and agricultural sources can increase the severity of eutrophication and cyanobacterial blooms, which affect the water directly via turbid conditions, foul odor, increased fish kills, and anoxia (Wang et al., 2001). Nutrient loading may be a potential risk to human health by promoting conditions favorable for the growth of waterborne diseases, particularly those contracted from bacterial sources (Dixit et al., 2017; Matthews & Bernard, 2015).

Although much effort has been focused on understanding how land use change impacts groundwater and perennial systems, relatively little monitoring has been conducted to understand how land use change impacts water quality in isolated pools in intermittent and ephemeral streams and how impacts may vary temporally. A case in point is the Edwards Aquifer region in south-central Texas. Some research has been conducted on stormwater runoff in ephemeral stream segments within the region, revealing steadily increasing concentrations of nutrients, pesticides, and trace metals (Opsahl, 2012). However, studies of isolated pools are rare and most previous research has been conducted on the water quality of perennial surface and groundwater systems. A study by Musgrove et al. (2016) revealed an increase in the concentration of nitrates into segments of the Edwards Aquifer most likely attributed to contamination from urban wastewater. Smith and Hunt (2018) further supported these findings during their analysis of the Barton Springs Aquifer, where increased pollutant loading called for the installation of an automated control system, in the form of a concrete vault with valves which closed during storm events and opened after to reduce contaminated storm water loading, as a best management practice to protect the resource. These studies show increasing impacts from urban development on water resources in the region, and suggest a potential impact on ephemeral stream pools, which warrants further study.

The objective of this study was to investigate whether and how urban land development impacts temporal patterns of water quality in standing water bodies within the Edwards Aquifer region. Two study approaches were taken to help accomplish the objective. First, levels of nitrates, total dissolved phosphorus, *E. coli*, and other coliform bacteria were sampled at two ephemeral stream sites of differing proximity to urban development, over a period of highly variable precipitation, to analyze how water quality varied with surrounding land use and how precipitation impacted pollutant concentrations over

time. It was assumed that concentrations of all measured pollutants would increase significantly following precipitation events in the more urbanized site, since runoff from fertilized golf courses, lawns, septic systems, public parks, and urban soils have been linked to increased contaminant loading into water sources (Ishii et al., 2006; Taylor & Owens, 2009; Winter & Dillon, 2005), whereas pollutant loading into water sources at the less developed site was predicted to be minimal to nonexistent. A perennial pond with a consistent water level over time was also sampled to help control for seasonal variability in water quality parameters unrelated to precipitation patterns. Secondly, temporal variability in water quality parameters was analyzed at 24 sites with publicly available data in the Edwards Aquifer region to determine whether precipitation-driven changes in water quality parameters at sampled ephemeral pools were similar to patterns seen across the region. The sites with publicly available data differed from the field-sampled sites in having more consistent flow, allowing a comparison between sites with a more standing-water type pool environment to those with more consistent flow patterns.

Methods

Study area

The Edwards Aquifer region has a moderately arid climate (Gustafson, 2015). Annual rainfall ranges from 76 to 89 cm in the Eastern portion and 51 to 64 cm in the Western portion, with the highest rates of rainfall occurring in the spring and fall. Periods of drought are common for the region, as temperatures may exceed 38°C, causing rapid evaporation of water from the region's thin soils (Fowler, 2005). The main geological subtype within the region is karstic limestone, which is a highly permeable system of faults and fractures that allows efficient recharge of the aquifer (George et al., 2011). Soils and surface water in the region are neutral to alkaline pH due to the limestone geology, but water in the aquifer is fresh, with total dissolved solids less than 500 mg/L. The aquifer itself serves as invaluable habitat for various endemic species, helps reduce inputs of freshwater into downstream estuaries, and provides drinking water for millions of people, including San Antonio (Bowles & Arsuffi, 1993; Fowler, 2005; George et al., 2011). Surface water sources over the aquifer are commonly owned and protected by the state, with landowners and other users of water needing legal permission to extract water from rivers (Gustafson, 2015). Temporal patterns of flow in the region result from the karst topography and precipitation patterns, which are characterized by short periods of intense precipitation within longer periods of drought. During periods of drought, surface flow ceases in streams and rivers not fed by groundwater springs, leaving only isolated pools in otherwise dry channels. Streamflow returns during intense precipitation events, refilling pools, and may persist for several days to weeks following precipitation.

Field collection of water quality samples was conducted at three locations within the Edwards Aquifer region: Ingram, Albert and Bessie Kronkosky State Natural Area (ABK Ranch), and Fair Oaks Ranch (Figure 1). All sites were similar regarding vegetation composition, temporal weather patterns, and presence of an isolated standing water pool. Soils were similar at sites as well, with Fair Oaks Ranch and ABK primarily gravelly clay loams in the Brackett-Real association, and soils at Ingram primarily clays in the Harper-Eckrant complex. However, sites differed in terms of surrounding land use; ABK Ranch was in a protected natural area and had no urban cover in the contributing watershed, Ingram was in a rural area, but also had no urban cover in the contributing watershed, and Fair Oaks Ranch was in a suburban housing development with 12% developed cover and 3.3% impervious cover in the contributing watershed. In addition, the specific type of standing water body varied between sites. Fair Oaks Ranch and ABK Ranch were isolated pools in ephemeral streams, which filled during rainfall and streamflow and dried slowly in between rainfall and flow events. Ingram was a pond fed by a spring via feeder pipe. This site served as a control for temporal variability because the water level remained stable throughout the duration of research, and thus fluctuations in water quality at this site could not be attributed to precipitation-driven runoff from the surrounding watershed.

Water quality sampling

Surface grab samples of water at Ingram, ABK Ranch, and Fair Oaks Ranch were collected weekly over the course of a 5-month period ranging from June to October of 2018. No water samples were collected in September at ABK Ranch, because the area was closed for access for the entire month due to substantial flooding and trail damage. Water for analysis of nitrate and total dissolved phosphorus was collected in 1-L acid-cleaned, polyethylene bottles and placed on ice until return to the laboratory located at the University of Texas at San Antonio (UTSA) campus. Upon return to the laboratory, samples were stored in a refrigerator at 4°C until processing, typically within 24 hours of collection. Laboratory blanks were analyzed in conjunction with field samples to identify any areas of potential contamination; nitrate, phosphorus, *E. coli*, and fecal coliform concentrations were negligible in all measured blank samples. Field samples were not filtered to comply with EPA analysis methodology.

Nitrate concentrations in water samples were analyzed using a brucine sulfate colorimetric reaction (EPA Method 352.1: Nitrogen, Nitrate (Colorimetric, Brucine) by Spectrophotometer). Samples and standards were mixed with a brucine sulfate solution and the final absorbance was read on a BioMate™ 3S spectrophotometer at 410 nm. Nitrate concentrations of samples were determined using an absorbance-concentration standard curve.
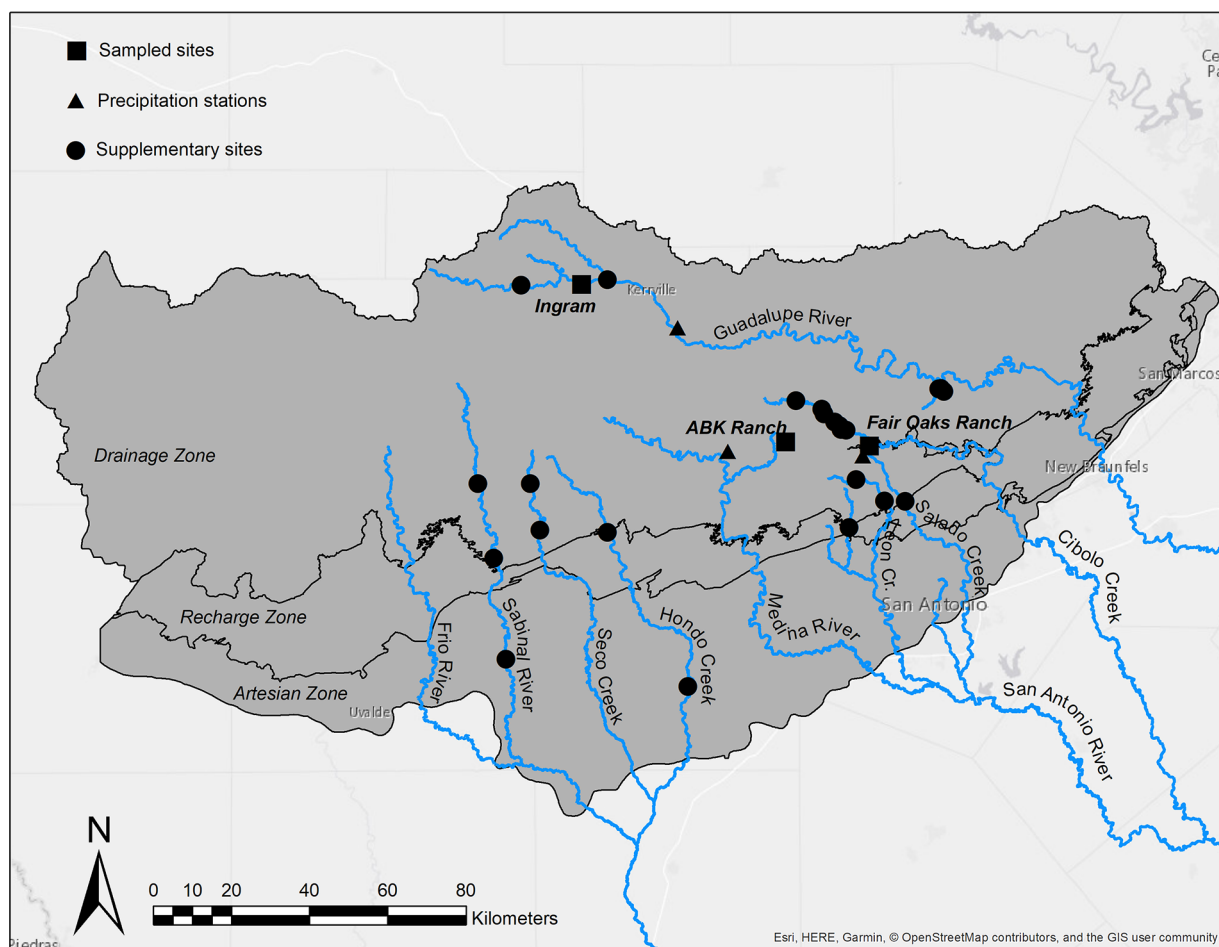
Figure 1. Map showing study sites, precipitation stations, and supplementary sites in relation to San Antonio. The Edwards Aquifer drainage, recharge, and artesian zones are shown in the gray outline.

Amounts of total dissolved phosphorus in water samples were determined using an ammonium persulfate digestion procedure (EPA Method 365.3: Phosphorus, All Forms (Colorimetric, Ascorbic Acid, Two Reagent)). Following digestion, samples were mixed with an ascorbic acid solution and the final absorbance was read on a BioMate™ 3S spectrophotometer at 650 nm. Concentrations of total dissolved phosphorus of samples were determined using an absorbance-concentration standard curve.

Coliform count plates (3M™ Petrifilm™) were used to measure the presence of *E. coli* and other coliform bacteria within the water samples. On field sampling days, plates were removed from refrigerated storage and placed in quart-size sealable bags prior to sampling to allow for the stabilization of the agar during travel to field sites. Within 15 minutes of water sample collection, a disposable glass pipette with a dropper bulb was used to place roughly 1 mL of sample onto the agar to allow for the immediate growth of bacterial colonies. Plates were then placed back into the bags to ensure the agar would not be disturbed during transport back to the laboratory. Once returned, the plates were placed in a box with a lid and allowed to incubate at room temperature (21°C–24°C) for approximately five days. The plates were then examined under a compound microscope at 50× magnification. The number of *E. coli* and other coliform bacteria colony forming units (CFUs/mL) was counted for each plate. Distinction between *E. coli* and other coliform bacteria colonies was determined based on their color on the plates; blue indicated the presence of *E. coli* CFUs while red indicated the presence of other coliform bacteria CFUs.

To determine the impact of precipitation on water quality, mean daily precipitation was determined at each site for the week prior to, and including the day of, each sampling event. Rainfall data for all three sites was obtained from Weather Underground (wunderground.com) at the stations nearest to the sampling sites (Kerrville Municipal-Schreiner Station for Ingram, Pipe Creek HQ/ABK Unit Station for ABK Ranch, and Cibolo Trails Station for Fair Oaks Ranch (Figure 1).

Supplemental water quality data

Data on nitrate, phosphorus, *E. coli*, and other fecal coliforms were obtained from multiple additional sampling sites within the Guadalupe, San Antonio, and Frio River watersheds in the Edwards Aquifer region (Figure 1). Water quality data were obtained from the Texas Commission on Environmental

Quality (TCEQ) Surface Water Quality Web Reporting Tool (https://www80.tceq.texas.gov/SwqmisPublic/index.htm) and the United States Geological Survey (USGS) Water Quality Data Web Interface (https://waterdata.usgs.gov/nwis). Water quality data submitted to TCEQ are collected using a standard procedure and subject to quality assurance protocols (Texas Commission on Environmental Quality (TCEQ) 2012, 2020). Water quality data available through USGS is also quality assured. River flow information for each supplemental water quality site was also obtained from the nearest USGS flow gage. Data from the period 2000 to 2018 was used in the analysis; although some sites had earlier data, this data was not used so that water quality data would better align with contemporary land use data, which was collected in 2016. Multiple supplemental water quality sites showed zero flow during dry periods; however, all water quality samples at supplemental sites were collected during periods with flowing water, except for a few collection dates at Hondo Creek at SH 173 SE Hondo (TCEQ site 18408) and Leon Creek at Raymond Russell Park (TCEQ site 12851). Thus, supplemental sites were not considered representative of pools in ephemeral streams but instead were used to determine whether flowing water sites had similar levels of water quality parameters as sampled ephemeral sites and whether water quality parameters responded similarly to sampled ephemeral sites during flood events. The sites were also used to explore whether response patterns of water quality parameters to flood events differed across a gradient of urban land development.

Analysis strategy

Weekly values of nitrate, total dissolved phosphorus, coliform counts, and *E. coli* were averaged for each month at each site and plotted to examine temporal trends. Correlation analysis (with significance level $\alpha = .05$) was conducted using weekly measured values to identify whether correlations between anthropogenic pollutants and weekly antecedent rainfall were significant. A one-way ANOVA was conducted for each site to determine whether average pollutant concentrations differed in "dry" (weekly precipitation ≤ 0.50 cm) and "wet" (weekly precipitation > 0.50 cm) conditions. Ingram, the control site, was excluded from both correlation analyses because the water level in the spring-fed pond remained consistent over the course of research, and thus was minimally impacted from rainfall events. An additional correlation analysis (with significance level $\alpha = .05$) was conducted using monthly averaged ambient temperature values and bacterial counts at both Fair Oaks Ranch and ABK Ranch to analyze the differences in bacterial growth based on temperature.

Median values of nitrate, total phosphorus, *E. coli*, and other fecal coliforms were calculated at 24 supplementary sites. Data from supplementary sites was restricted to the years 2000 to 2018 to ensure that water quality data was representative of contemporary land use. The relationship between precipitation events and water quality parameters

was also explored using data from supplementary sites. At supplemental sites, discharge level measured at the nearest gaging station was used as a measure of recent precipitation events. At each supplemental site, relationships between water quality parameters and weekly antecedent mean daily discharge were tested with linear regression analysis (with significance level $\alpha = .05$). An additional analysis was conducted to explore whether water quality parameters at sites in watersheds with greater urban development showed stronger responses to precipitation and flooding events. The slopes of relationships between discharge and water quality parameters were collected for all sites for each water quality parameter and correlated with percent impervious cover in the watershed. It was expected that sites with greater watershed impervious cover would show stronger water quality responses to flood events and thus have greater slope values compared to sites in less developed watersheds.

Results

Highest average monthly rainfall totals occurred in September and October at Ingram, whereas July had the highest average monthly rainfall at ABK Ranch and Fair Oaks Ranch (Figure 2). Temporal patterns at both ABK Ranch and Fair Oaks Ranch were similar for the duration of research, most likely due to the closer proximity of these sensors as compared to the sensor for the Ingram site. The highest daily precipitation total was 15.75 cm, which was recorded at Fair Oaks Ranch during the month of July. Following this rainfall event, flow rate increased substantially, and the site experienced a significant flood (Love & Laub, 2021). The stream at ABK Ranch did not flow during the summer months, but underwent significant flooding during the month of September, causing a delay in sample collection. As Ingram was an isolated pond, it underwent no visible water level changes throughout the duration of research, even during and following significant precipitation events.

Nitrates

Fair Oaks Ranch was consistently higher in nitrate concentrations than the other two study sites, with the highest average concentration of nitrates, 0.166 mg/L, occurring at this site during the month of July (Figure 3). Concentrations at ABK Ranch and Ingram remained low (<0.05 mg/L) throughout the duration of research, with ABK Ranch recording only slightly higher concentrations during dry conditions ($\bar{x} = 0.01$, SE $= 0.005$) than wet ($\bar{x} = 0.009$, SE $= 0.002$). There were no significant differences in means between dry and wet conditions within the natural water source at ABK Ranch ($p = .65$) or Fair Oaks Ranch ($p = .15$). Nitrates ($p < .01$) at Fair Oaks Ranch ($r_N = .67$) were found to have a moderate positive correlation to precipitation events, with a higher concentration of nitrates being observed during wet conditions ($\bar{x} = 0.12$, SE $= 0.05$) rather than dry ($\bar{x} = 0.03$, SE $= 0.02$) (Figure 4b).
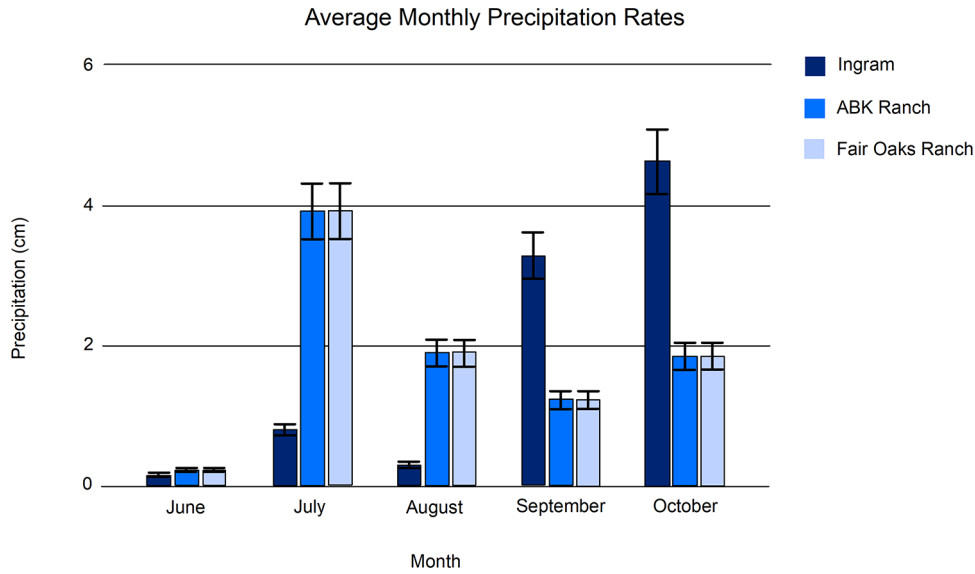
Average Monthly Precipitation Rates

Figure 2. Average weekly rainfall per month for the study sites from June to October 2018. Stations at ABK Ranch and Fair Oaks Ranch collected identical measurements over the duration of research due to their close proximity. Error bars indicate standard error in monthly precipitation rates at each study site.
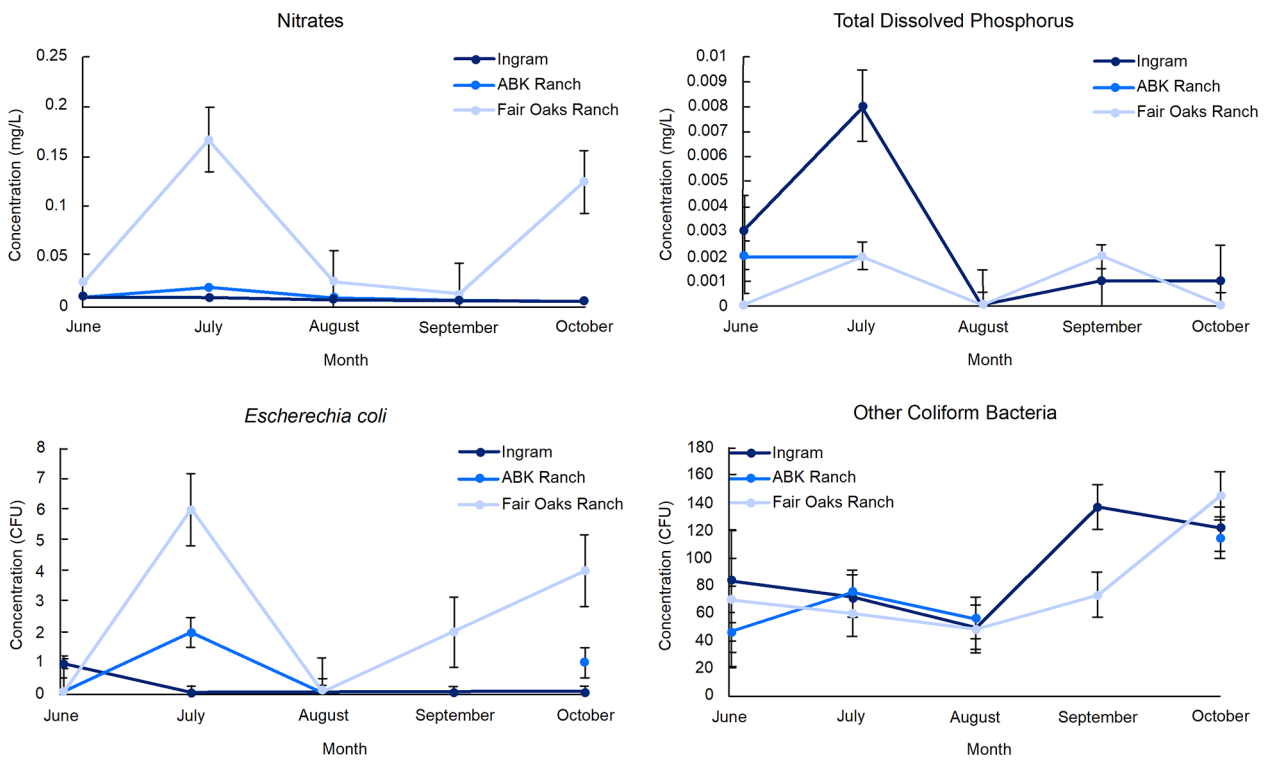

Figure 3. Monthly averages of pollutant concentrations at Ingram, ABK Ranch, and Fair Oaks Ranch from June to October 2018. ABK Ranch did not have a value in the month of September due to site closure. Error bars indicate variation in pollutant concentration averages during each month; errors bars are not present for pollutants that only had one measurement collected within the month.

Total dissolved phosphorus

Concentrations of total dissolved phosphorus were below detection limits (<0.01 mg/L) for most of this study at all three sites (Figure 3). The highest individual weekly value was 0.036 mg/L, recorded at Ingram in July. Monthly averages at both ABK Ranch and Fair Oaks Ranch did not exceed 0.002 mg/L. There was no significant difference in means between dry ($\overline{x} = 0.0015$, SE = 0.0007) and wet ($\overline{x} = 0.0007$, SE = 0.0004) conditions within the natural water source at ABK Ranch ($p = .39$). However, there was a significant difference in means between dry and wet conditions within the natural water source at Fair Oaks Ranch ($p < .01$), with a higher concentration of phosphorus occurring during dry conditions
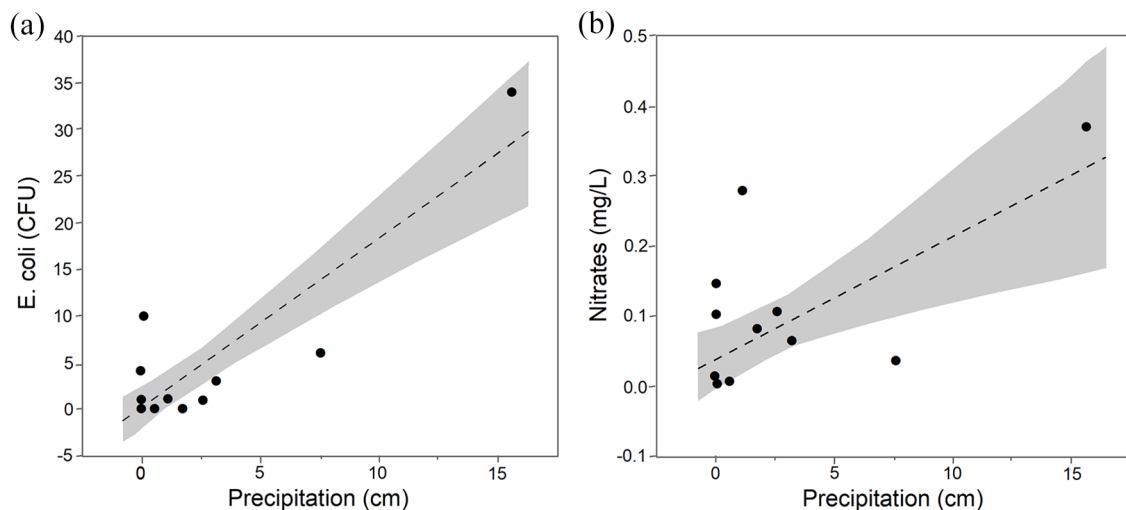
Figure 4. Correlation analysis results at Fair Oaks Ranch showing (a) relationship between weekly precipitation (cm) and *E. coli* (CFU) (*r* = .88) and (b) relationship between weekly precipitation (cm) and nitrates (mg/L) (*r* = .67). Gray shaded area represents the upper and lower 95% confidence band.

($\overline{x}$ = 0.0028, SE = 0.001) than wet ($\overline{x}$ = 0.0026, SE = 0.002). Concentrations of total dissolved phosphorus at neither site was significantly correlated to precipitation events.

Escherichia coli

E. coli CFU counts remained at relatively low levels (<10 CFUs/mL) throughout the study (Figure 3). The month of July at Fair Oaks Ranch saw the highest concentration, with 6 CFUs/mL being recorded on average. The highest monthly readings for Ingram and ABK Ranch were 1 and 2 CFU, respectively, with no variation in concentrations due to only having a singular measurement within the month for both sites. There was no significant difference in means between dry or wet conditions within the water source at Fair Oaks Ranch (*p* = .31). However, there was a significant difference in means between dry and wet conditions within the water source at ABK Ranch (*p* = .04), with a higher concentration of *E. coli* occurring during dry conditions ($\overline{x}$ = 1.60, SE = 0.91) rather than wet ($\overline{x}$ = 0.33, SE = 0.33). *E. coli* (*p* < .01) at Fair Oaks Ranch (r_E = 0.88) was found to have a strong positive correlation to precipitation events, with higher concentrations occurring during wet conditions ($\overline{x}$ = 6.88, SE = 4.06) than dry ($\overline{x}$ = 0.67, SE = 0.44) (Figure 4a).

Other coliform bacteria

Other coliform bacterial CFU counts were considerably higher than those of *E. coli* in the water source at all three sites, with fluctuations occurring similarly over the 5-month data analysis period (Figure 3). Higher coliform compared to *E. coli* counts is unsurprising as more generalized, opportunistic bacterial colonies are more likely to show rapid growth, particularly in stagnant water conditions. The highest weekly individual value was recorded at 145 CFUs at Fair Oaks Ranch. There was no

significant difference in means between dry ($\overline{x}$ = 68.56, SE = 16.23) and wet ($\overline{x}$ = 89.88, SE = 7.42) conditions within the natural water source at Fair Oaks Ranch (*p* = .28). However, there was a significant difference in means between dry and wet conditions within the natural water source at ABK Ranch (*p* = .02), with a higher concentration of other coliform bacteria occurring during wet conditions ($\overline{x}$ = 77.33, SE = 20.57) than dry ($\overline{x}$ = 56.40, SE = 10.08). Counts of other coliform bacteria CFUs at neither site were significantly correlated to monthly antecedent precipitation.

Supplementary sites

Water quality parameters at sampled ephemeral sites were within the range of values found at sites across the Edwards Aquifer region for nitrate (0.07–7.8 mg/L), *E. coli* (9–39,655 MPN/100 mL) and other fecal coliforms (17–2,860 number/100 mL) and were on the low end of the range for total phosphorus (0.01–1.1 mg/L), though methodological differences in phosphorus measurement may explain the somewhat low values found in sampled sites (Table 1). All sites showed either no significant relationship or a positive relationship between weekly antecedent discharge and *E. coli* concentration (Table 2), like that seen at Fair Oaks Ranch. Several sites also showed a positive relationship between weekly antecedent discharge and nitrate concentrations, but several sites showed a negative relationship. Relationships between watershed impervious cover and discharge-concentration slope were not significant for any water quality parameter (*p* > .18), suggesting no strong impact of impervious cover on the strength of water quality responses to flood events.

Discussion

The main objective of this study was to compare water quality conditions of two ephemeral stream systems that differed in

Table 1. Information for Supplementary Sites Analyzed, Including Median Concentrations of Water Quality Constituents.

SITE NAME AND NUMBER	COLLECTING AGENCY	WATERSHED AREA (HECTARES)	PERCENT IMPERVIOUS COVER	NITRATE (mg/L)	TOTAL PHOSPHORUS (mg/L)	*E. COLI* (MPN/100 mL)	FECAL COLIFORMS (NUMBER/100 mL)
Upper Cibolo SE of Boerne (12853)	TCEQ	23,750	2.9	0.6 (8)	1.1 (24)	150 (13)	–
Upper Cibolo Creek at Northrup Park (20821)	TCEQ	10,262	0.7	0.2 (15)	0.05 (1)	73 (21)	–
Upper Cibolo Creek at River Road Park (20823)	TCEQ	13,064	1.4	0.2 (3)	0.08 (5)	360 (14)	–
Upper Cibolo Creek at Sparkling Springs Drive (20830)	TCEQ	4,387	0.1	0.1 (2)	–	9 (14)	–
Cibolo Creek at Boerne City Park (12855)	TCEQ	19,370	2.1	0.9 (10)	0.2 (15)	190 (14)	385 (6)
Cibolo Creek at IH10 in Boerne (12857)	TCEQ	9,616	0.4	0.2 (11)	0.05 (10)	69 (47)	2,860 (5)
Cibolo Creek below Menger Creek (15126)	TCEQ	21,745	2.5	2.5 (20)	0.3 (27)	140 (30)	–
Cibolo Creek 1.6KM SH46 (16702)	TCEQ	20,558	2.1	0.4 (18)	0.6 (68)	84 (51)	120 (13)
Johnson Creek at SH 39 (12678)	TCEQ	44,201	0.5	0.4 (52)	0.01 (24)	50 (153)	60 (33)
Sabinal River at US 90 (12993)	TCEQ	82,573	0.2	7.8 (9)	0.05 (12)	65 (50)	–
Sabinal River at FM 187 (14939)	TCEQ	21,962	0.1	0.6 (2)	–	69 (10)	–
Sabinal River at Ranch Road 187 (21948)	TCEQ	61,217	0.2	0.5 (10)	0.05 (2)	32 (49)	29 (12)
Seco Creek at Miller Ranch (13013)	TCEQ	15,405	0.1	0.3 (9)	0.2 (2)	14 (24)	38 (12)
Seco Creek at SH 470 (13017)	TCEQ	4,462	0.1	0.2 (4)	–	84 (10)	–
Hondo Creek Downstream of RR 462 (13010)	TCEQ	33,128	0.2	0.3 (8)	0.08 (7)	26 (35)	33 (11)
Hondo Creek at SH 173 SE Hondo (18408)	TCEQ	146,075	0.2	2.2 (2)	0.04 (9)	19 (33)	–
Leon Creek (08180945)	USGS	3,469	1.3	0.4 (11)	0.2 (11)	39,655 (2)[a]	190 (1)[a]
Leon Creek at Raymond Russell Park (12851)	TCEQ	9,164	9.7	1.2 (16)	0.04 (19)	38 (35)	17 (5)
Salado Creek (08178585)	USGS	8,108	2.1	0.3 (5)	0.2 (5)	–	–
Honey Creek Trib (08167350)	USGS	41	0	0.2 (8)	0.06 (10)	–	–
Honey Creek Trib (08167353)	USGS	137	0	0.07 (9)	0.06 (12)	–	–
Honey Creek Trib (08167347)	USGS	91	0.4	0.07 (10)	0.06 (10)	–	–
North Fork Guadalupe River—Gaging Station (12682)	TCEQ	43,141	0.1	0.3 (54)	0.01 (24)	28 (151)	38 (30)
Helotes Creek (08181400)	USGS	5,115	0.5	0.4 (25)	0.1 (24)	3,500 (5)[a]	–

Note. Numbers in parentheses are number of samples. A dash indicates no data available.
[a]Units are colony forming units (CFUs) per 100 mL.

Table 2. Direction of Relationships Between Mean Weekly Antecedent Discharge and Water Quality Measures for Supplementary Sites.

SITE NAME AND NUMBER	NITRATE (mg/L)	TOTAL PHOSPHORUS (mg/L)	*E. COLI* (MPN/100 mL)	FECAL COLIFORMS (NUMBER/100 mL)
Upper Cibolo SE of Boerne (12853)	NS	Negative	Positive	–
Upper Cibolo Creek at Northrup Park (20821)	NS	NS	NS	–
Upper Cibolo Creek at River Road Park (20823)	NS	NS	NS	–
Upper Cibolo Creek at Sparkling Springs Drive (20830)	NS	NS	NS	–
Cibolo Creek at Boerne City Park (12855)	NS	NS	Positive	NS
Cibolo Creek at IH10 in Boerne (12857)	NS	NS	NS	NS
Cibolo Creek below Menger Creek (15126)	Negative	Negative	Positive	–
Cibolo Creek 1.6KM SH46 (16702)	NS	Negative	NS	NS
Johnson Creek at SH 39 (12678)	Positive	NS	NS	NS
Sabinal River at US 90 (12993)	Negative	NS	NS	NS
Sabinal River at FM 187 (14939)	NS	NS	Positive	–
Sabinal River at Ranch Road 187 (21948)	Positive	NS	NS	NS
Seco Creek at Miller Ranch (13013)	NS	NS	NS	NS
Seco Creek at SH 470 (13017)	NS	NS	NS	–
Hondo Creek Downstream of RR 462 (13010)	NS	NS	NS	NS
Hondo Creek at SH 173 SE Hondo (18408)	–	NS	NS	–
Leon Creek (08180945)	Positive	NS	–	–
Leon Creek at Raymond Russell Park (12851)	–	NS	Positive	–
Salado Creek (08178585)	NS	NS	–	–
Honey Creek Trib (08167350)	NS	NS	–	–
Honey Creek Trib (08167353)	NS	NS	–	–
Honey Creek Trib (08167347)	NS	NS	–	–
North Fork Guadalupe River—Gaging Station (12682)	Positive	NS	NS	NS
Helotes Creek (08181400)	NS	Positive	NS	–

Note. Values are only provided for significant relationships. NS = non-significant relationship, a dash indicates no data available to test the relationship.

urban land cover within the Edwards Aquifer region. ABK Ranch, a site with no urban development, and Fair Oaks Ranch, a site surrounded by a housing development and golf course, were subject to significant changes in water level over the course of research. Both varied from flowing streams to isolated pools, whereas Ingram, a site with light vegetation maintenance efforts but no immediate urban development, remained a consistently level pool.

While there were no consistent differences in most of the parameters between dry and wet conditions, some parameters were significantly different in dry versus wet conditions for at least one site. Analyses identified a strong positive correlation between weekly antecedent precipitation and *E. coli* (r_E = .88) at Fair Oaks Ranch (Figure 4). One explanation for this relationship is large areas of impervious cover funneling water-borne pollutants, mainly fecal bacteria, into receiving waters (Mallin

et al., 2000), and is supported by the fact that the undeveloped site at ABK Ranch did not experience a similar fluctuation in bacterial concentrations even following significant rainfall events. Moreover, all the supplementary sites that showed a significant positive relationship between *E. coli* and antecedent discharge, except one, had >2% impervious cover in the watershed, further suggesting urban development was a contributing factor to the *E. coli* increases with precipitation at Fair Oaks Ranch.

At ABK Ranch, elevated levels of *E. coli* were identified during dry conditions ($\bar{x}$ = 1.60, SE = 0.91), whereas other coliform bacteria concentrations were higher during wet conditions ($\bar{x}$ = 77.33, SE = 20.57). One potential explanation of this pattern is the isolated pool nature of the ABK Ranch site, combined with the varying ideal conditions for growth regarding *E. coli* and coliform bacteria. *E. coli* are more productive than other coliform bacteria at warmer ambient temperatures, such as those seen during dry conditions with low precipitation rates, while other coliform bacteria perform better at the lower ambient temperatures that occurred during wet conditions with high precipitation rates (Ishii et al., 2006). *E. coli* counts were not significantly correlated with ambient temperature values; however, other coliform bacteria counts were found to have a moderate negative correlation with ambient temperature at Fair Oaks Ranch ($r = -.59$), suggesting lower temperatures provided a more ideal growth environment for other fecal coliform bacterial colonies. Another potential explanation for differences between *E. coli* and other coliform counts in dry versus wet conditions is water salinity, which is typically elevated during dry conditions, and is known to influence the survivability of bacteria, including *E. coli* (Pachepsky & Shelton, 2011).

A significant peak in nitrates was observed at Fair Oaks Ranch following a sampling on July 10th; the week leading up to this sampling had high precipitation (15.75 cm), with the highest amount of precipitation occurring up to 2 days prior to sampling. Several lines of evidence suggest that urban development around the site contributed to the nitrate peak. Runoff from fertilized golf courses, lawns, and public parks, all of which are near the Fair Oaks Ranch sampling site, have been attributed to increased nitrate loading into other standing water bodies (Enwright & Hudak, 2009; Hudak, 2000; Winter & Dillon, 2005). Previous work has also shown that suspended solids, fine particles, heavy metals, and various nutrients and chemicals are often highest in concentration within the first 30 minutes of the runoff event, or the "first flush" (Baek et al., 2015; Ma et al., 2011; Park et al., 2010), whereas *E. coli* and total nitrogen concentrations appear to be higher toward the "end flush" of the runoff events (Bach et al., 2010). Since the site was sampled 2 days after the peak rainfall, the sampling likely caught the "end flush" of the event. Furthermore, as with bacterial concentrations, levels of nitrates at ABK Ranch did not rise substantially following precipitation as seen at Fair

Oaks Ranch, suggesting that a lack of urban development prevented these contaminants from entering the water body during stormwater runoff events. Some supplementary sites with low urban development also showed positive relationships between antecedent discharge and nitrate, suggesting some natural sources of nitrate contribute to increased levels during runoff events. However, the isolated pool nature of Fair Oaks Ranch may make it particularly susceptible to increases in nitrate during runoff events. In an isolated pool, there is likely low inputs of nitrate to the water in between runoff events, in contrast to perennial streams where nitrate may be contributed continuously by groundwater inputs or other upstream sources. Indeed, at the supplementary site Cibolo Creek below Menger Creek (TCEQ site 15136), which is a perennial site upstream from Fair Oaks Ranch, nitrate tended to decrease with increased discharge, opposite the pattern seen at the isolated pool at Fair Oaks Ranch.

Interestingly, phosphorus levels did not rise in equal concentrations as nitrates at Fair Oaks Ranch, whereas phosphorus levels were predicted to increase due to the two pollutants being commonly found in conjunction during nutrient loading into water sources (Pandey et al., 2014). One possibility for the lack of phosphorus response is that the precipitation event diluted phosphorus concentrations, such that they stayed at low levels during the runoff event. In support of this possibility, most supplementary sites that had a significant total phosphorus response to antecedent discharge showed a negative relationship. Since phosphorus levels were already near or below detection limits, further decreases in concentrations would not have been observed. Low phosphorus concentrations were found to be common in the study region, with more than half of supplementary sites having total phosphorous concentrations frequently below detection limits, including sites on Cibolo Creek upstream of the Fair Oaks Ranch sampling site.

Unlike the sites at both ABK Ranch and Fair Oaks Ranch, the isolated pool at Ingram remained at a consistent level throughout the duration of research and was only influenced by light vegetation management in its surrounding area. Thus, Ingram was used as a control site to observe whether water quality parameters fluctuated in the absence of a strong stormwater runoff influence. Ingram did record the highest individual weekly value of phosphorus, 0.036 mg/L, in July. Analysis performed on this parameter did not indicate a correlation with monthly precipitation levels, suggesting that a factor other than rainfall may have been a contributor to the increase in phosphorus concentrations. While not formally measured, visually noticeable levels of algae and, on occasion, significant "fishy" odors were emanating from the Ingram water source, suggesting the pool may have been subject to the process of eutrophication at minor levels (Matthews & Bernard, 2015). Additionally, this process may have been exacerbated by minor degradation of the surrounding pool bank following the vegetation management processes that occurred at this site during

research. Importantly, other parameters besides phosphorus remained consistently low throughout the study at Ingram, and nitrate and *E. coli* did not show similar spikes following rain events as observed at Fair Oaks Ranch, further supporting that stormwater runoff was a primary contributor to increases in nitrate and *E. coli* seen at Fair Oaks Ranch.

On average, the residential community of Fair Oaks Ranch saw a higher average monthly nitrate and *E. coli* level compared to Ingram and ABK Ranch, further suggesting that urban cover was a factor in determining water quality at Fair Oaks Ranch, a result consistent with previous work (Walsh et al., 2005). Another potential cause of water quality differences between sites is differences in soil properties within surrounding watersheds, such as soil salinity or nutrient concentrations. Although soil types were generally similar between sites, particularly Fair Oaks Ranch and ABK Ranch, further research could explore the potential of local soil properties as an influence on water quality differences. In addition, nitrate levels were on the low end of values seen at other supplementary sites with similar impervious cover, suggesting the isolated pool at Fair Oaks Ranch may be somewhat less impacted by urban sources of pollution compared to perennial sites, where leaky sewer pipes, septic systems, or wastewater discharge may provide continuous inputs of nitrates. Furthermore, Fair Oaks Ranch was still impacted by urban runoff events as discussed above and further research should explore whether other isolated pools in urban stream environments respond similarly to that seen at Fair Oaks Ranch.

Mammalian presence may also be a contributor to anthropogenic pollutant loading into standing water sources, with prior studies indicating that deer, feral hogs, and raccoons may play a direct role in the degradation of standing water sources through increased soil disturbance, water turbidity, and loading of fecal indicator bacteria (McDowell, 2007; Parker et al., 2013; Ram et al., 2007). These effects are often enhanced during periods of drought, where animals are more likely to congregate near the water sources and negatively influence already strained riparian resources through more direct defecation and concentrated use. However, the relatively low background levels of nitrate and *E. coli* observed at Fair Oaks Ranch, plus a strong increase in these parameters following storm events, suggests a more significant impact of pollutant runoff from urban development, rather than mammalian presence. In addition, mammalian use of the Fair Oaks Ranch water source was limited (Love & Laub, 2021). Previous work in the Cibolo Creek watershed identified livestock and atmospheric deposition as the largest contributors of nitrogen input and yield, making up 68.8% of nitrogen inputs, whereas wild animals including deer, feral hogs, and waterfowl only contributed 9.9% of nitrogen inputs (Sullivan & Gao, 2016). Nonetheless, wild animals may become important sources of nitrogen inputs in local areas during certain periods, such as droughts when animals may be concentrated around remaining water sources.

Further work to identify primary sources of pollution to standing water bodies and their spatial and temporal variability in the Edwards Aquifer region and elsewhere are warranted to gage the relative impacts of urban development versus other pollution sources on these unique environments.

Conclusions

Based on results of this study, anthropogenic pollutant loading into the standing water bodies of the Edwards Aquifer region, particularly nitrates and *E. coli*, may be attributed primarily to stormwater runoff from urbanization, a practice which is projected to exponentially grow each year as population numbers also increase. A year-round study, including more frequent sampling of the water sources both before and after storm events, would increase knowledge about exact sources of these pollutants and would be beneficial for remediation activities in the future. Furthermore, expanding the scope of this research to include multiple sites for each land use type—urban, rural, and forested—would assist in enhancing replicability and specification of anthropogenic pollutant sources.

Author Contributions

CHL collected water quality samples, performed laboratory analysis, and was the primary author for this paper. BGL assisted with study design, provided financial support for field and laboratory supplies, and contributed revisions for this paper. Both authors reviewed and approved of the final manuscript.

Data Availability Statement

Data collected as part of this research is available by contacting the authors.

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