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Stream Nitrogen Inputs Reflect Groundwater Across a Snowmelt-Dominated Montane to Urban Watershed

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Supporting Information

ABSTRACT: Snowmelt dominates the hydrograph of many temperate montane streams, yet little work has characterized how streamwater sources and nitrogen (N) dynamics vary across wildland to urban land use gradients in these watersheds. Across a third-order catchment in Salt Lake City, Utah, we asked where and when groundwater vs shallow surface water inputs controlled stream discharge and N dynamics. Stream water isotopes (δ^2H and δ^{18}O) reflected a consistent snowmelt water source during baseflow. Near-chemostatic relationships between conservative ions and discharge implied that groundwater dominated discharge year-round across the montane and urban sites, challenging the conceptual emphasis on direct stormwater inputs to urban streams. Stream and groundwater NO_3^- concentrations remained consistently low during snowmelt and baseflow in most montane and urban stream reaches, indicating effective subsurface N retention or denitrification and minimal impact of fertilizer or deposition N sources. Rather, NO_3^- concentrations increased 50-fold following urban groundwater inputs, showing that subsurface flow paths potentially impact nutrient loading more than surficial land use. Isotopic composition of H_2O and NO_3^- suggested that snowmelt-derived urban groundwater intercepted NO_3^- from leaking sewers. Sewer maintenance could potentially mitigate hotspots of stream N inputs at mountain/valley transitions, which have been largely overlooked in semiarid urban ecosystems.

INTRODUCTION

Urban and adjacent wildland areas experience elevated anthropogenic nitrogen (N) inputs that potentially impact water quality and the biotic composition and function of aquatic ecosystems.[1−5] Yet, despite the characterization of an urban stream syndrome,[6] impacts of urbanization on stream nutrient loading vary greatly as a consequence of interactions among land use patterns and the local biophysical context.[7−13] Few studies have assessed urbanization impacts on N cycling in semiarid montane watersheds and adjacent basins where streamflow is dominated by snowmelt. These landscapes include rapidly growing regions in western North America, central Asia, and South America.[14] They often exhibit strongly seasonal streamflow and nutrient inputs influenced by snow accumulation and melt,[15−17] and impacts of urbanization on these dynamics remain unclear. In other regions, leaking sanitary infrastructure[4,18] and ground/surface water interactions[5,11] have been shown to strongly impact urban stream N loading, but these factors have received little attention in semiarid and snowmelt-dominated urban watersheds.

Montane watersheds with a persistent winter snowpack often display a pulse in stream NO_3^- concentrations during spring snowmelt driven by NO_3^- transport along shallow subsurface flow paths.[15,19−26] Soil nitrification typically dominates stream NO_3^- inputs during snowmelt, although direct inputs of atmospheric NO_3^- from the melting snowpack can also occur.[24,25,27] Thus, montane watersheds in close proximity to urban areas, which experience greater N deposition than remote montane sites,[28,29] might display a particularly prominent snowmelt NO_3^- pulse to streams.

Urbanization adds additional complexity to snowmelt N dynamics. Urban landscapes receive substantial fertilizer N inputs[30] in addition to atmospheric deposition. In cities, first-order streams are often replaced with impervious infrastructure, decreasing the residence time of water in the subsurface.[11] Accordingly, terrestrial and aquatic N retention often decrease,

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while stream N exports increase in urban environments.[11,31−33] This response may be accentuated during snowmelt, when runoff from impervious surfaces can provide a major nutrient source to urban streams.[34]

Despite observations of NO_3^- flushing during snowmelt, many snow-covered environments also exhibit high capacity for biogeochemical N retention. The balance between microbial N mineralization, denitrification, and plant and microbial uptake during winter, and the spatial routing of hydrologic flow paths ultimately control soil N losses and stream inputs during snowmelt.[15,16,21,35,36] Nitrate can be attenuated by plant and microbial activity during transport, potentially minimizing a stream NO_3^- pulse.[27,37] The capacity of terrestrial ecosystems to retain NO_3^- during snowmelt is thought to vary with snow depth, which influences soil temperature, liquid water content, and subnivean biological activity.[16,17] Riparian groundwater can also represent an important zone of N removal during snowmelt[38] due to the confluence of dissolved organic carbon and NO_3^-[39] in a zone of buffered temperature variability.

Whereas groundwater flowpaths provide potential opportunities for biogeochemical N retention, they also represent a potential vulnerability in urban ecosystems, where groundwater can intercept a leaking sanitary infrastructure. Sewers provide a major source of stream N in humid temperate urban ecosystems[4,18,40] but have received little attention in semiarid snowmelt-dominated ecosystems. The routing of snowmelt to streams through groundwater may represent an especially important control on stream N dynamics in topographically complex landscapes at the intersection between mountains and valleys. Montane snowmelt sustains streamflow not only through high-elevation inputs but also via groundwater flowpaths that often emerge at the mountain/valley interface.[41−43] However, the relative importance of shallow surface vs groundwater flowpaths in structuring N inputs to urbanizing montane streams has received little attention.

We evaluated two alternative hypotheses: 1) Stream N concentrations peak during snowmelt as a consequence of NO_3^- flushing from surface soils and impervious surfaces, a pattern that is amplified along urban stream reaches; 2) Stream N concentrations are relatively static over time due to the dominance of groundwater inputs but vary spatially as a function of biogeochemical N retention and groundwater interception of subsurface N sources. To address relationships between water sources, flowpaths, and N inputs across an urbanization gradient, we compared spatial and temporal patterns of dissolved solutes and stable isotopes of H_2O and NO_3^- along a stream spanning forested montane headwaters in the Wasatch Mountains to urban Salt Lake City, Utah during snowmelt and baseflow, avoiding individual storm events. The relative importance of shallow surface vs groundwater contributions at these sites was assessed using solute concentration/discharge relationships and comparisons with potential source end members. For example, water flowing through shallow soils typically exhibits lower concentrations of rock-derived cations and higher concentrations of DOC than groundwater.[44,45] We partitioned water inputs from snow and rain and NO_3^- inputs from nitrification and atmospheric sources, using stable isotope mixing models. A shift from snow to rain over time or with downstream distance would implicate new water sources as opposed to well-equilibrated groundwater pools. Similarly, shifts in NO_3^- sources from microbial nitrification to atmospheric inputs would implicate surface vs subsurface flowpaths.

MATERIAL AND METHODS

Study Area. Red Butte Creek is a third-order stream that flows from a forested watershed in the Wasatch Mountains into Salt Lake City, UT. This gradient represents an abrupt transition from a protected area to an extensive urban landscape.[46] The reach examined here spans 13 km from montane headwaters at 2100 m to a residential neighborhood at 1300 m. The first 8 km include the protected area. Subsequently, the stream transits the University of Utah campus, commercial development, and residential neighborhoods. Additional characteristics are described in the Supporting Information.

We measured streamwater chemical composition at three montane and three urban sites. The upper montane site was located near the headwaters, and the midmontane site was 5.7 km downstream. The Central Utah Water Conservancy regulates discharge from a reservoir downstream of the midmontane site, and the lower montane site was below the reservoir. Subsequently, Red Butte Creek flows adjacent to gardens, lawns, and parking lots to the upper urban site. Further downstream, the mid urban site abuts commercial development and receives stormwater discharge. The lower urban site was located in a residential neighborhood with sewers dating from the early 1900s. Spring water inputs from the stream bank were visible at this site, beginning shortly upstream (after km 11).

Water Sampling. Stream water was sampled from the thalweg at each site using a syringe or drill pump, filtered through precombusted Whatman GF/F filters, transported on ice, and frozen. Water from precipitation, soils, and groundwater was similarly processed. Stream water was collected on a weekly to monthly basis from November 2013 to November 2014 (total n = 191 samples distributed among 40 sampling dates), with increased sampling frequency from February through May. Samples were not intended to characterize stream chemical composition during individual rainfall events, which produced flashy hydrographs at the mid urban site (Figure 1). Winter sample collection was sporadic at the upper montane site due to avalanches. Separate stream samples were collected approximately monthly from May 2013 to June 2014, and a representative subset (n = 75) was analyzed for δ^2H and $\delta^{18}O$ of H_2O.

Soil water was sampled from tension lysimeters in a natural riparian meadow and fertilized urban lawn located near the mid montane and upper urban sites, respectively, throughout 2014 (n = 202). Precipitation was sampled from multiple sites across the catchment on an event basis during 2014 for ion analysis (n = 177), and a representative subset from one site was analyzed for H_2O isotopes (n = 74). We sampled shallow riparian groundwater from wells adjacent to the stream at the upper montane and mid montane sites and from springs adjacent to the lower urban site on a weekly to monthly basis throughout 2014 (n = 148). Additional details are provided in the Supporting Information.

Chemical Analysis. Samples were analyzed for ion concentrations (Cl^-, SO_4^{2-}, PO_4^{3-}, NO_3^-, F^-, Na^+, Mg^{2+}, Ca^{2+}, K^+, NH_4^+) by ion chromatography. Dissolved organic carbon (DOC) and total dissolved N concentrations were measured on a representative subset of samples. Dissolved organic N (DON) was calculated as the difference between total dissolved N and inorganic N. Water isotopes ($\delta^{18}O$ and δ^2H) were measured by infrared spectroscopy. A representative subset of streamwater samples was analyzed for NO_3^- isotopes

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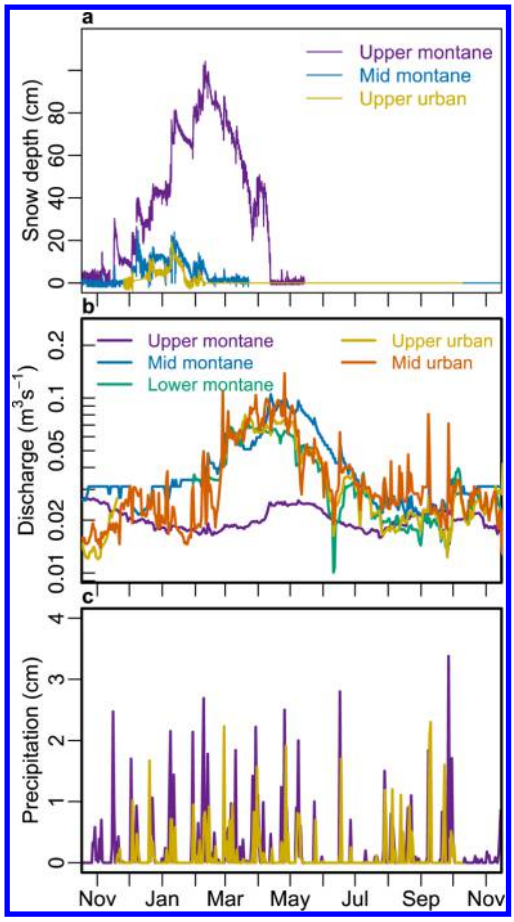

Figure 1. Snow depth (a), daily mean discharge on a logarithmic scale (b), and daily precipitation (c) at sites along Red Butte Creek. Line colors denote sites as indicated in the legends.

(δ^{15}N and δ^{18}O) using the denitrifier method.[47] Additional details are provided in the Supporting Information.

Discharge and Precipitation Measurements. Stream stage was measured at all sites (except the lower urban) with a vented pressure transducer logged at 15 min intervals. Discharge was estimated from stage measurements using a rating curve defined by periodic velocity-area flow measurements. Discharge measurements were averaged over daily time steps for the present analyses. At the mid montane site, discharge was measured by the U.S. Geological Survey (Station 10172200, Red Butte Creek at Fort Douglas). Continuous discharge could not be measured at the lower urban site. Several manual measurements suggested that baseflow discharge was similar to the mid urban site, so we used these data to calculate semiquantitative relationships between solutes and discharge. Precipitation was measured with rain gauges at the upper montane and upper urban sites.

Statistical Analysis. To assess changes in streamwater sources across the gradient, we estimated contributions of snow and rain to streamwater at each site using mixing models incorporating variation in mixtures and sources.[48] The isotopic composition of snow and rain was estimated by mass-weighted precipitation samples, where mixed rain/snow events were classified as snow. Orographic effects may have impacted water isotope composition in the catchment headwaters. We also present mixing model estimates corrected for the elevation difference (0.5 km) between the sampling site and catchment headwaters, conservatively assuming that all snow water equivalent was deposited in the headwaters. We used a lapse rate of −2.9‰ km^{-1} for δ^{18}O and corresponding changes in δ^{2}H based on the local meteoric water line.[49] Additional caveats associated with vapor exchange are discussed in the Supporting Information.

In streamwater downstream of the reservoir, evaporation was indicated by deviations from the meteoric water line. We approximated pre-evaporated water at each site using the intersection of the evaporation line and the local meteoric water line. We report raw mixing model results from measured isotope values given the minor impact of evaporation on the estimated snow contribution (±0.04). To provide another metric of evaporation, we present δ^{2}H excess as $\delta^{2}H - 8\delta^{18}O$ and line-conditioned δ^{2}H excess as $\delta^{2}H - a\delta^{18}O - b$, where a and b are the coefficients of the local meteoric water line.[50]

To evaluate changes in water sources and flowpaths within and among sites, we assessed relationships between ion concentrations and discharge using linear regressions of log-transformed variables.[51] Differences in response variables among water pools and sites were evaluated using ANOVA and posthoc pairwise comparisons with $\alpha = 0.01$.

RESULTS

Trends in Snow Cover, Precipitation, and Discharge. Cumulative precipitation for water year 2014 measured 84, 53, and 46 cm at the upper montane, mid montane, and upper urban sites, respectively. Accumulated snow peaked in mid January and completely melted by early February at the mid montane and upper urban sites and peaked in February and completely melted by mid April at the upper montane site (Figure 1a). Discharge peaked in mid April at all sites, with least temporal variation at the upper montane site (Figure 1b). The precipitation amount was distributed relatively evenly throughout the year at all sites (Figure 1c). Discharge responses to individual rainfall events were prominent only at the mid urban site (Figure 1b,c). Reservoir management contributed to small disparities in discharge between the mid montane and lower montane sites during snowmelt (Supporting Information).

Water Isotope Composition of Precipitation and Streamwater. Precipitation water isotopes in individual snow and rain samples varied between −157.8 and −29.0‰ for δ^{2}H and −20.8 and −3.3‰ for δ^{18}O (Figure 2, Supporting Information). These values fell tightly ($R^2 = 0.98$) along a local meteoric water line with a slope of 7.6. The isotope composition of snow and rain differed significantly ($p < 0.0001$). Mass-weighted δ^{2}H measured −127.7 ± 4.6‰ (mean ± standard error) in snow and −92.6 ± 4.6‰ in rain, and δ^{18}O measured −16.8 ± 0.6‰ and −12.5 ± 0.6‰, respectively. Stream water isotope composition was similar to mass-weighted mean snow at all sites and showed little temporal variability relative to precipitation isotope composition (Figure 2a). Stream water isotope composition was most stable over time at the upper montane site, which measured −124.9 ± 0.3‰ for δ^{2}H and −16.8 ± 0.1‰ for δ^{18}O, and was increasingly variable downstream (Figure 2b, Supporting Information).

Mixing models implied that a large proportion (0.92 ± 0.11) of upper montane streamwater was derived from snow. Adding the assumption that orographic isotope effects impacted all of the precipitation inputs to the headwaters decreased the modeled contribution of snow to 0.77 ± 0.10; actual proportions likely fell between these two scenarios. Regardless of the end members used, and potential impacts of sublimation (Supporting Information), estimated snow contributions

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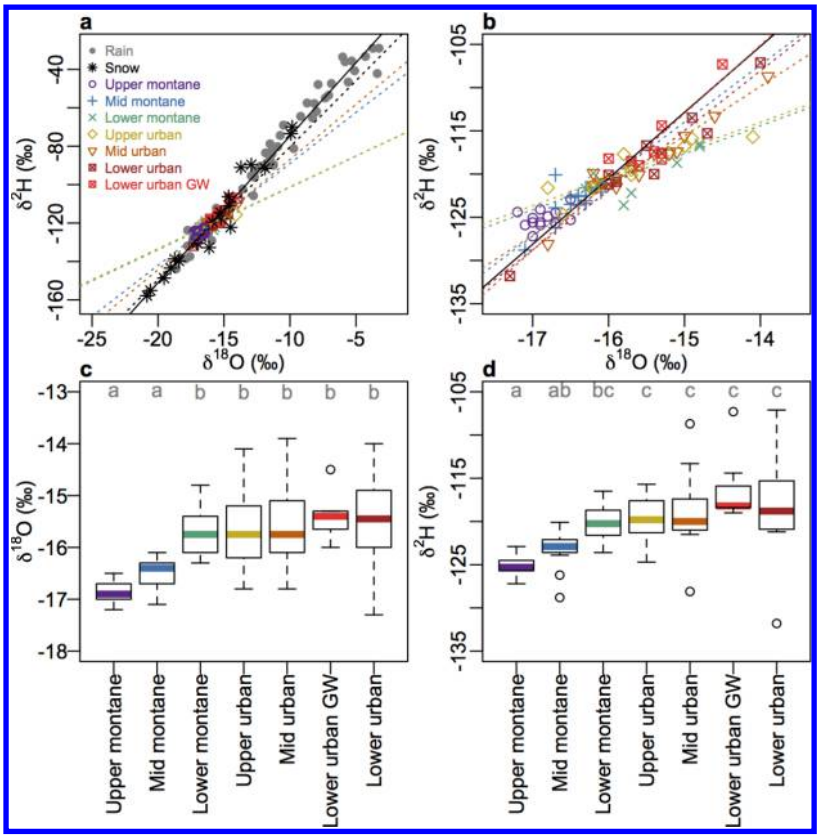

Figure 2. Precipitation and streamwater $\delta^{18}O$ and $\delta^{2}H$ (a). The solid black line represents the local meteoric water line, and dotted colored lines represent regressions of streamwater $\delta^{2}H$ on $\delta^{18}O$ for each site. See the Supporting Information for regression coefficients and statistical significance. The panel to the right (b) is an enlarged version of (a) focusing on the streamwater samples. Boxplots of streamwater $\delta^{2}H$ by site (c), where boxes represent medians and the interquartile range, and data >1.5 times the range from the box to the whiskers are denoted as outliers (circles). "Lower urban GW" denotes groundwater inputs adjacent to the lower urban site. Different letters denote significant differences in water $\delta^{2}H$ composition among sites. Boxplots of streamwater $\delta^{18}O$ by site (d).

decreased slightly but steadily with downstream distance to a minimum proportion of 0.74 ± 0.11 or 0.61 ± 0.09 at the lower urban site. Water isotopes from the lower urban spring also implied a predominance of snow (0.67 ± 0.11 or 0.56 ± 0.10) despite the much greater contribution of rain to total precipitation at the urban sites.

Stream water samples at three sites downstream of the reservoir (lower montane, upper urban, and mid urban) showed decreased $\delta^{2}H/\delta^{18}O$ slopes indicative of evaporative enrichment (Figure 2b,c,d, Supporting Information). Evaporation isotope effects were most prominent at the lower montane and upper urban sites, where $\delta^{2}H/\delta^{18}O$ slopes measured 3.2 ± 0.8 and 3.2 ± 0.4, respectively. Line-conditioned $\delta^{2}H$ excess (Supporting Information) also tended to decrease at sites below the reservoir, indicative of evaporation, although deviations were small (<2‰). Spring water isotope composition at the lower urban site was similar to the adjacent stream and closely paralleled the local meteoric water line (slope = 7.9 ± 1.9), and lined-conditioned $\delta^{2}H$ excess suggested no evaporation (Supporting Information).

Relationships between Stream Ion Concentrations and Discharge. Most ions in streamwater samples showed log/log slopes between concentration and discharge ranging from nonsignificant (zero) to weakly negative relationships (Figure 3, Supporting Information). However, the sites often had significantly different concentration/discharge relationships for a given ion, likely indicative of spatial heterogeneity in geological characteristics and flowpaths (i.e., shallow subsurface vs groundwater contributions). Chloride and Na^{+} concentrations showed no relationship to discharge at all sites except the lower urban, where concentrations decreased strongly with discharge as local groundwater inputs were diluted by upstream inputs (Figure 4). Magnesium concentrations decreased with discharge at the mid montane site, as well as at the lower urban site. Potassium concentrations decreased with discharge at all sites except the upper montane, and F^{-} concentrations showed no relationship with discharge at any site. In contrast to the other ions, SO_4^{2-} concentrations increased slightly but significantly with discharge at the lower montane and upper urban sites and showed no relationship with discharge at the other sites.

Concentrations of NO_3^{-}, DON, and DOC also showed variable relationships with discharge among sites (Figure 3). Nitrate concentrations decreased strongly with discharge at most sites (mid montane, lower montane, upper urban, and lower urban) and showed no relationship with discharge at the upper montane and mid urban sites. Concentrations of DON increased with discharge in the lower montane site, possibly reflecting flushing of algal detritus from the reservoir, and showed no relationship with discharge at the other sites. Concentrations of DOC increased strongly and highly significantly with discharge in the mid montane site and showed no relationship with discharge at the other sites. Ammonium was below detection (<0.01 mg N L^{-1}) in most (273) stream and groundwater samples. Relationships between NH_4^{+} and discharge were not significant.

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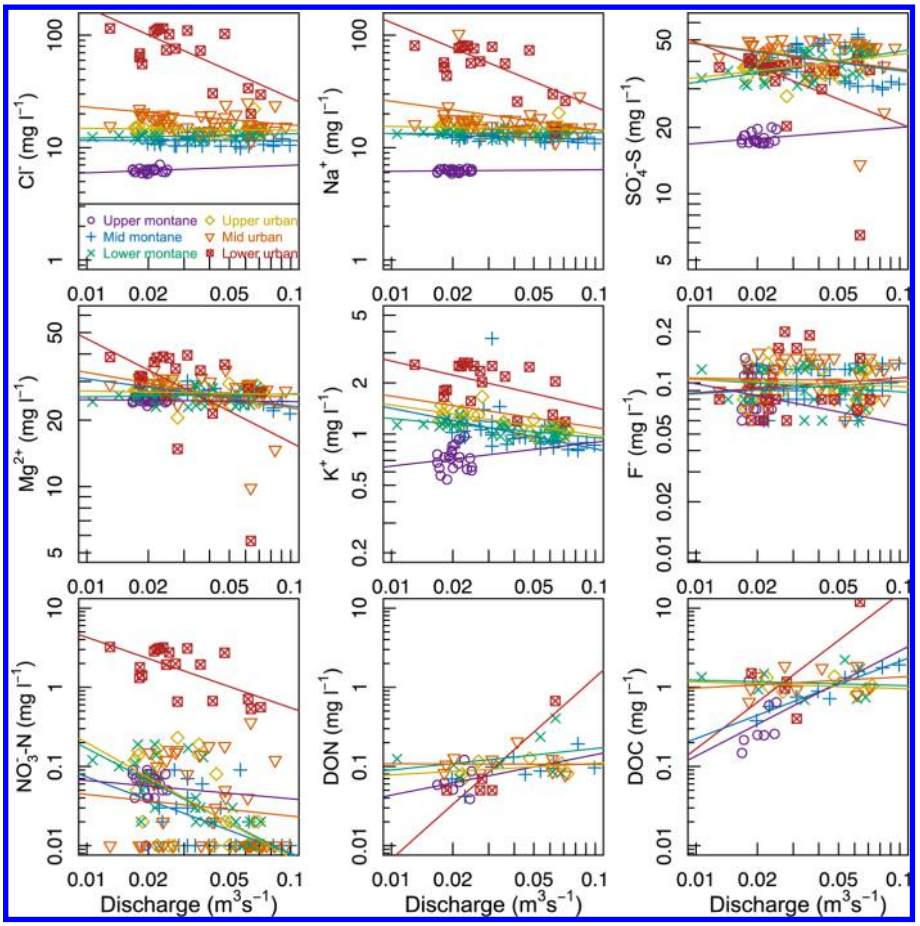

Figure 3. Log–log relationships between solute concentrations and discharge at montane and urban sites along Red Butte Creek. See the Supporting Information for linear regression coefficients and statistical significance. Discharge at the lower urban site was estimated using values from the mid urban site. Note the differences in *y*-axis scales among the panels.

Comparing Dissolved Solute Concentrations Across Water Pools and Sites. Solute concentrations varied by up to 3 orders of magnitude among precipitation, soil water, groundwater, and streamwater samples from different sites (Figure 4). Chloride and Na^+ concentrations were statistically similar in precipitation, soil water, riparian groundwater, and streamwater across most sites but were significantly elevated (5–10-fold greater) in upper urban soil water, lower urban groundwater, and lower urban streamwater. Concentrations of SO_4^{2-} were very low in precipitation and mid montane soil water (0.7 and 1.5 mg L^{-1}) relative to most groundwater and stream samples, which were 10–30-fold greater. Stream SO_4^{2-} concentrations were generally similar to co-occurring groundwater samples at the mid montane and lower urban sites. However, mean SO_4^{2-} concentrations in upper montane streamwater measured only 40% of concentrations in riparian groundwater at the same site, and groundwater SO_4^{2-} did not vary among sites.

Patterns in Mg^{2+} concentrations among the different water pools and sites were broadly similar to SO_4^{2-}. Magnesium concentrations in precipitation (0.43 ± 0.05 mg L^{-1}) and mid montane soil water (3.89 ± 0.48 mg L^{-1}) were lower by 1 or 2 orders of magnitude than in riparian groundwater (31.19 ± 0.37 mg L^{-1}) and streamwater (26.77 ± 0.29 mg L^{-1}). However, Mg^{2+} concentrations in mid urban soil water (45.43 ± 3.50 mg L^{-1}) and lower urban groundwater (36.41 ± 1.50 mg L^{-1}) were significantly greater than the other stream and groundwater pools. Concentrations of K^+ were statistically similar between precipitation (0.95 ± 0.13 mg L^{-1}) and most other pools of water, but, as with Mg^{2+}, they were also significantly greater in the upper urban soil water (19.19 ± 0.87 mg L^{-1}) and lower urban groundwater (3.31 ± 0.51 mg L^{-1}) than the other pools. Concentrations of F^- increased from precipitation to groundwater due to geological inputs, but F^- did not vary along the stream. Fluoride was significantly greater (1.4 ± 0.04 mg L^{-1}) in the upper urban soil water than all other pools.

Nitrate concentrations were greater in precipitation (0.47 ± 0.03 mg N L^{-1}) and soil water (0.39 ± 0.10 mg N L^{-1}) than most groundwater and streamwater samples along Red Butte Creek. Nitrate concentrations at sites along the stream between upper montane and mid urban averaged 0.01 ± 0.01 and 0.04 ± 0.01 mg N L^{-1} in groundwater and streamwater, respectively, and showed no differences between montane and urban stream samples. However, mean NO_3^- concentrations increased 50-fold at the lower urban site relative to the upstream sites, measuring 2.05 ± 0.08 and 1.96 ± 0.44 mg N L^{-1} in groundwater and streamwater, respectively. Concentrations of DON were similar across all sites and measured 0.10 ± 0.01 and 0.11 ± 0.02 in groundwater and streamwater, respectively. Stream DON concentrations typically exceeded NO_3^--N at all sites with the exception of the lower urban. Soil water from the upper urban site had much greater DON concentrations (2.40 ± 0.18 mg N L^{-1}) than the other water pools. Ammonium

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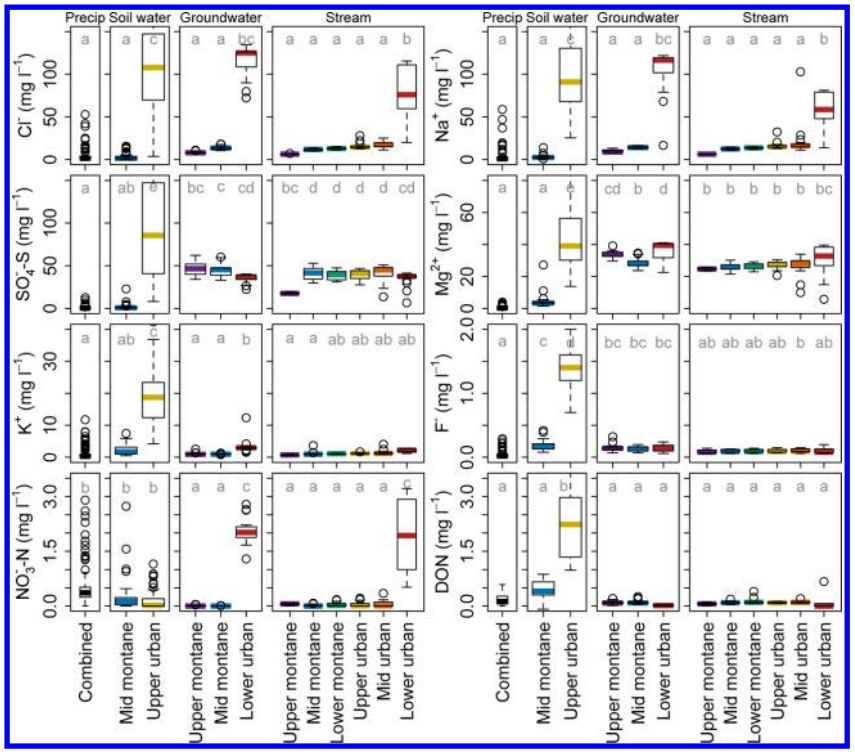

Figure 4. Solute concentrations in precipitation, soil water, groundwater, and streamwater at sites along Red Butte Creek. Boxplots with different letters denote significant differences in concentration for a given solute.

concentrations were highest in precipitation (0.48 ± 0.03 mg N L^{-1}) and mostly below detection in the stream (0.01 mg N L^{-1}).

Variation in Stream and Groundwater NO_3^- Isotope Composition. Nitrate $\delta^{15}N$ and $\delta^{18}O$ values in stream and spring water from the lower urban sites were higher and less variable than the other sites (Figure 5). In contrast, NO_3^- samples from the other sites had highly variable $\delta^{15}N$ and $\delta^{18}O$. Mean $\delta^{18}O$ of precipitation NO_3^- measured 81.9 ± 4.0‰. Assuming that $\delta^{18}O$ of nitrified NO_3^- measured approximately −15‰ (consistent with soil water from nearby montane sites), a two-source mixing model implied a small mean atmospheric NO_3^- contribution (9 ± 2%) at all sites. However, elevated $\delta^{18}O$ of NO_3^- in two samples from the mid urban site (Figure 5) indicated sporadic increases in atmospheric NO_3^- contributions to 52−56%.

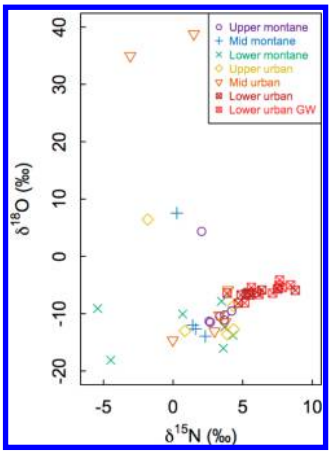

Figure 5. Nitrate isotope composition ($\delta^{18}O$ and $\delta^{15}N$) in streamwater at sites along Red Butte Creek; groundwater sampled from springs at the lower urban site is denoted "Lower urban GW" in the legend.

DISCUSSION

Groundwater Dominated Stream Discharge Even during Snowmelt. Temporal and spatial consistency in streamwater δ^2H and $\delta^{18}O$, δ^2H excess, and dissolved ion concentrations indicated the importance of well-mixed snow-derived groundwater sources even in the urban stream reaches, in contrast to previous work showing a large impact of impervious surfaces during snowmelt.[34] Contrary to our first and supporting our second alternative hypothesis, near-static relationships between conservative ion concentrations and discharge implied that geochemically equilibrated groundwater, as opposed to water traversing shallow or impervious flowpaths, generally dominated discharge across the land use gradient. Similar relationships between ions and discharge have been observed elsewhere on an annual basis.[51] However, the importance of groundwater demonstrated here has received much less attention in the context of snowmelt, where meltwater can potentially entrain nutrients from shallow flowpaths, leading to a stream NO_3^- pulse.[15,19−26] Previous work in Red Butte Canyon implied a large hyporheic or alluvial exchange volume approximately 30-fold greater than the stream channel.[52] Mixing of snowmelt with this reservoir likely minimized temporal variation in conservative solutes and provided opportunities for biogeochemical N removal.

The importance of groundwater was also illustrated by consistently elevated concentrations of rock-derived solutes (SO_4^{2-}, Mg^{2+}) in streamwater relative to montane soil water and precipitation. Stream solutes mirrored groundwater at all sites where we could measure both pools. In contrast, soil water at the upper urban site had K^+ and F^- concentrations 20- and 14-fold greater than streamwater at all sites, suggesting a minor

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direct contribution of these soils to urban discharge. The small but significant decrease in Mg^{2+} and corresponding increase in DOC (Figure 3) at the mid montane site provided the only evidence of increasing soil water contributions during snowmelt, where rising groundwater tables ultimately intersected carbon-rich surface soil horizons with lower concentrations of rock-derived cations.[44,45] Spatial variability in interactions among the stream and groundwater reservoirs[53] along Red Butte Creek likely contributed to subtle differences in the slopes of ion concentration/discharge relationships among sites (Supporting Information). Small linear increases in several stream solutes (Cl^-, Na^+, K^+) between the first five sites likely reflected evapotranspiration by riparian vegetation.

Snowmelt Did Not Produce a Pulse in Stream NO_3^- Concentrations. Numerous studies have shown that stream NO_3^- concentrations typically peak during spring snowmelt in temperate catchments, presumably due to flushing of soil NO_3^-.[15,19−26] This pattern might be expected in the montane and urban reaches of Red Butte Creek due to fossil fuel emissions from the Salt Lake Valley and associated N deposition.[29] Bulk N deposition measured in individual precipitation events totaled approximately 4.5 kg N ha y^{-1} and likely underestimated dry deposition. This estimate was comparable to N critical loads for other western montane ecosystems[28,54] and was further augmented by fertilizer N inputs along the urban reach.[55]

Contrary to our first alternative hypothesis and supporting our second, we found that stream NO_3^- concentrations decreased or showed no relationship with increasing discharge during snowmelt at all sites across the montane to urban gradient. Concentrations of DON were also constitutively low, contrasting with recent findings of high DON in other urban watersheds.[5] Rather, stream NO_3^- concentrations tracked spatial patterns in groundwater. We reiterate that this study focused on seasonal discharge patterns and did not quantify discrete rainfall events, where stormwater generated flashy hydroperiods at the mid and lower urban sites (Figure 1). However, comparing hydrographs between the upper urban and mid urban sites implied a relatively small stormwater influence on cumulative discharge at the mid urban site (approximately 15%). The negative relationship between NO_3^- concentrations and discharge was most notable in the lower urban site, which received groundwater inputs with high NO_3^- that were diluted by increased discharge during peak snowmelt. This finding contrasts with previous work demonstrating substantial urban snowmelt NO_3^- inputs from impervious surfaces in Minneapolis, MN.[34] It also contrasts with a suburban montane stream in Colorado where septic NO_3^- inputs were greatest during snowmelt[56] but similarly emphasizes the importance of groundwater rather than surface flowpaths in controlling stream N dynamics in semiarid montane ecosystems.

The absence of a snowmelt NO_3^- pulse (Figure 3) likely reflected the importance of subsurface biological N retention and/or denitrification. Surface soils contributed to N uptake and removal during snowmelt, illustrated by decreasing inorganic N between precipitation and soil water in the montane and urban sites and echoing many previous studies.[16,35] However, we suggest that N biogeochemical cycling in alluvial and riparian groundwater was especially important along Red Butte Creek, given 1) the dominant importance of groundwater to discharge, 2) the static low NO_3^- concentrations in montane groundwater relative to soils, and 3) indices of an anaerobic environment suitable for denitrification. The latter was implied by evidence of SO_4^{2-} reduction, particularly at the upper montane site: stream SO_4^{2-} concentrations were consistently lower than in groundwater, and we consistently smelled hydrogen sulfide (the product of SO_4^{2-} reduction) while sampling these wells. Thermodynamic constraints imply that NO_3^- was consumed via denitrification in sulfidic sediments, confirmed by consistent groundwater NO_3^- values below detection limits at this site. Denitrification in riparian groundwater has been widely documented,[39] and riparian N retention during snowmelt has been demonstrated in montane streams lacking a major urban influence.[38] Here, these processes likely contributed to constitutively low stream NO_3^- along most of the montane to urban gradient.

Stream NO_3^- and Ion Concentrations Varied Little Across the Montane to Urban Boundary. Intriguingly, stream NO_3^- concentrations did not vary with elevation or across the montane to urban gradient (Figure 4), as one would expect if variation in terrestrial NO_3^- inputs were a dominant factor as hypothesized previously.[33] Water isotope mixing models suggested a small shift in streamwater sources and an increasing contribution of rain or lower-elevation precipitation to discharge with downstream distance. While the absence of downstream spatial variation in NO_3^- concentrations has often been observed over small scales (i.e., < 0.5 km) in headwater streams,[57] our data show that static NO_3^- can persist even across larger land use transitions (~10 km).

This finding is interesting given the large differences in precipitation, snow cover, temperature, and land use across this gradient, which have been proposed to control stream NO_3^- inputs via their effects on N inputs, soil biogeochemical processes, and hydrologic flow paths.[11,16,17,33] Given the absence of increased baseflow NO_3^- concentrations, the substantial fertilizer N inputs in the landscape adjacent to the upper and mid urban sites (~100 kg N ha y^{-1}; L. Lopez, University of Utah, personal communication) were likely retained or denitrified rather than exported to the stream, echoing findings from mesic urban ecosystems.[4,58]

Urban Groundwater Dominated Stream NO_3^- Inputs. Stream N peaked dramatically at the lower urban site following groundwater NO_3^- inputs from urban springs, which dominated discharge at this site as reflected by similarities between urban groundwater and stream ion composition (Figure 4). Increased groundwater inputs at the mountain front/valley boundary were documented in a geographically similar watershed[42] and may represent a widespread regional phenomenon. The isotopic composition of urban groundwater implied a dominant snow contribution, either from montane recharge emerging along the mountain front and/or from urban snowmelt.

Municipal water in Salt Lake City is also primarily derived from snowmelt and could contribute to groundwater recharge via infiltration of irrigation water or leaking supply pipes. Fluoride is added to local municipal water at ~0.7 mg L^{-1} and provides a useful tracer given that water isotopes cannot distinguish groundwater contributions from natural snowmelt vs municipal water. Fluoride increased in irrigated soil, indicating evapoconcentration of municipal water, but did not increase in either the lower urban groundwater or stream, indicating a relatively small contribution of municipal water to groundwater at the lower urban site.

Nitrate stable isotopes (Figure 5) and dissolved ions (Figure 4) indicated that increased NO_3^- concentrations in the lower

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urban groundwater likely reflected interactions between natural flow paths and leaking sewers, as opposed to infiltration of fertilizer/soil N or atmospheric deposition. Sewage total N concentrations likely exceeded F^- > 100-fold, explaining increased groundwater NO_3^- despite no change in F^-. If fertilizer/soil N were important, we would expect increased groundwater F^- from irrigated urban soils. Transport of fertilizer to groundwater recharge areas via overland flow over sidewalks and roads is also possible, which would minimize interactions with surface soils. However, $\delta^{18}O$ of fertilizer NO_3^- measures 17−25‰,[59] much greater than the NO_3^- $\delta^{18}O$ we observed in lower urban stream and groundwater. Similarly, NO_3^- in local atmospheric deposition also has much higher $\delta^{18}O$ (81.9 ± 4.0‰) than we observed at this site. Rather, elevated $\delta^{15}N$ and consistent $\delta^{18}O$ of NO_3^- point to leaky sewers in explaining the 50-fold increase in NO_3^- between the mid and lower urban sites. Many sewers in this watershed were installed in the early 1900s and may be deteriorating; septic systems are not present here.

Reports of $\delta^{15}N$ of NO_3^- from human waste (2−25‰[59]) overlapped with $\delta^{15}N$ of NO_3^- from lower urban stream and groundwater. The absence of a linear relationship between $\delta^{15}N$ and $\delta^{18}O$ of NO_3^- at the lower urban site suggested that a human waste source rather than denitrification was responsible for increased $\delta^{15}N$ values at this site relative to upstream.[60] More likely, variation in $\delta^{15}N$ (Figure 5) at this site was driven by fractionation during nitrification[61] of excess sewer NH_4^+. Differences in NO_3^- $\delta^{18}O$ between the lower urban and upstream samples likely reflected water sources in the nitrifying environment and the extent of $\delta^{18}O$ exchange.[62]

Implications of Groundwater Control of N Inputs to Semiarid Streams. The importance of a well-equilibrated groundwater reservoir in controlling discharge to the montane reaches of Red Butte Creek suggests that temporal and spatial variability in surface biogeochemical processes, particularly coupled to snow accumulation and melt, may have had less impact on stream N dynamics than previously proposed.[16,17] Rather, increased water residence times in the subsurface may enhance N retention by riparian plants and microbes as well as denitrification,[38,39] thus avoiding deleterious snowmelt NO_3^- pulses.

In contrast, interactions between streams and urban groundwater represent an important vulnerability for water quality.[11] The importance of leaking sewers to urban stream N inputs has been well-documented in humid temperate ecosystems[4,18,40] but has received little attention as a N source to semiarid urban streams (as opposed to septic systems[56,63]). Leaking sewers in arid Arizona watersheds could explain elevated groundwater NO_3^-,[64] but deposition, fertilizer, and soils dominated NO_3^- inputs to ephemeral streams.[65,66] Regional water quality reports highlighted the importance of point discharges by publicly owned treatment works but not the potential importance of leaking sewage infrastructure.[67]

Groundwater interception of leaking sanitary infrastructure, and consequent impacts on surface water quality, may represent a generalizable characteristic of urban ecosystems irrespective of climate and hydrogeological characteristics. Enhanced sewer infrastructure monitoring and maintenance could likely mitigate the primary source of N to Red Butte Creek. The fact that groundwater NO_3^- inputs were concentrated in a discrete region at the mountain front/valley transition could also facilitate the use of targeted stream restoration and engineered green infrastructure (i.e., treatment wetlands) for N attenuation in this and geographically similar ecosystems.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b04805.

Study site description and map of sampling sites; sampling and chemical analysis details; water isotope data; statistical relationships between ion concentrations and discharge (PDF)

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Notes

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