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Geochemically Heterogeneous Shallow Groundwater in an Urban Stream's Floodplain Contributes Negligible Quantities of Municipal Water Types to the Stream

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ABSTRACT

In urban environments, municipal water sources (e.g., drinking water and wastewater) can contribute considerably to regional groundwater resources. However, little is known about municipal water fluxes between streams and shallow groundwater at the floodplain scale. Understanding surface water–groundwater interactions in urban floodplains is essential for protecting both human and ecosystem health, sustainably managing water resources, and informing efforts to upgrade municipal water infrastructure as cities continue to expand. To address this research gap, we investigated whether the shallow groundwater in an urban floodplain transports drinking water and untreated wastewater to a stream. Our study focused on the urban Deer Creek watershed, near St. Louis, Missouri, United States, where we collected samples from the stream and three shallow (<4 m deep) groundwater wells situated in its floodplain <0.5 km apart. Stream and shallow groundwater samples were obtained weekly over 2.6 years and analysed for municipal water tracers (e.g., optical brighteners, faecal coliform bacteria, and F^-) as well as other water quality parameters (e.g., temperature, specific conductivity, major anions, and total element concentrations) to understand water sourcing and exchange in this urban catchment. Although municipal water tracer signatures were elevated in Deer Creek, the shallow groundwater in its floodplain exhibited low concentrations for these tracers. Our findings suggest that the shallow groundwater is not a meaningful source of drinking water or untreated wastewater to the stream. However, if municipal water types migrate deeper into the groundwater profile than the depths we sampled, deeper groundwater could still deliver drinking water and untreated wastewater to Deer Creek, potentially explaining the elevated municipal water signatures observed in the stream. Nevertheless, we found that the shallow groundwater was geochemically heterogeneous despite the proximity of the observation wells. Variations in shallow groundwater characteristics among the wells are likely driven by differences in water depth, floodplain geomorphology, water residence time, mineral precipitation and dissolution processes in the substrate, and localised urban land use. Such differences over the small spatial extent we explored imply that municipal water types could still locally impact shallow groundwaters in urban catchments.

1 | Introduction

Urbanisation has impacted the hydrological cycle by altering natural fluxes of water and introducing new water sources in developed areas. While contributions of precipitation to groundwater are hindered in urban settings due to high levels of impervious surface area (Miller et al. 2014; Marx et al. 2021), municipal waters, including drinking water, untreated wastewater, and treated wastewater, have become substantial sources of groundwater recharge in many cities (Vázquez-Suñé et al. 2010; Sanzana et al. 2019; Beal et al. 2020). The addition of municipal waters to the urban water cycle has implications for both water quantity and quality in urban catchments.

Drinking water enters the environment through deliberate uses (e.g., lawn irrigation; Fillo et al. 2021) or infrastructure failures (e.g., water main breaks). Drinking water contributions to the environment can be determined by assessing surface water and groundwater resources for tracers like F^- since drinking water is commonly fluoridated to a known concentration above natural background levels in the United States for dental health (USHHS 2015; Lockmiller et al. 2019; Finegan and Hasenmueller 2023a). High levels of drinking water in surface water and groundwater resources waste water and economic resources, prompting the potential need for infrastructure updates.

Both untreated and treated wastewaters can be released into the environment through intentional means (e.g., constructed sewer outfalls or effluent discharge sites; Kuhlemann et al. 2021; Marx et al. 2021; Oswald et al. 2023) or unintentional pathways (e.g., leaking infrastructure; Paul et al. 2004; Sercu et al. 2011; Lee et al. 2015). While both types of wastewater can cause water quality impairments, untreated wastewater entering the environment is a more considerable water quality concern as it has a greater potential to contribute microorganisms, nutrients, heavy metals, and emerging contaminants to water resources per unit volume (Cheung et al. 1990; Petelet-Giraud et al. 2009; Dickenson et al. 2011). Common tracers for detecting untreated wastewater in waterbodies include faecal coliforms like *Escherichia coli* (*E. coli*), optical brighteners (synthetic whitening compounds present in laundry detergents and paper products; Tavares et al. 2008; Cao et al. 2009; Dubber and Gill 2017; Corsi et al. 2021; Finegan and Hasenmueller 2023a), and B concentrations and isotope compositions (since B can be sourced from household detergents; Vengosh et al. 1994; Hasenmueller and Criss 2013; Lockmiller et al. 2019). Elevated F^- concentrations have also been used to indicate wastewater inputs to water resources since F^- amendments for drinking water can be retained in the wastewater signature (Lockmiller et al. 2019).

While drinking water and wastewater have been found to be significant inputs to urban watersheds, most studies examining municipal water recharge of urban groundwater resources occur at the watershed, city, or regional scale (Paul et al. 2004; Wolf et al. 2006; Luque-Espinar et al. 2015; Barthel and Banzhaf 2016; Vystavna et al. 2018; Sanzana et al. 2019; Beal et al. 2020; Kuhlemann et al. 2021). For example, an assessment of Barcelona, Spain, found that municipal water leaks accounted for 52% of urban groundwater recharge, with 22% originating from the drinking water supply and 30% coming from wastewater infrastructure (Vázquez-Suñé et al. 2010). In Lima, Peru, drinking water main leaks contributed 40% of the total aquifer recharge (Lerner 1986).

These regional scale studies are important for understanding the water budgets of cities, particularly when estimating human-sourced recharge to the groundwater (Wallace et al. 2021), but they often generalise the heterogeneities in water fluxes and contamination levels that might be observed at smaller spatial extents. Few studies examine fluxes of municipal water types between surface water and groundwater reservoirs at higher spatial resolutions, like floodplain or hyporheic scales (Banzhaf et al. 2013; Keefe et al. 2019), despite the shallow groundwater usually being more impacted by infrastructure issues (Paul et al. 2004; Wolf et al. 2006; Lee et al. 2015). Thus, studies with high spatial resolution are necessary to understand local exchanges between surface water and groundwater resources and the potential flux of municipal waters across them.

This study therefore investigates whether shallow groundwater in stream floodplains can serve as a source of legacy drinking water and wastewater to urban stream systems. To address this objective, we conducted a comprehensive geochemical assessment of an urban stream, the shallow groundwater within its floodplain, and representative sources of drinking water and untreated wastewater for the catchment. We also examined natural controls on stream and shallow groundwater geochemistry to evaluate the spatial and temporal connectivity between these water resources and how such interactions might influence the transport of municipal water types through the basin. Our integrated approach provides insight into both the sources and exchange pathways of municipal waters in urban watersheds as well as the geochemical evolution of urban water resources at a floodplain scale.

2 | Methods

2.1 | Study Site

This study was performed in the Deer Creek watershed, near St. Louis, Missouri, United States (Figure 1a), which is a 95.3 km^2 catchment that is almost entirely covered by developed land use classifications (Figure 1b). We selected the urbanised Deer Creek basin to examine if shallow groundwater plays a role in transmitting municipal waters to surface waterbodies for several reasons. First, the only municipal water types that can potentially be sourced to the watershed are drinking water and untreated wastewater. The untreated wastewater produced within the catchment is transported to a treatment facility outside of the basin via the sewer infrastructure network and, therefore, treated wastewater is not a confounding third municipal water endmember for our study location. Second, only 42 parcels within the entire Deer Creek basin potentially use septic systems (Deer Creek Watershed Alliance 2023), so septic systems have a comparatively limited capacity to source wastewater to the catchment. Third, a regional scale sewer infrastructure renovation that was completed on 31 July 2022 removed sewer overflows from the watershed prior to our study, thereby eliminating direct inputs of untreated wastewater to the stream (Finegan and Hasenmueller 2025).

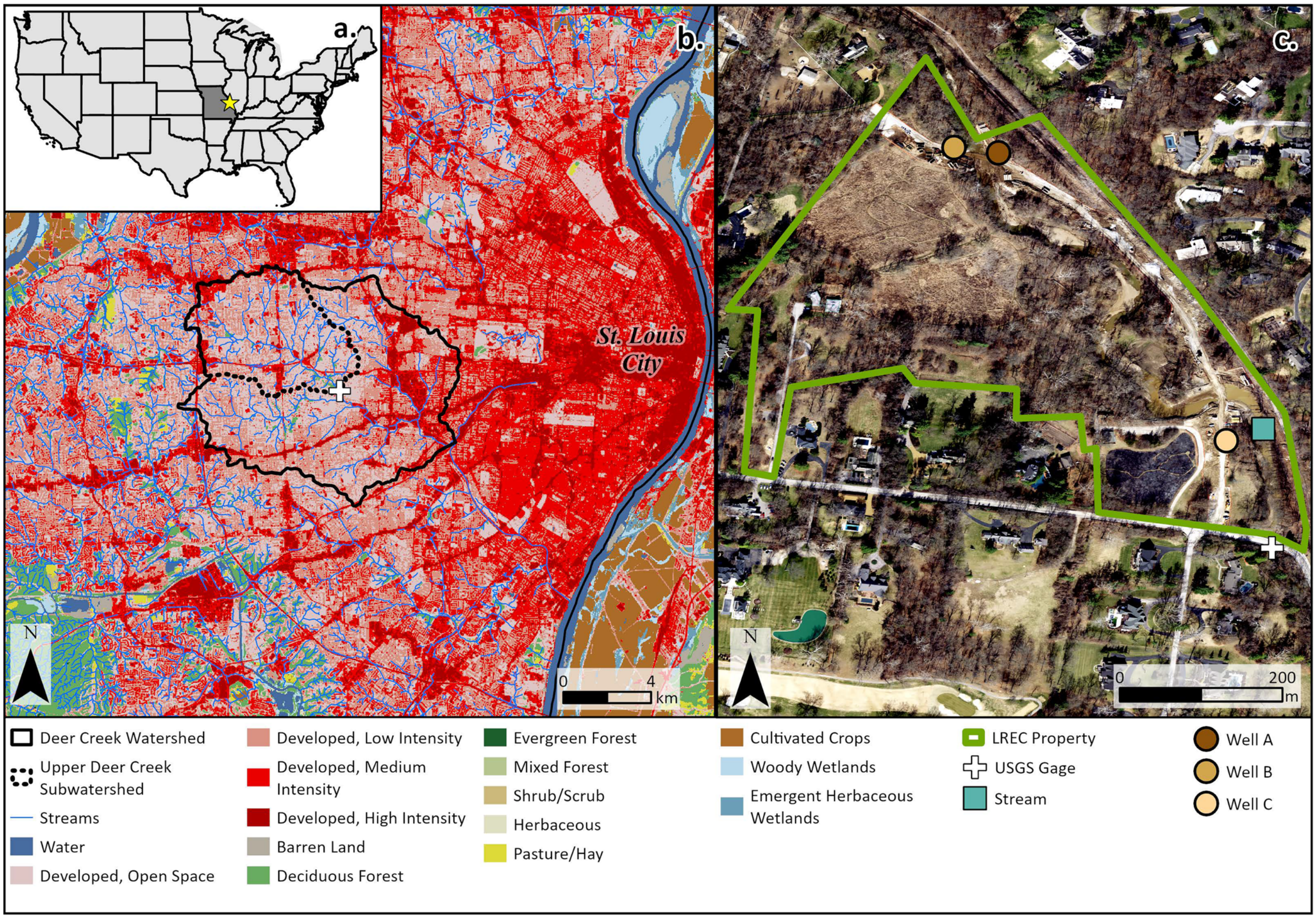

FIGURE 1 | Maps illustrating (a) the study site's location (star) in relation to the contiguous United States, (b) the St. Louis Metropolitan area showing land use classifications (USGS 2024) and the boundaries for both the upper Deer Creek subwatershed (which drains to USGS gage 07010055) and the entire Deer Creek watershed, and (c) the Litzsinger Road Ecology Center (LREC), with the stream sampling site, shallow groundwater sampling sites, and USGS stream gage location from (b) on an aerial image (St. Louis County 2021).

The efforts to remove the sewer outfalls in the Deer Creek basin have improved the stream's water quality (Finegan and Hasenmueller 2025). Nevertheless, concentrations of tracers for both untreated wastewater and drinking water in Deer Creek are still elevated relative to rural streams in the region (Lockmiller et al. 2019; Finegan and Hasenmueller 2025), suggesting that these two municipal water types may still be sourced to the stream due to failing subsurface water infrastructure or irrigation. Shallow groundwater discharge has been hypothesised as a potential vector for municipal water contributions to streams in the region (Lockmiller et al. 2019), including Deer Creek (Buckley 2020). However, these prior studies did not acquire the needed hydrological and geochemical data to determine if the shallow groundwater could serve as a potential legacy source for municipal waters to urban streams.

We focused our assessment of shallow groundwater as a potential conveyer of municipal water types to a gaining reach of Deer Creek (MoDNR 2025) at the Litzsinger Road Ecology Center, which is a 0.16 km^2 private education and restoration site situated at the centre of the Deer Creek watershed (Figure 1b,c). A United States Geological Survey (USGS) stage and discharge station (gage 07010055; USGS 2025) is just downstream of our study location and collects data for the 31.1 km^2 upper Deer Creek subcatchment (Figure 1b,c). The upper Deer Creek subbasin mostly contains low to medium density urbanised land use and has 32.2% impervious surface area, but the Litzsinger Road Ecology Center property is unique because it features restored tallgrass prairie and bottomland woodland habitats (Figure 1b,c; USGS 2024). Despite these ecological restoration efforts, the property managers have reported instances of sewer laterals leaking into a vernal pool at the site, demonstrating the potential for the shallow groundwater to transmit municipal waters to proximal surface waterbodies.

Three preexisting shallow groundwater wells (i.e., Well A, Well B, and Well C; Figure 1c) were available on the property for our study, with all having been installed on 13 June 2022. The wells' depths range from 2.93 m to 3.81 m below the surface, with Well A being the shallowest and Well C being the deepest. All three shallow groundwater wells are located within the floodplain of Deer Creek, ranging from 10 m to 30 m from the stream's channel. The western floodplain, which includes Well B and Well C, is inundated more frequently than the eastern floodplain due to topographic differences. While the bedrock geology of the upper Deer Creek watershed includes both Mississippian carbonates and Pennsylvanian siliciclastic sedimentary rocks, the study site overlies Mississippian St. Louis Limestone (Harrison 1997; MoDNR 2025).

2.2 | Stream and Shallow Groundwater Physicochemical Characterisation

Our study site was visited approximately weekly from 15 September 2022 through 1 May 2025. During each field visit, in situ measurements and samples were collected from Deer Creek and the three shallow groundwater monitoring wells installed in the stream's floodplain (Figure 1c). At the stream, in situ water quality measurements were collected for temperature, specific conductivity, pH, and dissolved O_2 using a YSI Professional Plus Multiparameter Instrument and optical brighteners using a Turner Designs AquaFluor Handheld Fluorometer (with units reported as reference fluorescence units (RFU)). At the three observation wells, the shallow groundwater's depth was determined using a Solinst 102 Water Level Indicator. To prevent the sampling of stagnated water, water was pumped out of each well prior to sample collection using a Geotech Geopump Peristaltic DC Pump following the United States Environmental Protection Agency's (USEPA) groundwater sampling procedures for the low flow method (Puls and Barcelona 1996; USEPA 2013). Briefly, the shallow groundwater was pumped from each well at a low flow rate while specific conductivity, pH, and dissolved O_2 measurements were checked for stability every 0.10–0.25 L of water pumped using the handheld YSI Professional Plus Multiparameter Instrument. Pumping continued until the shallow groundwater measurements stabilised to within 5% for specific conductivity, 0.1 units for pH, and 10% for dissolved O_2 among three consecutive measurements per the USEPA's groundwater stabilisation criteria (Puls and Barcelona 1996; USEPA 2013). Once these parameters were stable, the same in situ measurements that were obtained for the stream were acquired for the three shallow groundwater wells.

We also collected water samples from the stream and shallow groundwater locations for analyses of anion (i.e., F^-, Cl^-, SO_4^{2-}, and NO_3^-–N) concentrations during every site visit, while samples for measurements of total element (i.e., B, Na, Ca, Mg, Sr, K, and Si) and *E. coli* concentrations were obtained from 15 September 2022 to 1 January 2024. The samples for anion and total element analyses were field-filtered with 0.2-μm cellulose acetate filters into 50-mL polypropylene sample vials and transported back to the laboratory on ice. The samples that were used for determining anion concentrations were stored at −18°C until analysis on a ThermoFisher Dionex Integrion High Pressure Ion Chromatograph (IC), while the samples for total element analysis were acidified to 1% HNO_3, stored at 4°C, then analysed on a PerkinElmer 8300 Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). Instrument accuracy and precision were within 5% for the IC and within 10% for the ICP-OES based on blanks, check standards, and sample replicates. To evaluate *E. coli* levels, stream and shallow groundwater samples were collected into autoclaved 150-mL polypropylene bottles and transported to the laboratory on ice for immediate processing with the USEPA approved IDEXX Colilert Quanti-Tray System (USEPA 2017) and autoclaved glassware. Given the high levels of *E. coli* in the stream, we diluted the stream samples with autoclaved ultrapure (18.2 MΩ cm) water using a 1:5 ratio for our analyses. The *E. coli* data are reported in colony forming units per 100 mL (CFU/100 mL).

2.3 | Physicochemical Characterisation of Potential Endmember Contributions to the Stream and Shallow Groundwater

We obtained drinking water and untreated wastewater samples to measure their physicochemical attributes to determine how these endmembers might impact the stream and shallow groundwater at our study location. We collected four drinking water samples on 29 August 2023, 5 September 2023, 16 November 2023, and 21 December 2023 from a tap at the Litzsinger Road Ecology Center. On 12 October 2023, we received a 24-h composite influent wastewater sample from the Metropolitan St. Louis Sewer District's wastewater treatment plant that receives the untreated wastewater from the Deer Creek basin. All the municipal water endmember samples were processed for the same analytes as the stream and shallow groundwater samples (see Section 2.2 for more detail). We compared our results for the stream, shallow groundwater, and municipal water endmember samples from the Deer Creek catchment to published data for 18 rural spring samples, 8 rural stream samples, 17 drinking water samples, and 24 untreated wastewater samples collected in the St. Louis region (Lockmiller et al. 2019; Finegan and Hasenmueller 2023a).

To understand how the floodplain substrate might influence the characteristics of the shallow groundwater, we analysed an archive of sediment samples that had been collected when the wells were originally installed. These archived substrate samples consisted of 120–160 cm^3 of homogenised floodplain sediment obtained from the top, middle, and bottom of 0.46 m long sections of well core that had been collected at depths of 0.30–0.76 m, 1.06–1.52 m, and 1.83–2.29 m for all the wells and 3.20–3.66 m for Well C. The sediment sample collection had been stored at −18°C in glass jars prior to our analyses. Gravimetric water content for each thawed sediment sample was determined by weighing 10 g of sediment, drying the sediment at 105°C for at least 48 h, measuring the resulting dry sediment mass, and calculating the percent water loss. Each of these dried sediment samples was subsequently measured for organic matter content by heating the dry sediment in a muffle furnace at 550°C for 4 h, allowing it to cool overnight, weighing the new mass, and calculating the percent organic matter loss (Heiri et al. 2001). Exchangeable cations (i.e., Na, Ca, Mg, and K) in the substrate were analysed by weighing 10 g of untreated sediment for each sampling interval, allowing the sediment to air dry for 4 days, and creating as many 2.5 g replicates as possible (which resulted in 2–4 replicates per sediment sample). Each dried 2.5 g sediment replicate was mixed with 25 mL of 0.1 M $BaCl_2$-NH_4Cl, then the slurry was shaken for 30 min after which time it was left to settle overnight (Amacher et al. 1990). The supernatant from each mixture was subsequently gravity-filtered using an 11-μm filter and acidified to 1% HNO_3 prior to analysis for exchangeable cations on the ICP-OES.

2.4 | Data Calculations, Visualisations, and Statistics

We were unable to test our water samples for HCO_3^- and CO_3^{2-}, but we could estimate their values through ion balance

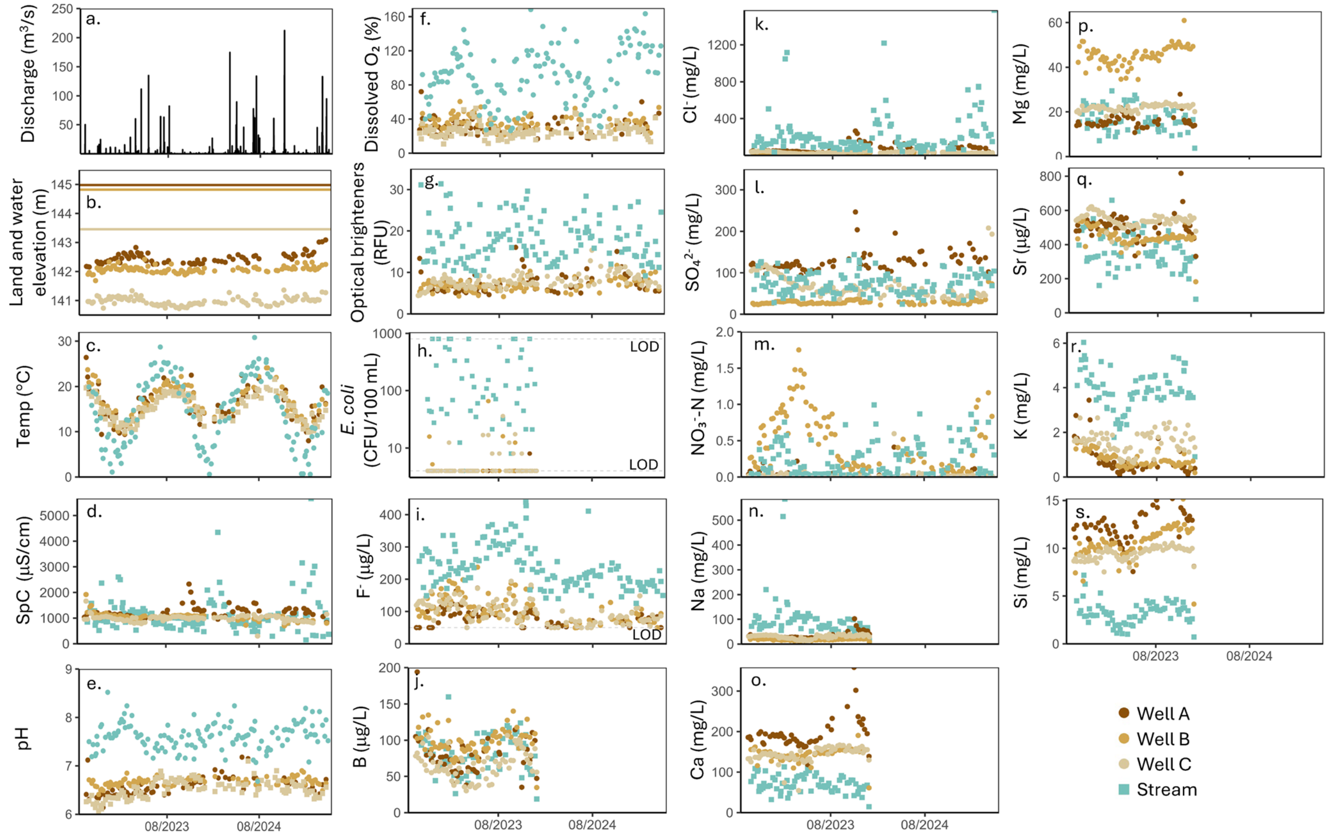

FIGURE 2 | (a) Discharge for Deer Creek (USGS 2025) and (b) the shallow groundwater elevation in the observation wells, with the land surface elevation for each well indicated by a solid line of the same colour. Water quality data are shown for (c) temperature (temp), (d) specific conductivity (SpC), (e) pH, (f) dissolved O_2, (g) optical brighteners, (h) *E. coli*, (i) F^-, (j) B, (k) Cl^-, (l) SO_4^{2-}, (m) NO_3^--N, (n) Na, (o) Ca, (p) Mg, (q) Sr, (r) K, and (s) Si. When applicable, lower and upper limits of detection (LOD) for our methods are indicated on the plots with dashed grey lines.

using concentration data for the measured major anions (i.e., Cl^-, SO_4^{2-}, and NO_3^-) and total elements that typically speciate as cations (i.e., Na, Ca, Mg, Sr, and K). To complete the ion balance for each sample, we presumed respective cation charges of Na^+, Ca^{2+}, Mg^{2+}, Sr^{2+}, and K^+, summed the anions and cations (as mEq/L) in RStudio using base R functions (R version 3.6.1; R Core Team 2024), and assumed that the excess cation concentration would equal the total concentration of both HCO_3^- and CO_3^{2-} (in mEq/L). The calculated HCO_3^- and CO_3^{2-} values were combined with measured analyte concentrations in The Geochemist's Workbench to create Piper diagrams.

Other data visualisations were created in R using *ggplot2* (Wickham 2016), and summary statistics for the stream and shallow groundwater data were calculated using R's *rstatix* package (Kassambara 2023). We applied the Kruskal-Wallis test to the non-normally distributed physicochemical data to determine significant differences among the stream and shallow groundwater samples using the *ggpubr* package (Kassambara and Mundt 2020). A Wilcoxon rank sum test was employed with the "wilcox_test" function of the *rstatix* package (Kassambara 2023) to establish which groups were significantly different. We used a significance level of $\alpha = 0.01$ for all statistical analyses. Any relationship that is hereafter described as "significant" has met this threshold.

3 | Results

3.1 | Stream and Shallow Groundwater Physicochemical Characteristics

During the monitoring period, continuous discharge for Deer Creek (Figure 2a), measured at USGS gage 07010055 (USGS 2025), had an average value of $0.48\,m^3/s$ and a median value of $0.06\,m^3/s$. The stream responded rapidly to precipitation events, with the largest flood events most frequently occurring in the spring months. However, we intentionally collected our weekly samples for the stream when discharge was low (i.e., $< 5\,m^3/s$). The shallow groundwater well levels all fluctuated < 1 m over the monitoring period, but the water levels tended to be highest in the wells in the early spring and lowest in the late summer and early fall (Figure 2b). While Well B and Well C typically had sufficient water volumes to collect samples, Well A was periodically dry or so close to dry that we were unable to pump sufficient volumes of water for the physicochemical parameters to stabilise for our measurement and sample collection (these periods are indicated by dates without data for Well A in Figure 2b).

Our water quality measurements highlighted physicochemical differences between the stream and shallow groundwater sampling sites. While we found no significant differences among the sites' temperatures over the monitoring period, the

TABLE 1 | Averages and standard deviations for the physicochemical parameters for the stream and three shallow groundwater monitoring sites.

Parameter	Stream (n = 130)	Well A (n = 75)	Well B (n = 107)	Well C (n = 108)
Water table elevation (m)	NA	142.46 ± 0.19	142.07 ± 0.11	140.98 ± 0.14
Water table depth (m)	NA	2.52 ± 0.19	2.75 ± 0.11	2.48 ± 0.14
Temperature (°C)	14.1 ± 7.7	15.3 ± 3.9	16.4 ± 3.6	15.2 ± 2.9
Specific conductivity (μS/cm)	1040 ± 749	1206 ± 236	1031 ± 117	978 ± 111
pH	7.63 ± 0.27	6.56 ± 0.17	6.69 ± 0.09	6.52 ± 0.18
Dissolved O_2 (%)	92.0 ± 33.9	31.9 ± 9.5	35.8 ± 7.9	26.3 ± 8.0
Optical brighteners (RFU)	18.1 ± 5.7	7.4 ± 2.4	6.9 ± 1.4	7.9 ± 1.7
E. coli (CFU/100 mL)[a]	113 ± 4[a]	4 ± 1[a]	5 ± 2[a]	5 ± 2[a]
F^- (μg/L)	237 ± 65	82 ± 26	105 ± 42	98 ± 33
B (μg/L)	80 ± 26	79 ± 26	99 ± 18	66 ± 19
Cl^- (mg/L)	221.4 ± 233.8	76.2 ± 47.4	26.1 ± 5.9	32.8 ± 9.8
SO_4^{2-} (mg/L)	74.2 ± 25.3	125.9 ± 24.6	29.7 ± 7.4	68.2 ± 29.1
NO_3^--N (mg/L)	0.25 ± 0.24	0.04 ± 0.06	0.51 ± 0.41	0.03 ± 0.06
Na (mg/L)	98.9 ± 85.1	34.5 ± 15.6	18.5 ± 3.2	29.9 ± 7.2
Ca (mg/L)	70.3 ± 20.7	193.7 ± 38.4	144.1 ± 16.3	143.5 ± 18.8
Mg (mg/L)	17.1 ± 5.3	16.1 ± 3.0	44.9 ± 5.6	21.8 ± 1.3
Sr (μg/L)	366 ± 104	503 ± 75	446 ± 53	541 ± 40
K (mg/L)	3.9 ± 0.9	0.8 ± 0.7	0.8 ± 0.3	1.6 ± 0.5
Si (mg/L)	3.3 ± 1.2	12.1 ± 1.6	10.5 ± 1.6	9.4 ± 0.7
Mg:Ca (mM/mM)	0.40 ± 0.05	0.14 ± 0.03	0.51 ± 0.02	0.26 ± 0.05

[a]Geometric means and geometric standard deviations are reported for *E. coli*.

shallow groundwater temperatures fluctuated less than those of the stream (Table 1; Figure 2c). Specific conductivity was elevated in the stream during the winter months, but the shallow groundwater wells did not demonstrate the same seasonal fluctuations (Figure 2d). Nevertheless, Well A had elevated specific conductivity values following prolonged dry periods when the well would go dry (Figure 2b,d). The pH values of the shallow groundwater sites were also significantly lower than the stream's pH measurements (Table 1; Figure 2e). We observed higher pH in the winter and lower pH in the summer for the stream, but the shallow groundwater did not exhibit this behaviour. The average dissolved O_2 percent saturation values for the shallow groundwater sites were less than half those for the stream, and Well C had dissolved O_2 saturation values that were typically lower than the other two wells (Table 1; Figure 2f).

Optical brightener values were significantly higher in the stream relative to the shallow groundwater wells (Table 1; Figure 2g). The *E. coli* levels were also elevated in the surface water compared to the shallow groundwater, with the *E. coli* geometric mean of the stream being > 20× higher than the shallow groundwater sampling sites (Table 1; Figure 2h). We observed no significant differences in either optical brightener or *E. coli* levels among any of the shallow groundwater wells. The F^- levels were significantly higher in the stream compared to all the shallow groundwater wells (Table 1; Figure 2i). Stream F^- concentrations were most distinct from the shallow groundwater during the summer and fall. However, in the winter, the F^- concentrations for the stream and shallow groundwater wells began to converge (Figure 2i). The highest F^- levels we observed during the study (up to 444 mg/L from 14 to 16 November 2023; Figure 2i) occurred in the stream and coincided with a reported drinking water main break upstream. The B concentrations were indistinguishable among all water types throughout the monitoring period (Table 1; Figure 2j).

The Cl^- levels were highest and most variable in the stream (Table 1), with concentration peaks occurring in the winter (Figure 2k). The Cl^- concentrations in Well A were higher than in the other two wells (Table 1), especially following the periods when the well would go dry (Figure 2b,k). Throughout the study period, Well A consistently had the highest SO_4^{2-} values of all our monitoring sites, while Well B featured the lowest SO_4^{2-} concentrations (Table 1; Figure 2l). Well C had SO_4^{2-} concentrations that were similar to Well A at the beginning of the monitoring period, but they gradually decreased over the course of the study period towards the values observed in Well B (Figure 2l). As with other analytes, SO_4^{2-} concentrations increased in Well A following dry periods (Figure 2b,l). The NO_3^-–N values were not significantly different between Well A and Well C, but both Well B and the stream had significantly

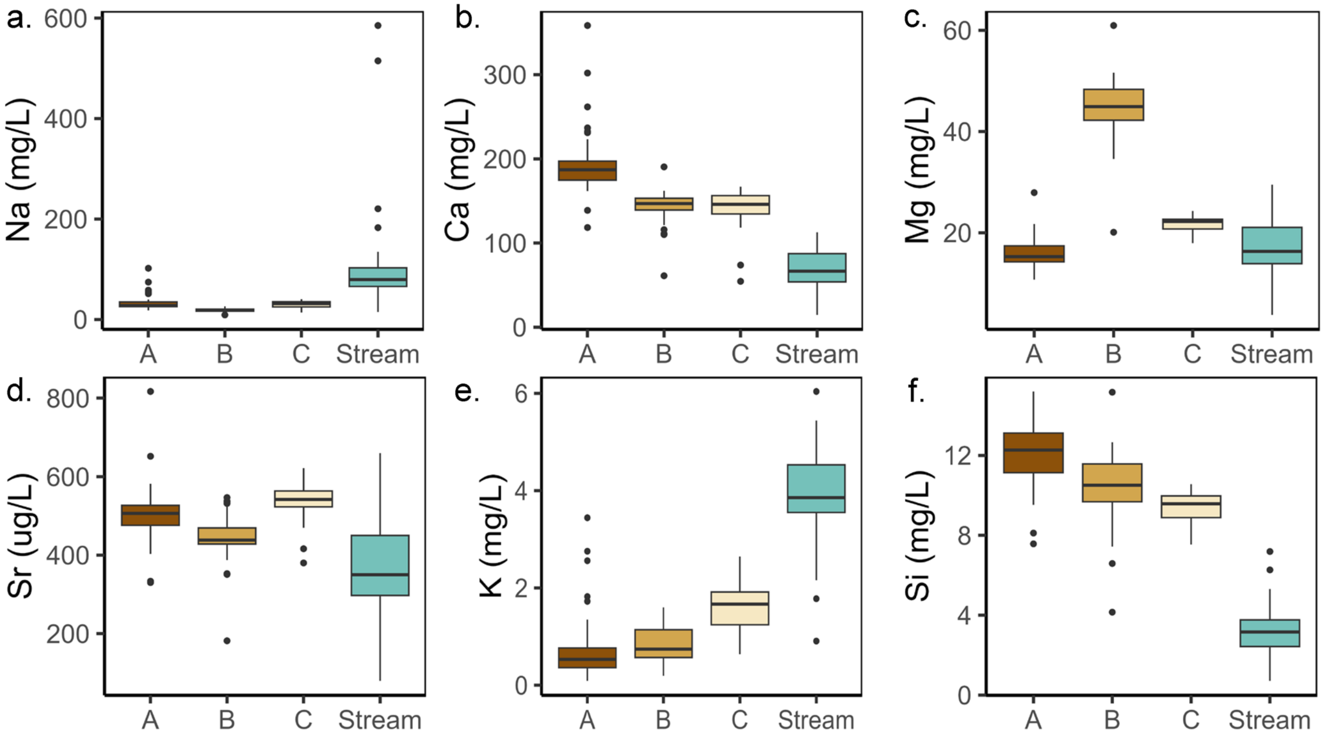

FIGURE 3 | Box and whisker plots for (a) Na, (b) Ca, (c) Mg, (d) Sr, (e) K, and (f) Si for the stream and shallow groundwater monitoring sites across the entire sampling period.

higher NO_3^-–N concentrations compared to the other two wells (Table 1). While no seasonal patterns in NO_3^-–N were observed in Well A and Well C, both Well B and the stream exhibited high NO_3^-–N concentrations in the spring and early summer followed by declining NO_3^-–N values later in the summer and into the fall (Figure 2m).

Our total element data (Figure 2n–s) showed that the stream had significantly lower concentrations of Ca, Sr, and Si compared to the three shallow groundwater monitoring sites, while concentrations of Na and K were significantly higher in the stream relative to the shallow groundwater (Table 1; Figure 3a,b,d-f). Average Mg concentrations in the stream were similar to Well A and Well C (Table 1; Figure 3c). When comparing significant differences among the wells, we found that Well A had the highest Ca and Si concentrations, Well B had the lowest Na concentrations but the highest Mg concentrations, and Well C had the highest K concentrations (Figure 3a-c,e,f). All three wells had similar Sr values (Figure 3d). In our evaluation of temporal patterns for our sites, we found the stream had elevated Na in the winter months compared to the rest of the year (Figure 2n). Well A had elevated concentrations of Na, Ca, Mg, Sr, and Si (Figure 2n–q,s) following a period of prolonged drought (Figure 2b), which coincided with elevated specific conductivity readings for that well (Figure 2d).

3.2 | Endmember Physicochemical Characteristics

Our drinking water and wastewater endmember samples had municipal water tracer and other analyte values that were typically close to the ranges presented in prior studies for the region (Lockmiller et al. 2019; Finegan and Hasenmueller 2023a; see Table 2). Untreated wastewater always had elevated optical brightener levels relative to Deer Creek and the shallow groundwater in its floodplain (Table 2). Drinking water and untreated wastewater F^- concentrations were commonly elevated relative to the stream and shallow groundwater samples from the Deer Creek watershed (Table 2). While B concentrations were generally lower in the stream and shallow groundwater samples compared to drinking water and untreated wastewater, we observed more overlap in B values between the watershed samples and both municipal water types than we did with the other tracers (Table 2). Our Deer Creek stream samples also had elevated municipal water tracer ranges relative to stream and spring samples collected at rural sites in the region (Table 2).

Our evaluation of the floodplain sediment samples collected when the wells were originally installed showed that the substrate had similar gravimetric water content across comparable depths for all the well sites (Figure 4a). While organic matter content values were similar among the sites for the deeper floodplain sediment samples, Well C had ~2× higher organic matter levels near the ground surface compared to the other two wells (Figure 4b). The cation exchange capacities of the substrate for all the well sites were within 5 $cmol_c$/kg for similar depths, but their values generally decreased with depth for Well A and Well C and increased with depth for Well B (Figure 4c). The floodplain sediment's exchangeable Mg:Ca molar ratio at Well A increased then decreased with depth, but it consistently increased with depth for Well B (Figure 4d). Well C's exchangeable Mg:Ca molar ratios did not notably change as a function of substrate depth (Figure 4d). The exchangeable Na percentage for the floodplain sediment was >4× higher at Well A compared to Well B and Well C

TABLE 2 | Analyte value ranges for samples from drinking water, untreated wastewater, streams, and shallow groundwater obtained in this and other studies.

Water type	Data source and sample number	Optical brighteners (RFU)	F^- (µg/L)	B (µg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	NO_3^--N (mg/L)	Na (mg/L)	Ca (mg/L)	Mg (mg/L)	Sr (µg/L)	K (mg/L)	Si (mg/L)
Drinking water	This study $n=4$	6.4–9.4	517–661	109–137	22.6–33.5	155.3–199.8	0.10–0.92	57.0–74.0	18.6–20.8	16.2–22.9	177–226	6.2–7.0	3.5–6.0
	Regional studies[a] $n=17$	5.3–20.2	517–748	41–102	13.3–28.5	56.3–187.7	1.8–11.2	17.2–59.5	16.9–28.1	5.4–25.0	119–212	4.6–5.9	3.0–5.8
Untreated wastewater	This study $n=1$	64.1	519	245	84.0	226.4	0.08	98.3	40.5	21.6	277	11.3	4.4
	Regional studies[a] $n=24$	50.1–248.0	369–911	94–275	74.1–92.2	92.2–259.8	0.11–8.61	74.6–194.0	29.5–86.6	14.1–27.0	176–308	8.4–17.5	0.6–5.0
Rural waters[b]	Regional studies[a] $n=26$	3.1–13.0	56–129	18.3–43.7	21.6–112.4	11.6–53.2	0.21–3.05	13.7–56.1	64.0–106.1	8.1–24.8	100–183	1.4–2.7	4.0–7.7
Deer Creek watershed: stream	This study $n=130$	9.2–39.4	125–439	19–160	37.0–1574.3	24.3–144.1	0.01–0.99	14.9–585.2	14.7–112.8	3.8–29.5	80–660	0.9–6.0	0.7–7.2
Deer Creek watershed: shallow groundwater	This study $n=290$	4.2–16.0	50–237	30–194	12.8–265.6	22.3–246.6	0.01–1.75	9.2–102.0	54.54–358.4	10.7–60.9	182–817	0.1–3.4	4.2–15.2

[a]Samples were characterised by Lockmiller et al. (2019) and Finegan and Hasenmueller (2023a).
[b]Samples were collected from rural springs and streams.

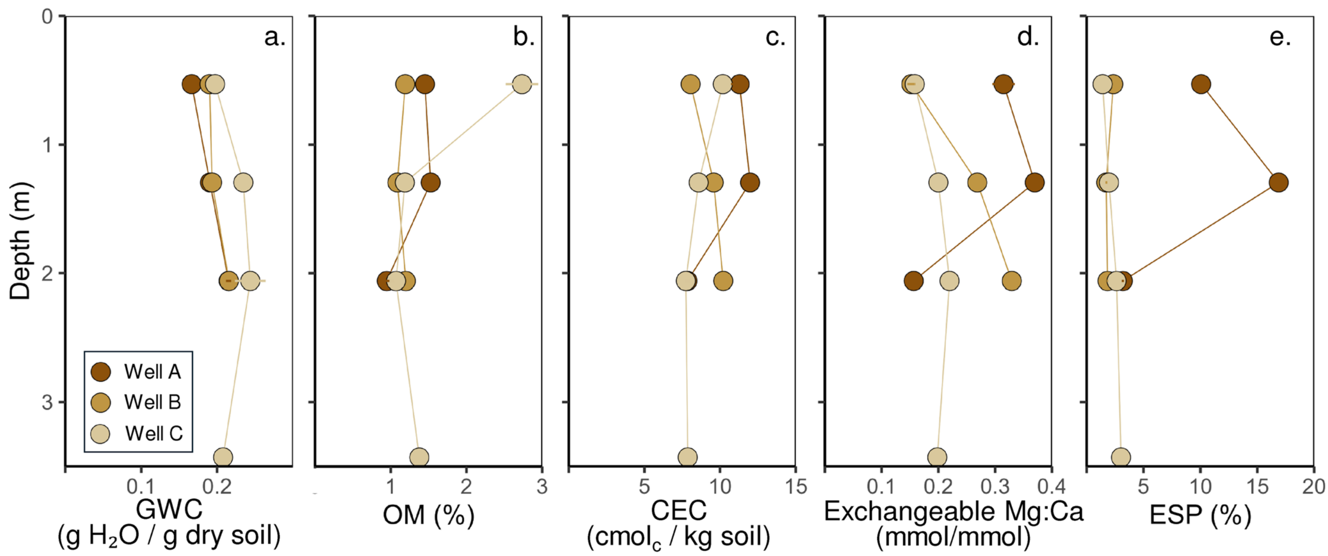

FIGURE 4 | Physicochemical characterisations of the floodplain sediment substrate at each of the shallow groundwater well sites. Replicate averages (points) and standard deviations (bars; note that the standard deviations were less than the point size in most cases) are provided for (a) gravimetric water content (GWC), (b) organic matter (OM) content, (c) cation exchange capacity (CEC), (d) exchangeable Mg:Ca ratios, and (e) exchangeable Na percentages (ESP) at each depth interval.

for the two shallowest sampling depths (Figure 4e). However, the deepest sediment sample for Well A had an exchangeable Na percentage value that was analogous to the other well sites (Figure 4e).

4 | Discussion

4.1 | Drinking Water and Untreated Wastewater Signatures in an Urban Watershed

Across the 2.6 years we monitored stream and shallow groundwater physicochemical attributes in the Deer Creek catchment, standard tracers of drinking water and untreated wastewater were often elevated in the stream relative to the shallow groundwater in its floodplain (Tables 1 and 2; Figure 2). Indeed, optical brighteners and *E. coli*, which are used as untreated wastewater indicators, were higher in Deer Creek relative to the wells and had a significant and positive ($r = 0.50$) correlation for the stream samples. These findings suggest that Deer Creek continues to receive untreated wastewater contributions despite the prior sewer renovation (Hartel et al. 2008; Tavares et al. 2008; Finegan and Hasenmueller 2023a). We expect that the optical brighteners and *E. coli* were mainly sourced to the stream from untreated blackwater since they were found at high levels together rather than independently (e.g., individually elevated optical brightener levels can suggest contributions from greywater, while high *E. coli* concentrations alone can indicate inputs from wildlife). We nevertheless acknowledge that these other potential sources may impact Deer Creek to a minor degree given the moderate strength of the stream's optical brightener and *E. coli* correlation. Interestingly, the shallow groundwater wells had low optical brightener and *E. coli* levels (Table 1; Figure 2g,h), and the parameters were not correlated for the well samples. Low values for these tracers in the shallow groundwater suggest limited sourcing of untreated wastewater to the observation wells.

Concentrations of F^- that are elevated above background levels in natural waterbodies can indicate either drinking water or untreated wastewater inputs. Like our optical brightener and *E. coli* data, Deer Creek's F^- concentrations were almost always higher than those in the shallow groundwater samples (Tables 1 and 2; Figure 2i). The highest F^- concentrations for the stream usually occurred in the summer, while the shallow groundwater generally exhibited elevated F^- levels in the winter. These differences in F^- behaviour between the surface water and shallow groundwater may respectively be due to lawn irrigation with fluoridated drinking water impacting the stream in the summer and water main breaks in the subsurface contributing drinking water to the shallow groundwater in the winter. Seasonal variations in drinking water contributions to the Deer Creek basin are consistent with previous observations for an urban catchment in Austin, Texas, United States, where drinking water inputs accounted for $< 1\%$ to nearly 100% of the total recharge to the studied basin during the wet and dry seasons, respectively (Passarello et al. 2012). We even captured the signal of a large drinking water main break around 14–16 November 2023 that impacted Deer Creek. During the event, stream F^- concentrations increased from 246 mg/L to 444 mg/L and corresponded with an increase in discharge over the 2 days of the drinking water main break event (Figure 2a,i). While we clearly documented the considerable and immediate input of drinking water to the stream, we could not ascertain if the subsequent increases we observed in F^- concentrations for the shallow groundwater in the winter of 2023–2024 were the result of this specific main rupture event or multiple leaks. Indeed, the shallow groundwater sites exhibited elevated F^- concentrations across multiple winters during the study period. Untreated wastewater may also source F^- to the stream given Deer Creek's elevated optical brightener and *E. coli* signatures, but, as noted earlier, low values for these parameters in the well samples suggest that untreated wastewater is an unlikely source of F^- to the shallow groundwater.

While the Deer Creek watershed historically contained constructed sewer overflows upstream of our sampling location, they were removed by 31 July 2022 (Finegan and Hasenmueller 2025), which was 1.5 months before our study started on 15 September 2022. With the stream no longer receiving rapid and direct inputs of sewage, any untreated wastewater entering Deer Creek would likely be sourced from faulty infrastructure in the watershed. We thus hypothesised that the shallow groundwater was delivering untreated wastewater as well as drinking water to the stream, which had been previously suggested for urban streams in the St. Louis region (Lockmiller et al. 2019; Buckley 2020). Nevertheless, we found that Deer Creek had higher drinking water and untreated wastewater tracer concentrations compared to the shallow groundwater, which was not our anticipated result. Our findings instead indicate that the shallow groundwater we sampled was not a meaningful transporter of legacy drinking water and untreated wastewater to this urban stream system.

One possible reason for the low municipal water tracer concentrations in the shallow groundwater samples might be our observation well depths. We originally assumed that sampling the shallow groundwater at the depths at which the wells occur would be sufficient to capture drinking water and untreated wastewater signals because the study site is situated such that leaking water infrastructure at residences uphill would travel downhill with the groundwater towards the stream. Our F^- data suggest this process probably occurred to some degree for drinking water since the F^- signature in the well sites was elevated during the winter months (Figure 2i). However, F^- concentrations in the wells rarely exceeded those in the stream.

The phenomenon of untreated wastewater leaking at shallow depths in the subsurface was in fact previously observed by the land managers at the Litzsinger Road Ecology Center when a sewer lateral pipe ruptured, causing raw sewage to upwell into a vernal pool on the property. Despite past examples of subsurface sewage infrastructure failures leading to untreated wastewater contributions to surface waterbodies at the site, we suspect the potentially heterogeneous nature of the sewage infrastructure leaks meant we did not capture their signatures where we were monitoring. Deeper samples of the groundwater may exhibit stronger untreated wastewater signals when the water homogenises as it travels farther into the subsurface. Additionally, while our wells reached depths up to 3.81 m below the surface, sewer lateral pipes can range from 1 m to 5 m in depth (Lee et al. 2015) and the recently installed sanitary tunnel in the watershed that collects untreated wastewater from the lateral pipes and trunk sewer networks is approximately 10 m below the surface (MSD 2020). If wastewater exfiltrates from faulty sewer pipes at depths > 3.81 m, deeper groundwater may have elevated untreated wastewater tracer concentrations compared to the shallower groundwater that we sampled. Indeed, leaking wastewater infrastructure has been shown to contaminate groundwater at depths up to 23 m (Wolf et al. 2006; Lee et al. 2015). Deer Creek is mapped as a gaining stream at our study site (MoDNR 2025), and, should deeper groundwater be its supply, then groundwater could still be a vector for delivering municipal waters to the stream.

With these variables in mind, future studies should examine groundwater geochemistry across larger depth ranges in conjunction with shallow aquifer properties (though information on the characteristics of shallow aquifers is often limited in many regions). We also note that future work should consider the potential for groundwater to infiltrate into the wastewater infrastructure. Given that our selected site features groundwater depths that are shallower than components of the wastewater infrastructure network, movement of groundwater through the sewer system is a strong possibility (Zeydalinejad et al. 2024) and may vary seasonally with groundwater level (Figure 2b).

Another unexpected outcome of our study was the similarity of the B signatures across our monitoring sites (Tables 1 and 2; Figure 2j). The B signal in water resources is often used as an indicator of wastewater pollution since B can be added to wastewater from household detergent use (Vengosh et al. 1994; Hasenmueller and Criss 2013; Lockmiller et al. 2019). If B were only sourced to our sites from untreated wastewater contributions, our B results would suggest that the stream and shallow groundwater are similarly impacted by untreated wastewater inputs. However, this hypothesis is inconsistent with our findings for the other municipal water tracers. A mixing diagram for the B and F^- concentrations in our samples from the Deer Creek watershed sites as well as potential endmembers (i.e., unimpacted water types from rural areas in the region, drinking water, and wastewater) showed that our stream samples had a combination of the characteristics of regional rural water types and municipal waters (Figure 5). All the wells occasionally had samples that fell between the signatures of the rural waterbodies and drinking water, indicating some drinking water contributions to the shallow groundwater. However, many shallow groundwater samples fell outside of the mixing diagram where they had high B but low F^- concentrations (Figure 5). Thus, an uncharacterised source of B to the shallow groundwater confounds the municipal water signatures, and, consequently, using B concentrations alone appears to be an infeasible method to detect untreated wastewater at our shallow groundwater sites. We suspect weathering processes in the floodplain substrate may be the source of the elevated B levels in the shallow groundwater (Mavromatis et al. 2015), but the Deer Creek watershed samples, municipal water types, and any additional B endmembers would need to be better constrained through quantifying their $\delta^{11}B$ values as has been done in other systems (Vengosh et al. 1994; Barth 1998; Petelet-Giraud et al. 2009; Guinoiseau et al. 2018).

4.2 | Drivers of Shallow Groundwater Heterogeneity

While all the shallow groundwater wells had low levels of municipal water tracers (i.e., optical brighteners, *E. coli*, and F^-) compared to the stream, we found that the shallow groundwater was surprisingly heterogeneous for other analyte signatures (Tables 1 and 2; Figures 2 and 3) given the proximity of the wells (i.e., all within 0.5 km of each other; Figure 1c). We anticipated that the anions and total element concentrations would exhibit a gradient between the shallowest groundwater well (i.e., Well A) and the stream, but no consistent geochemical trend emerged among the monitoring sites (Figures 2 and 3). Thus, to better constrain the sourcing and evolution of shallow groundwater in

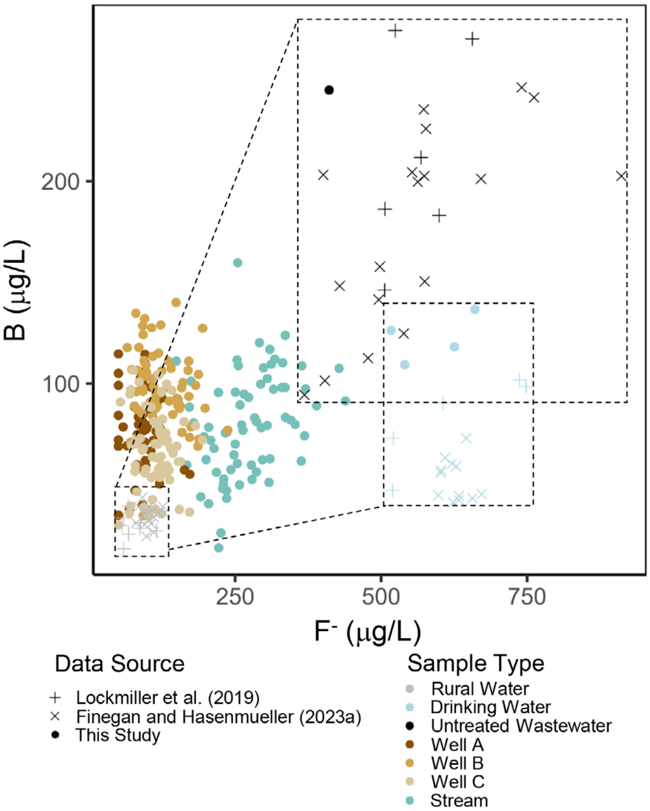

FIGURE 5 | A mixing diagram for B and F^- data for our Deer Creek watershed stream and shallow groundwater samples as well as our drinking water and untreated wastewater endmember samples. We also include previously published data for rural springs and streams, drinking water, and untreated wastewater in the region (Lockmiller et al. 2019; Finegan and Hasenmueller 2023a). The endmember B and F^- concentration ranges are indicated by the boxes with dashed outlines.

the urban Deer Creek catchment, we assessed potential drivers of geochemical variability at the floodplain scale for our watershed sites.

Natural drivers of shallow groundwater geochemistry can include contributions from precipitation, losses via evapotranspiration, spatiotemporal variations in flowpaths, fluctuations in water table depth, connections with surface waterbodies, changes in topography, and interactions with the substrate (e.g., soil, sediment, or rock; Gao et al. 2020). Of these processes, spatial variations in the water budget from precipitation and evapotranspiration should be minimal at our study location given its floodplain scale and are thus unlikely drivers of the heterogeneity in the shallow groundwater's geochemistry. While watershed lithology can influence the assemblages of dissolved species in groundwater (Négrel et al. 1993; Blum et al. 1998; Roy et al. 1999; Jin et al. 2008; Wu et al. 2014), our shallow groundwater wells sit above or at the contact with the bedrock, where the same unit is mapped for the entire study area. Therefore, variations in geology are probably not an important factor controlling geochemical heterogeneity in the floodplain's shallow groundwater.

Other hydrological factors, including infiltration processes, preferential flowpaths, and flow rates, can impact the geochemistry of the shallow groundwater via water retention times, which may affect water-substrate interactions at our well sites. In the floodplain, the sediment properties and water flow along the contact between the sediment and rock, particularly for Well C, which extends to the surface of the bedrock, are likely major controls on the shallow groundwater's flow and geochemical evolution. Moreover, fluxes between the surface water and shallow groundwater can change seasonally, leading to the stream experiencing either gaining or losing conditions (Prajapati et al. 2021). We periodically observed evidence for such surface water-groundwater exchanges, including through potential first flushing events, where certain anions and total element concentrations increased concurrently for the well sites and Deer Creek (Figure 2). Prominent examples of possible first flush events included when SO_4^{2-} concentrations simultaneously increased for Well A and Deer Creek during small discharge events for the stream that followed dry periods (Figure 2a,b,l), though other analytes and wells could exhibit similar behaviour (Figure 2).

Some of the shallow groundwater heterogeneities in the floodplain could be attributable to the depth of the wells and, thus, the residence time of the water they were collecting. Well A had the highest variability in temperature and a variety of geochemical parameters (e.g., specific conductivity, Cl^-, Na, Ca, Sr, and K), seasonally went dry after periods of drought, and was the most saline after those dry periods (Table 1; Figures 2 and 3). Well A therefore perhaps represents the youngest water in our shallow groundwater system and, consequently, is more impacted by temporal fluctuations in precipitation and water table level than the other wells (Crowther and Pitty 1982; Constantz 2008). Since Well B and Well C typically featured less variability for many of their geochemical signatures compared to Well A, they likely exemplify deeper and better mixed water sources within the system.

Another possible cause of the shallow groundwater's geochemical variability is the geomorphology of the floodplain (Nolan et al. 2003; Akbariyeh et al. 2018). Well A is situated atop a steep cutbank, while the other two wells are located at lower elevations on the opposite bank (Figure 1c). Thus, the Well B and Well C sites are more frequently inundated during Deer Creek's flood events due to the lower ground surface elevation. The Well A site being flooded less frequently than the other sites could lead to drier sediment conditions that cause the precipitation of evaporite minerals during periods of drought, leading to higher salinity in the sediment (Figure 4e). The dissolution of those minerals following rainfall events could indeed explain the periodic first-flushing events that we observed at the site.

We also explored potential water flowpaths and surface water–groundwater interactions at our sites using the Mg:Ca molar ratios in our water samples (Fairchild et al. 2006; Williams et al. 2007; Musgrove et al. 2010). When we plotted the Mg:Ca molar ratios for our Deer Creek basin samples (Figure 6), we observed that the trendlines varied considerably among our stream and shallow groundwater monitoring sites despite the local scale of the study. While we did not assess the mineralogy of the substrate in which the wells are located, we suspect the divergent Mg:Ca molar ratios among the wells may represent differing mineral weathering and precipitation processes

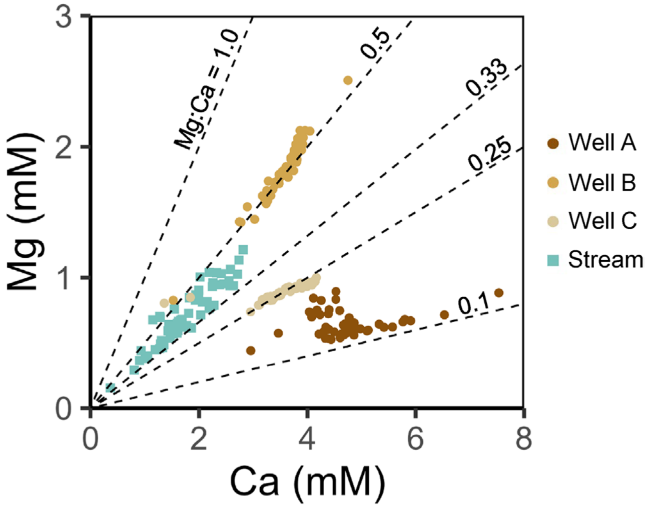

FIGURE 6 | Mg:Ca molar ratios for the stream and shallow groundwater samples.

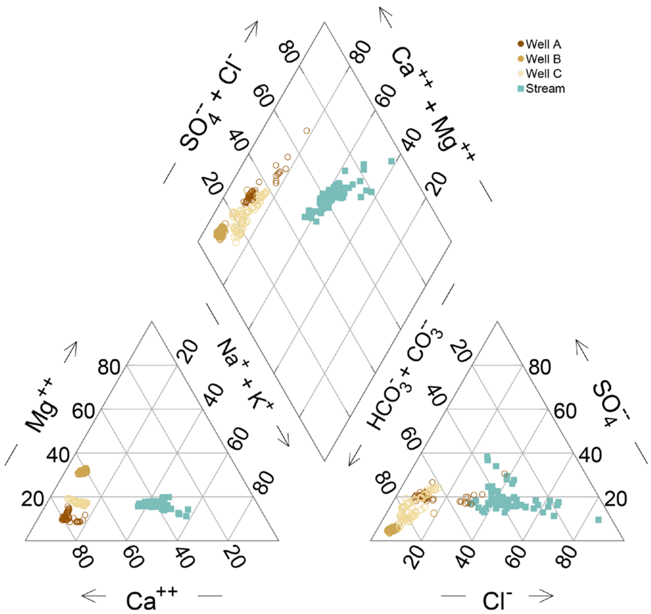

FIGURE 7 | A Piper diagram for the stream and shallow groundwater samples.

across the sites. For example, the Mg:Ca molar ratios are lowest in Well A, which also featured large Ca and SO_4^{2-} pulses during first flush events following dry periods (Figure 2b,l,o). These Ca and SO_4^{2-} peaks in Well A's water may represent an influx of gypsum weathering products from the floodplain substrate, and geologic maps of the area indeed indicate the presence of evaporite minerals in the limestone bedrock (Harrison 1997). Pulses of gypsum weathering products would elevate the Ca concentrations in Well A but would not similarly increase the Mg concentrations. This process would subsequently lead to the relatively low Mg:Ca molar ratios for Well A compared to the other sampling sites. Future work to characterise the substrate's mineralogy would help resolve the causes of the diverse Mg:Ca molar ratios for the stream and shallow groundwater sites.

Our Piper diagram further demonstrated the geochemical variability among our stream and shallow groundwater sites (Figure 7). Our data for Well B clustered tightly within the Ca-Mg-HCO_3^--type water field (Figure 7) and had Mg:Ca molar ratios (Figure 6) most representative of calcite weathering (Williams et al. 2007). These characteristics of Well B likely result from the underlying limestone at the study location (Harrison 1997; MoDNR 2025). While Well A also mostly plotted in the Ca-Mg-HCO_3^--type water field, some samples trended to Ca-Mg-SO_4^{2-}-type waters (Figure 7). This behaviour may be related to the first flushing events we observed at Well A (e.g., SO_4^{2-} pulses; Figure 2l). Like the other two wells, Well C plotted in the Ca-Mg-HCO_3^--type water field, but its data extended between the more tightly clustered data of the other two shallow groundwater sites as well as the stream (Figure 7). Similarly, Well C had Mg:Ca molar ratios that fell between the values obtained for the stream and the other two shallow groundwater wells (Figure 6).

Compared to the shallow groundwater samples, the stream water was shifted into the Ca-Mg-SO_4^{2-}-type and Na-Cl^--type water compositions (Figure 7) because Cl^- and Na concentrations were elevated in Deer Creek during the winter (Figure 2k,n). High levels of Cl^- and Na in the stream are unsurprising since deicing salts are applied in our study catchment (Finegan and Hasenmueller 2023b) to increase roadway safety during snowy and icy conditions in the winter (Hintz et al. 2022). In contrast, the shallow groundwater samples exhibited low concentrations and variability in their Cl^- and Na signatures, except Well A following first flushing events (which typically occurred in the late summer and early fall; Figure 2k,n). Prior studies have shown that road salt related ions can accumulate in groundwater over time, with annual Cl^- increases of 1–6 mg/L (Godwin et al. 2003; Kelly et al. 2008; Perera et al. 2013; Robinson and Hasenmueller 2017). However, we suspect that the limited road salt signature in the observation wells is due to the distance between our monitored sites and nearby roadways, which likely restricted the exposure of the shallow groundwater at these locations to deicer contamination events (Baraza and Hasenmueller 2021).

While all the shallow groundwater sites in the floodplain of Deer Creek were relatively unimpacted by road salt pollution (Table 1), other land use associated pollutants behaved differently among the wells. For example, Well B featured elevated NO_3^-–N concentrations in the spring (up to nearly 2.0 mg/L) compared to the other wells that always had NO_3^-–N levels of < 0.6 mg/L (Figure 2m). The stream also featured springtime increases in NO_3^-–N (Figure 2m), but the average NO_3^-–N value for the stream was half that of Well B (Table 1). The high NO_3^-–N concentrations in Well B may be sourced from a small horse farm ~100 m upgradient of the well (Figure 1c) that may likewise impact the stream. Our discovery of high heterogeneity for pollutants like NO_3^-–N across the well sites illustrates the importance of understanding small scale land use variations in urban floodplain environments. Although shallow groundwater did not appear to be a major pathway for transmitting municipal water types to the nearby stream, the high variability of analytes such as NO_3^-–N across the floodplain monitoring wells suggests that the shallow groundwater's role in transporting drinking water and untreated wastewater to streams may vary across urban watersheds.

5 | Conclusions

Our integrated, floodplain scale study of the physicochemical characteristics of an urban stream and its adjacent shallow groundwater showed that the shallow groundwater was not a meaningful source of the elevated drinking water and untreated wastewater signatures observed in the stream. Although the shallow groundwater at our monitoring sites played a limited role in conveying municipal waters to the stream, we observed striking geochemical differences among the observation wells. At this local scale, factors such as precipitation, evapotranspiration, and geology did not appear to drive this observed variability. Instead, the geochemical heterogeneity among the wells likely reflects differences in groundwater depth, geomorphology, residence time, mineral precipitation and dissolution processes, and urban land use. While the shallow groundwater did not act as a major conduit for municipal water types to the surface water at our study location, the high variability in other analytes across the floodplain's shallow groundwater suggests that its role in transmitting drinking water and untreated wastewater to streams may vary across urban catchments. Future studies should monitor more locations and a wider range of groundwater depths within urban stream floodplains to better identify where municipal water transmission may occur.

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Data Availability Statement

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

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