**Restored Streams** 2 3 Joseph T. Malin<sup>1,2</sup>, Sujay S. Kaushal<sup>1</sup>, Paul M. Mayer<sup>3</sup>, Carly M. Maas<sup>1,4</sup>, Steven P. Hohman<sup>5</sup>, Megan A. 4 Rippy<sup>6,7,8</sup> 5 6 7 8 9 <sup>1</sup>: Department of Geology & Earth System Science Interdisciplinary Center, University of Maryland, 10 College Park, Maryland 20742, USA 11 <sup>2</sup>: Environmental Quality Resources, L.L.C., 2391 Brandermill Blvd., Suite 301, Gambrills, MD 21054, 12 USA <sup>3</sup>: Environmental Protection Agency, 805 SW Broadway #500, Portland, OR 97205, USA 13 14 4: United States Geological Survey, 1730 E Parham Road, Richmond, VA 23228, USA <sup>5</sup>: Environmental Protection Agency, 1650 Arch St, Philadelphia, PA 19103, USA 15 16 6: Occoquan Watershed Monitoring Laboratory, The Charles E. Via, Jr. Department of Civil and Environmental Engineering, Virginia Tech, 9408 Prince William Street, Manassas VA, USA 17 7: Center for Coastal Studies, Virginia Tech, 1068A Derring Hall (0420), Blacksburg, VA, USA 18 19 8: Disaster Resilience and Risk Management (DRRM), 1068A Derring Hall, 405 Perry Street, Blacksburg, 20 VA 24061, USA. 21 22 23 24 Joseph T. Malin: joemalin@umd.edu

Longitudinal Stream Synoptic (LSS) Monitoring to Evaluate Water Quality in

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### Abstract

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26	Impervious surface cover increases peak flows and degrades stream health, contributing to a variety of
27	hydrologic, water quality, and ecological symptoms, collectively known as the urban stream syndrome.
28	Strategies to combat the urban stream syndrome often employ engineering approaches to enhance stream-
29	floodplain reconnection, dissipate erosive forces from urban runoff, and enhance contaminant retention,
30	but it is not always clear how effective such practices are or how to monitor for their effectiveness. In this
31	study, we explore applications of longitudinal stream synoptic (LSS) monitoring (an approach where
32	multiple samples are collected along stream flowpaths across both space and time) to narrow this
33	knowledge gap. Specifically, we investigate: (1) whether LSS monitoring can be used to detect changes in
34	water chemistry along longitudinal flowpaths in response to stream-floodplain reconnection, and (2) what
35	is the scale over which restoration efforts improve stream quality. We present results for four different
36	classes of water quality constituents (carbon, nutrients, salt ions, and metals) across five watersheds with
37	varying degrees of stream-floodplain reconnection. Our work suggests that LSS monitoring can be used
38	to evaluate stream restoration strategies when implemented at meter to kilometer scales. As streams flow
39	through restoration features, concentrations of nutrients, salts and metals significantly decline (p $<$ 0.05) or
40	remain unchanged. This same pattern is not evident in unrestored streams, where salt ion concentrations
41	(e.g. Na <sup>+</sup> , Ca <sup>2+</sup> , K <sup>+</sup> ) significantly increase with increasing impervious cover. When used in concert with
42	statistical approaches like Principal Component Analysis, we find that LSS monitoring reveals changes in
43	entire chemical mixtures (e.g., salts, metals, and nutrients), not just individual water quality constituents.
44	These chemical mixtures are locally responsive to restoration projects, but can be obscured at the
45	watershed scale and overwhelmed during storm events.

47 Keywords

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48 Urban streams, restoration, water quality assessment, nutrient pollution, freshwater salinization

#### Introduction

Urbanization and its impacts on water quality are degrading many kilometers of streams in the Chesapeake Bay watershed and across the U.S. Urbanization can impact a watershed's physical, chemical, and biological characteristics (FISRWG, 1998; Paul & Meyer, 2001; Walsh et al., 2005) and ultimately reduce water quality. Impervious surface cover increases peak flows and degrades stream health, contributing to a variety of hydrologic, water quality, and ecological symptoms, collectively known as the urban stream syndrome (Walsh et al., 2005). Pollution from nutrients, metals, and salts impact sensitive downstream receiving waters such as drinking water supplies or coastal waters. Stream restoration strategies are diverse (Newcomer-Johnson et al., 2016) and the goal of many stream restoration projects is to reconnect streams with floodplains and riparian wetlands that are sinks for carbon and nutrients. Billions of dollars are spent on rehabilitating water quality through stream restoration and engineering stream channels and floodplains in the U.S. and elsewhere (Bernhardt et al., 2005; Newcomer-Johnson et al., 2016). Despite the growing prevalence of stream restoration, questions remain whether stream restoration using engineering approaches actually improve urban water quality and how to effectively restore and monitor streams. Stream-floodplain reconnection has been shown to increase nutrient retention along stream flowpaths (Bukaveckas, 2007; Kaushal et al., 2008; Mayer et al., 2022; McMillan & Noe, 2017), but there can be spatial and temporal variability across stream reaches and restoration projects that can make it difficult to assess the effectiveness of stream restoration practices (Booth et al., 2004; Filoso & Palmer, 2011; Kaushal et al., 2023a,b; Sivirichi et al., 2011).

Runoff and contaminants are more efficiently transported to urban streams due to flashy runoff from impervious surfaces and storm drains (Askarizadeh et al., 2015; Walsh et al., 2005). Runoff from impervious surfaces is discharged to urban streams from storm drains with minimal opportunity for biogeochemical retention of pollution from nonpoint sources such as leaky sewer pipes underneath streams, road salts, fertilizers, vehicles, and other sources (Cooper et al., 2014; Galella et al., 2021; Kaushal et al., 2020; Maas et al., 2023; Mayer et al., 2010; Morel et al., 2020). Increased runoff decreases hydrologic connectivity between the stream and its floodplain, which causes polluted water to bypass the upper soil horizons of floodplains (with ample organic matter and plant roots for retention of contaminants) (Groffman et al., 2002; Kaushal et al., 2008; Walsh et al., 2005). Increasing impervious surface cover due to urbanization leads to less infiltration of precipitation and more overland flow during storm events (Booth & Jackson, 1997; Fanelli et al., 2017; Paul & Meyer, 2001). An urban stream can become hydrologically disconnected from its floodplain due to increased runoff and erosion of stream banks contributing to channel incision (Groffman et al., 2002) and other geomorphic changes (Leopold et al., 2005). Shallow groundwater flowing through the riparian zone cannot adequately interact with

vegetation and organic matter in upper soil horizons (Fanelli et al., 2017; Groffman et al., 2002; Kaushal et al., 2008), and can result in decreased retention of pollutants such as nitrogen (Forshay et al., 2022; Hanrahan et al., 2018; Kaushal et al., 2008) and phosphate (Davis et al., 2015; McMillan et al., 2014). Specific conductance can be an indicator of surface water contributions during storms versus groundwater contributions during baseflow (Kaushal et al., 2019; Occhi, 2011; Pellerin et al., 2008). Overall, restoring hydrologic connectivity between streams and floodplains and shallow groundwater can be critical for influencing biogeochemical reactions (Kaushal et al., 2008; Mayer et al., 2010; Mayer et al., 2022).

Stream restoration is used to reduce impacts from urbanization; approaches are diverse and may include channel or in-stream hydromorphic methods, restoring riparian zones, or entire watershed actions. Stream restoration goals may include enhancing water quality, channel stability, riparian or in-stream habitats, biodiversity, or any combination of these (Newcomer-Johnson et al., 2016; Palmer et al., 2014). Diverse approaches for stream restoration are described in detail in Newcomer-Johnson et al. (2016), but the most common approaches that have shown the potential to improve water quality are (1) stream-floodplain reconnection, which can enhance N uptake in streams and hyporheic zones and foster denitrification (Kaushal et al., 2008; Mayer et al., 2022; Newcomer-Johnson et al., 2016); (2) enhancing hydrologic connectivity between streams and oxbow wetlands, which can enhance denitrification and N removal (Harrison et al., 2011, 2012a); (3) creating stream-wetland complexes (Filoso & Palmer, 2011; Forshay et al., 2022; Newcomer et al., 2014); and (4) regenerative stormwater conveyance (Duan et al., 2019; Williams & Filoso, 2023). There are also other engineered restoration approaches such as natural channel design (Rosgen, 1996, 2011) in which stream channels are widened, point bars or cutbanks are added, or the sinuosity of the channel is increased.

Most work evaluating the effects of stream restoration on water quality has focused on nutrient retention in restored streams while neglecting the fate and transport of salts, metals, and organics together (Kaushal et al., 2023a,b; Maas et al., 2023). Assessing stream restoration effectiveness using conventional monitoring approaches that rely only on monitoring one or a few contaminants over time at just one or a few fixed locations can be difficult. Urban watersheds have spatial and temporal dimensions, which influence water quality along a continuum of flowpaths (Kaushal & Belt, 2012; Kaushal et al., 2023a,b, 2014b; Maas et al., 2023). Here, we explore a longitudinal stream synoptic (LSS) monitoring approach in which we have sampled along the entire flowpath or a large reach of flowpath at a fixed frequency at the same locations. We used this repeated LSS monitoring approach to analyze multiple chemicals to assess the effectiveness of stream restoration across both space and time, and to identify whether restoration features can attenuate multiple contaminants, such as nutrients, salts, and metals, along flowpaths. In our study, LSS monitoring was performed across a wide range of discharges, storm events, and specific

conductance fluctuations driven by salting events in these streams. The presence of any emergent or consistent longitudinal patterns in water chemistry along the flowpaths can provide valuable information regarding the spatial heterogeneity of water quality along the streams and the functioning of the stream restoration.

Many restoration studies monitor water quality at one or a few sites in restored streams after the restoration has occurred. Typical monitoring approaches are: sampling streams on a weekly or bi-weekly basis over a decade (Mayer et al., 2022); collecting groundwater along water well transects on a monthly basis (Wood et al., 2022); and/or using combinations of bi-weekly sampling and longitudinal synoptic sampling (Newcomer-Johnson et al., 2014; Pennino et al., 2016b; Sivirichi et al., 2011). Assessing stream restoration effectiveness depends greatly on when and where monitoring is conducted along a stream network (Kaushal et al., 2023a,b; Newcomer-Johnson et al., 2014; Sivirichi et al., 2011) and whether multiple contaminants are monitored (Kaushal et al., 2022; Maas et al., 2023). Repeated LSS monitoring can also help identify which restoration approaches may be effective over spatial and temporal scales (Kaushal et al., 2023a,b; Maas et al., 2023). Here, we asked whether we are missing important changes in water quality associated with different forms of stream restoration by not incorporating high resolution LSS monitoring where streams are sampled frequently along the entire flowpath.

In order to answer this question, we use repeated LSS approaches to evaluate the effects that stream restoration can have on water chemistry by sampling across various spatial and temporal scales. The results from this effort allow us to address: (1) whether LSS monitoring can be used to detect changes in water chemistry along longitudinal flowpaths in response to stream-floodplain reconnection, and (2) what is the scale over which restoration efforts improve stream quality. Overall, there are many challenges when it comes to evaluating restorations, depending on available time, resources, and money. Therefore, it is important to understand both the advantages and disadvantages of sampling across different spatial and temporal scales when designing monitoring programs. Consideration of multiple spatial and temporal scales allows for improved comparisons of seasonality, hydrologic conditions, pollution events, and land use management practices within and among watersheds (Kaushal et al., 2023a, b; Maas et al., 2023). Basically, we explore applications of LSS monitoring repeated over time to evaluate water quality along restored stream flowpaths. The LSS monitoring approach used here evolved from methods described in Kaushal et al. (2023a,b), Kaushal et al. (2014b), Maas et al. (2023), Newcomer-Johnson et al. (2014), Pennino et al. (2016b), and Smith et al. (2017). In this study, we repeated LSS monitoring over time and across seasons and hydrologic events in order to better understand potential water quality tradeoffs in response to restoration and the potential for co-management of pollutants. We

found that the implementation of multifunctional nature-based solutions in the form of restoring urban stream reaches can have a positive impact on streamwater quality.

#### Methods

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LSS Study Design: Monitoring the Impacts of Restorations Along Watershed Flowpaths
Across Space and Time

Five watersheds with stream restoration efforts were monitored along their flowpaths at different spatial and temporal scales to explore the impacts of watershed restoration projects on stream chemistry. We sampled streams longitudinally at least once per season to capture changes in water chemistry along the flowpath. In this study, all streams were sampled longitudinally repeatedly between 4 and 10 times. The lack of higher frequency synoptic sampling datasets can lead to limitations in the ability to explore the full benefits of LSS. Longitudinal stream synoptic (LSS) monitoring was conducted according to the approaches and methods described by Kaushal et al. (2023 a,b) and Maas et al. (2023). LSS monitoring is also described in greater detail further below when discussing specific detailed field and lab methods. All stream sampling sites were located along the thalweg of each stream. The same sampling sites were chosen for each longitudinal synoptic (Figure 1). During longitudinal sampling, automated stream samplers were placed at each stream to capture diurnal stream chemistry data. Streams were monitored (1) bi-weekly over an annual cycle to capture the influence of seasonality on water quality changes; (2) seasonally during baseflow and stormflow to characterize differences in water chemistry during these conditions; and (3) hourly over diurnal cycles to capture the short-term influence of brief storm events. In all five watersheds, the following water quality constituents were measured throughout the study: total dissolved nitrogen (TDN), dissolved organic carbon (DOC), dissolved and particulate elements (B, Ba<sup>2+</sup>, Ca<sup>2+</sup>, Cu, Fe, K<sup>+</sup>, Mg<sup>2+</sup>, Mn, Na<sup>+</sup>, S, and Sr<sup>2+</sup>), temperature, DO, conductivity, total dissolved solids, salinity, pH, and oxygen reduction potential.

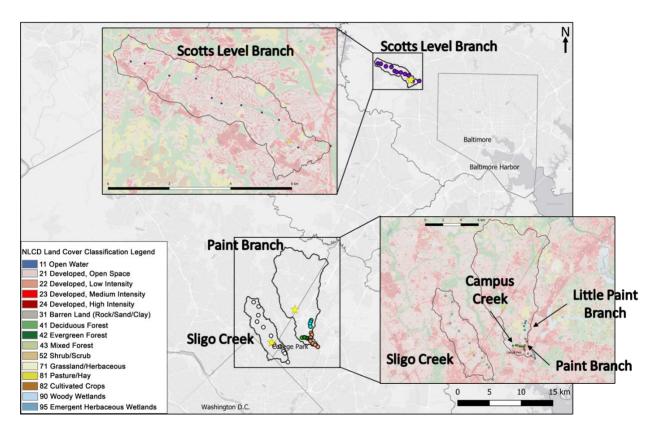


Fig. 1 Site Map. Scotts Level Branch, Sligo Creek and Paint Branch watersheds are outlined. Circle markers depict longitudinal sampling sites at Scotts Level Branch (purple), Sligo Creek (white), Campus Creek (green), Paint Branch (orange), and Little Paint Branch (teal). Stars represent USGS Stream Gauge locations. Map colors depict land cover characteristics described by the National Land Cover Database Classification Legend (NLCD, 2021)

#### Site Descriptions

All five watersheds are located within Maryland, USA and are tributaries of the Chesapeake Bay (Figure 1). Four of the watersheds are within the Anacostia Watershed. Brief descriptions of the five studied watersheds and their restoration strategies are summarized below and in Table 1. The watersheds differ in percent impervious surface cover, percent forest cover, and drainage area (Figure 2). The stream restoration strategies were dependent upon local hydrology, watershed size, accessibility of the stream channel's surrounding floodplain, and the extent of urban infrastructure in and around the stream



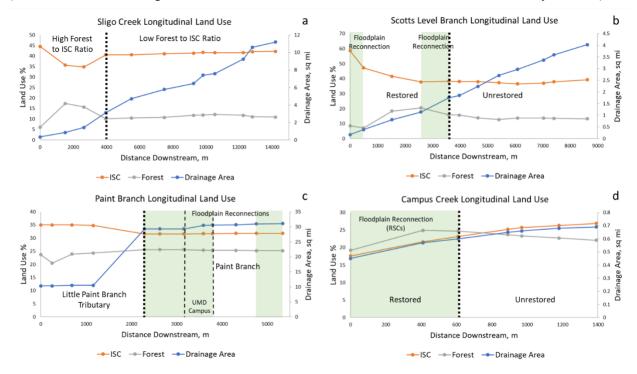


Fig. 2 Longitudinal patterns in land use and cumulative drainage area of all five flowpaths plotted against distance downstream. 0 m represents the most upstream point of the sampled flowpath. Percent impervious surface cover (ISC) and forest cover are plotted. Green bars represent restored areas along the flowpaths. Thick dashed lines divide watersheds into two comparable sections of flowpath; Sligo Creek is divided by relative forest cover to ISC (a), Scotts Level Branch (b) and Campus Creek (d) are divided by restored and unrestored flowpath, and Paint Branch is divided by tributary and main stem. Additional dashed lines along the Paint Branch flowpath represent the location of the University of Maryland, College Park campus

Two paired watersheds in this study, Sligo Creek and Scotts Level Branch, offered a unique opportunity to compare the effectiveness of different stream restoration approaches. Sligo Creek has undergone channel-based restoration efforts, while Scotts Level Branch has been exposed to floodplain reconnection strategies along sections of its flowpath. These two watersheds are in similar geographic regions, have comparable land use and land cover along their flowpaths, and similar hydrology including similar seasonal precipitation (Online Resource 1). Annually, precipitation, evapotranspiration, and runoff peak at similar times at Sligo Creek and Scotts Level Branch. Sligo Creek usually has higher annual precipitation, while Scotts Level Branch has more outlier flooding events due to heavy rainstorms. Otherwise, precipitation levels and hydrology between the two watersheds are quite similar (Online

Resource 1). Both watersheds have an average impervious surface cover of 41% and similar average forest covers at 12-14% (Table 1). Sligo Creek and Scotts Level Branch both have decreasing impervious surface cover in the beginning of their flowpaths, and they both have similar patterns in stable impervious cover further downstream (Figure 2).

We also investigated and compared longitudinal water quality responses in nested watersheds. Little Paint Branch and Campus Creek are both small, nested watersheds within the larger Paint Branch watershed (Figure 1), which allows us to compare them to each other. Campus Creek was restored using regenerative stormwater conveyance (RSC), a technique in which a series of step pools are added to reduce the velocity of the water moving along the flowpath, whereas Little Paint Branch has experienced "natural floodplain reconnection" due to sedimentation following the construction of a major highway upstream (Blanchet, 2009). Comparing longitudinal patterns in chemistry along these two sites might tell us if engineered and natural floodplain reconnections confer different water quality benefits.

One of the reasons to explore hydrologic and seasonal changes in the context of this study is that they have the potential to complicate the detection of restoration effects using longitudinal stream synoptic monitoring (there may be different longitudinal patterns across streamflow conditions). Given that our first objective of this study was to explore whether changes in water chemistry can be detected along longitudinal flowpaths in response to floodplain reconnection, our second objective was to evaluate how might this change by season, flow condition, and spatial scale. We used linear regression of repeated LSS monitoring data to help address the first objective and used PCA and changes on a diurnal scale to address the second objective. The comparison of higher resolution tributary samples (which can resolve short-duration effects) in Campus Creek and Little Paint Branch and lower resolution watershed-scale samples (which reveal broader trends) across the entire Paint Branch watershed were also used to address our second objective, which explores the scales over which restoration efforts improve stream quality.

# Sligo Creek Watershed (Minimal Floodplain Reconnection but Changes in Impervious Surface Cover)

Sligo Creek is a 14.2 km stream within a 29.0 km² watershed that flows through Montgomery and Prince George's County in Maryland. Sligo Creek is a tributary of the Northwest Branch of the Anacostia River, which flows into the Potomac River. The watershed has an average impervious surface cover of 41% and a forest cover of 12% (U.S. Geological Survey, 2019). Silgo Creek has not undergone floodplain reconnection due to a narrow stream corridor and residential development in close proximity to the stream channel. Restoration efforts have focused primarily on stream channel stabilization and a series of stormwater management projects. The Sligo Creek watershed restoration project has undergone six

phases since 1989 when Montgomery County decided to restore water quality and habitat conditions in the stream (George, 2012). Phases I-IV (conducted in 1989, 1992-1994, 1996, and 1999) created stormwater retention ponds and wetlands into the watershed. Phase V (conducted in 2005-2007) introduced low-impact development (LID) stormwater management bioretention systems, and Phase VI (conducted in 2010-present) implemented additional stormwater management techniques across 48% of the upper Sligo Creek subwatershed. Restoration projects at Sligo Creek have resulted in a 41% reduction in peak flow discharge and overall improvements in water quality (George, 2012).

Sample collection at Silgo Creek was conducted at twelve sites spanning from headwaters to the confluence. Sample collection sites were spaced between 550-2,000 m apart and were primarily chosen based on access to the stream channel. Sampling was conducted at the same locations during each LSS sampling campaign. Sligo Creek was sampled two times during baseflow and two times during stormflow conditions; diurnal sampling was conducted three times and automated samplers were placed at sites SC2 (1,525 m), SC7 (9,249 m), and SC12 (14,202 m) (Table 2).

#### Scotts Level Branch Watershed (Floodplain Reconnection Along Headwater Reaches)

Scotts Level Branch is an 8.7 km stream within a 10.4 km² watershed in Baltimore County, Maryland. Scotts Level Branch is a tributary of Gwynns Falls, which is a tributary of the Middle Branch of the Patapsco River. This watershed drains residential development and has an average impervious surface cover of 41% and a forest cover of 14% (U.S. Geological Survey, 2019). Two restoration projects involving floodplain reconnection have been implemented along the flowpath at Scotts Level Branch (Scotts Level Branch Stream Restoration Project, 2019). The most upstream restoration project, constructed in 2019, is from sample site SLB1 (0 m) to SLB2 (491 m), while the second stream restoration project, completed in 2014, extends from sample site SLB4 (2,576 m) to SLB5 (3,584 m). A third floodplain reconnection project focused on a first-order tributary (which flows into the channel upstream of site SLB5) was under construction in the Fall of 2022. Two additional projects are still in design. The goal of these projects was to regrade the landscape around deeply incised reaches of the flowpath to reconnect the stream to its floodplain and reduce sediment and nutrient runoff into the stream (Ryan, 2022). Additionally, plants native to Maryland watersheds were reintroduced to the floodplain, and stream sinuosity was increased where possible to slow stream water flow and reduce the probability of further incision.

As with Silgo Creek, sample collection at Scotts Level Branch was conducted at twelve sites from the headwaters to the confluence. Sample collection sites were spaced between 375-1,220 m apart and were primarily chosen based on access to the stream channel. Sampling was conducted at the same

locations during each LSS sampling campaign. Scotts Level Branch was sampled four times during baseflow, four times during stormflow conditions, and two times following road salting events; diurnal sampling was conducted four times and automated samplers were placed at sites SLB1 (0 m), SLB7 (4,650 m), and SLB10 (7,035 m) (Table 2).

### Paint Branch Watershed (Streambank Stabilization and Minimal Floodplain Reconnection) and

### Subwatersheds

Paint Branch is a 22.5 km stream that flows through Montgomery and Prince George's Counties in Maryland. This 80.5 km² watershed is a fourth-order tributary of the Northeast Branch of the Anacostia River which feeds into the Potomac River and is the largest watershed of this study. The watershed has an average impervious surface cover of 33% and a forest cover of 24% (U.S. Geological Survey, 2019). The Paint Branch watershed has undergone multiple restorations including one performed by the U.S. Army Corps of Engineers in 2015 and another sanctioned by the MDOT Maryland Transit Administration and finished in 2021 as part of the Purple Line mass transit project. The 2015 project was designed to restore fish passage and habitat connectivity along the stream corridor (Roach, 2018). The project ultimately included floodplain reconnection strategies when the U.S. Fish and Wildlife Service identified that floodplain connectivity was a main contributor to impairment in the stream (USFWS, 2015). This restoration project also focused on restabilizing eroding stream banks through the University of Maryland at College Park campus. The project spans sampling sites PB5 (2,290 m) through PB9 (3,790 m). The more recent 2021 restoration project, sampled at sites PB11 (4,760 m) and PB12 (5,340 m), also included floodplain reconnection strategies as well as ways of improving habitat and overall stream stability (Paint Branch Stream Restoration, 2021) (Figure 2).

The entire Paint Branch watershed (from headwaters to outflow; 22 km transect) was sampled once at 22 locations along its flowpath. Repeated LSS monitoring was performed at 12 locations along the downstream-most reach of flowpath (PB 1 (0 m) through PB 12 (5,340 m). Sample collection sites were spaced between 200-1,130 m apart and were primarily chosen based on access to the stream channel. Sampling was conducted at the same locations during each LSS sampling campaign. Two subwatersheds of Paint Branch were also monitored; Little Paint Branch and Campus Creek (described further below). Paint Branch was sampled one time during baseflow and four times during stormflow conditions; diurnal sampling was conducted five times and automated samplers were placed at sites PB1 (0 m), PB6 (2,630 m), and PB9 (3,790 m), or only at PB8 (3,590 m) (Table 2).

#### Little Paint Branch (Natural Floodplain Reconnection from Sedimentation)

The Little Paint Branch tributary flows into the downstream reach of the main Paint Branch flowpath. The watershed has an average impervious surface cover of 35% and a forest cover of 23% (U.S. Geological Survey, 2019). Little Paint Branch tributary has undergone a natural floodplain reconnection (Blanchet, 2009) following the construction of an interstate connector highway (Interstate-495) just upstream of our study's first sampling site. Samples were collected at four sites from Interstate-495 (PB1 - 0 m) to the confluence with the main Paint Branch flowpath (PB4 - 1,160 m). Sampling was conducted at the same location during each LSS synoptic (Figure 2).

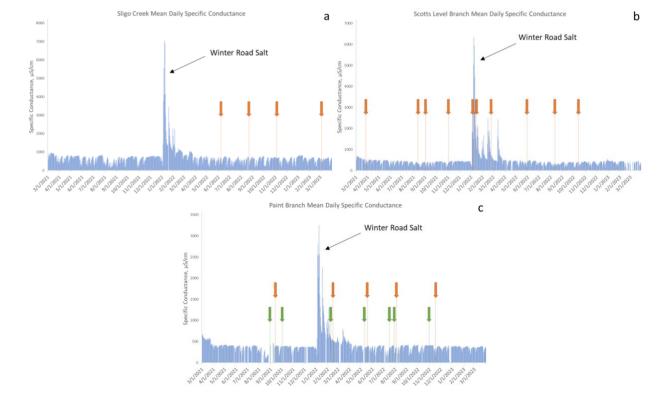
## <u>Campus Creek Watershed (Floodplain Reconnection with Regenerative Stormwater Conveyance</u> along Headwater Reach)

Campus Creek is another tributary of Paint Branch that intersects the main Paint Branch flowpath just upstream of sample site PB8 (3,509 m). Unlike Little Paint Branch, it experienced extensive engineering of its channel and the construction of RSCs (Kaushal et al., 2022; Wood et al., 2022). Campus Creek is a 1.4 km stream located in College Park, Maryland. Campus Creek's 1.8 km² watershed is the smallest of this study, flowing from the College Park Golf Course at the headwaters through the University of Maryland campus. The watershed has an average impervious surface cover of 24% and a forest cover of 23%. The restoration project at Campus Creek, completed in November 2019, was designed to address stormwater runoff and erosion of the stream channel (Carmichael, 2020). The project was sampled from sample site CC6 (0 m) through CC4 (610 m). The strategies used in this watershed included small wetland-like overflow areas, where runoff from heavy rainfall events could be temporarily stored, as well as the addition of regenerative stormwater conveyance (RSCs). This project spanned about 900 linear meters, over half of the watershed's flowpath, starting just downstream of its headwaters.

Samples were collected from seven sites spanning from the headwaters to the confluence with the main Paint Branch flowpath. Sample collection sites were spaced between 80-280 m apart and were primarily chosen based on access to the stream channel. Sampling was conducted at the same locations during each LSS monitoring campaign until July 2022 when a heavy storm made the site farthest downstream (CC0) inaccessible and sampling was moved twenty meters further downstream. Campus Creek was sampled four times during baseflow and three times during stormflow conditions; diurnal sampling was conducted five times and automated samplers were placed at sites CC6 (0 m), CC4 (610 m), and CC1 (1,180 m) or CC0 (1,390 m) (Table 2).

#### Longitudinal Stream Synoptic Monitoring

We conducted a survey of each stream and its floodplain to determine monitoring site locations along the flowpaths. LSS monitoring occurred primarily during baseline levels of specific conductance, although there was some LSS monitoring during winter road salt events, particularly at Scotts Level Branch (Figure 3b). Similar to other studies, many monitoring sites along the flowpaths were located upstream of road crossings or pedestrian bridges over the channels for easier access to the stream (Wayland et al., 2003). We collected all water samples from the stream channel at each site while monitoring longitudinally downstream. We collected grab samples in 125 mL bottles after rinsing in stream water three times. A Yellow Springs Instrument (YSI) ProQuatro multiparameter meter was used in conjunction with the grab sample to collect *in-situ* data for temperature, DO, conductivity, total dissolved solids (TDS), salinity, pH, and oxidation-reduction potential (ORP). The YSI handheld meter has an accuracy of  $\pm 0.1$  mg/L for DO,  $\pm 0.2$ °C, 0.001 mS/cm for conductivity,  $\pm 0.1$  ppt for salinity,  $\pm 0.2$ units for pH, and  $\pm 20$  mV for ORP (YSI, n.d.). When applicable, grab samples and field probe measurements (Online Resource 2-6) were collected at the same time as an automated sample collection. All longitudinal synoptic sampling events are listed in Table 2, while Figure 3 shows each synoptic event on a relative time scale plotted against specific conductance at that location. Orange and green arrows depict when repeated LSS monitoring campaigns were performed.



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Fig. 3 Mean daily specific conductivity measurements are provided by USGS gauges at each stream. Orange arrows depict when LSS monitoring campaigns were performed. The Paint Branch USGS gauge is not located along the repeated LSS monitoring flowpath but is included to show seasonal patterns similar to the other watersheds (c). Campus Creek does not have a USGS gauge along its flowpath, so green arrows depict Campus Creek repeated LSS monitoring campaigns

#### Diurnal Sampling Along Stream Flowpaths During Baseflow and Storms

We deployed Teledyne ISCO portable automated samplers at select monitoring sites along the flowpath to collect samples on a diurnal cycle to characterize baseflow conditions and capture brief storm events (Table 2). Automated samplers were programmed to collect one sample every hour for a full twenty-four-hour diurnal cycle. The measured diurnal cycle usually started the day of or the day before the longitudinal sampling. If more than one automated sampler was deployed in nearby streams, they were all programmed to collect samples simultaneously. At the end of the diurnal cycle, samples collected by the automated samplers were transferred to 125 mL bottles and filtered in the lab.

#### External Datasets

Aside from field data collection, multiple resources were used to collect additional watershed information. The USGS database provided changes in stream conditions over time, such as discharge and specific conductance, *via* stream gauge data collection, as well as geologic maps of Maryland and spatial analytical tools through StreamStats (U.S. Geological Survey, 2019). USGS stream gauge data were used to supplement high density collection for discharge and specific conductance measurements. StreamStats was used to determine approximate land use percentages for forest cover and impervious surface cover in each watershed. The Maryland Topography Viewer, provided through the Maryland Mapping & GIS Data Portal, was used to determine site elevations. Precipitation data were obtained through Parameter-elevation Regressions on Independent Slopes Model (PRISM) which is based on the National Weather Service (NWS) data (Online Resource 1).

#### Discharge Measurements and Calculations

Three of the five watersheds (Sligo Creek, Scotts Level Branch and Paint Branch) have USGS gauges and high-frequency sensors for monitoring continuous water quality. USGS stream gauges collect data every five minutes (U.S. Geological Survey, 2016). The gauges at Sligo Creek (USGS Gauge 01650800 near Takoma Park, MD) and Paint Branch (USGS Gauge 01649190 near College Park, MD) measure gauge height (ft), discharge (cfs), DO (mg/L), pH, specific conductance (µS/cm at 25 °C), temperature (°C), and turbidity (FNU). The stream gauge at Scotts Level Branch (USGS Gauge 01589290

at Rockdale, MD) measures the same parameters, minus DO. Discharge measurements used in this study are average daily discharge, maximum peak discharge, and average annual discharge. The gauges at Sligo Creek and Scotts Level Branch are located along flowpaths evaluated in this study. The Paint Branch gauge is near, but outside, our monitored flowpath. Additional discharge measurements were performed at Scotts Level Branch during a longitudinal synoptic (March of 2021) to explore the role of hydrologic factors on changes in chemical concentrations and loads along the flowpath.

Longitudinal discharge measurements were performed at Scotts Level Branch during March 2021. At each synoptic site along the longitudinal flowpath, stream velocity measurements were collected with a Hach FH950 Portable Flow Meter System to calculate discharge, and channel width and depth measurements were collected to build cross-sectional plots. Relationships between stream chemistry and discharge with respect to longitudinal distance from headwaters were assessed. Cross-sectional velocity measurement locations were chosen at each site by considering accessibility of the stream in that area of the flowpath. For each discharge measurement, total stream width was measured, followed by incremental depth and velocity measurements to determine discharge and cross-sectional topography (similar to Kaushal et al., 2014, Kaushal et al., 2023, Newcomer-Johnson et al., 2014, and Sivrichi et al., 2011). A velocity measurement taken at two-thirds depth was used to calculate stream discharge (Holmes et al., 2001).

#### Sample Processing and Water Chemistry Analyses

Laboratory methods for sample processing and elemental analyses followed those described in Galella et al. (2021), Haq et al. (2018), Kaushal et al. (2019), and Maas et al. (2023). Samples were usually processed and prepped for analysis within 24 hours. Each sample was pumped through pre-ashed 0.7 µm glass fiber filters using a vacuum. Sample bottles were triple rinsed in deionized water and filters were replaced between each sample to prevent cross contamination. 30 mL of each filtered sample was acidified to 0.5% using ultra-pure nitric acid to prevent biological activity and flocculation between particles within the sample.

Non-acidified samples were frozen until analyzed on a Total Organic Carbon Analyzer (TOC-L; Shimadzu, Columbia, Maryland) to measure total dissolved nitrogen (TDN) and dissolved organic carbon (DOC). Samples were injected in the TOC-L with hydrochloric acid (HCl) to transform inorganic carbon into carbon dioxide. The organic carbon content was calculated by subtracting the inorganic carbon from the total carbon in the sample. Total dissolved nitrogen concentrations were calculated by combusting each sample and passing it through a non-dispersive infrared detector (Galella et al., 2023; Haq et al., 2018; Maas et al., 2023; Wood et al., 2022). The TOC-L has a detection limit of  $4 \mu g/L$  for carbon

measurements and 5 μg/L for nitrogen measurements, and a maximum reproducibility coefficient of variation of 1.5% (*Total Organic Carbon Analyzer*, 2011). We recognize that manufacturer-stated uncertainties may not always be achievable in real applications due to potential matrix effects sometimes. However, all laboratory analyses in this project use standards methods, and all laboratory protocols and methods have been approved as Quality Assurance/Quality Control Plans by the U.S. Environmental Protection Agency (Galella et al., 2020; Shelton et al., 2023). All standards analyzed as samples were within 10% of true values of commercially certified standard values (Galella et al., 2020; Shelton et al., 2023). All samples in this project were considerably elevated above the detection limits of measurement.

Acidified samples were analyzed via inductively coupled plasma optical emissions spectrometer (ICP-OES) using a Shimadzu Elemental Spectrometer (ICPE-9800, Shimadzu, Columbia, Maryland, USA) to measure base cation (Ca<sup>2+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>) and other elemental (B, Ba<sup>2+</sup>, Cu, Fe, Mn, S, and Sr<sup>2+</sup>) concentrations. Comparisons to external commercial check standards were used to assess instrument accuracy. All standards analyzed as samples were within 10% of true values of commercially certified standard values (Galella et al., 2020; Shelton et al., 2023). As reported by the manufacturer, the ICP-OES has uncertainties of 0.6, 10, 0.6, and 0.6 μg/mL for Ca<sup>2+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, and Na<sup>+</sup>, respectively (Sellers, 2014).

As mentioned above, all measured values in urban polluted streams were considerably elevated above the detection limits. All analytical methods followed those described in US Environmental Protection Agency Quality Assurance Plans and followed in previous studies (Galella et al., 2021; Galella et al., 2023; Shelton et al., 2023).

#### Statistical Analyses

Linear regression was used to explore relationships between chemical concentrations and distance downstream. Each watershed provided a natural experiment, in which we could compare the differences in linear regressions between restored and unrestored stream reaches. Separate models were developed for flowpaths through restoration or forest features and flowpaths through degraded conditions or increasing impervious surface cover. Linear regression calculations were performed using MATLAB version R2022b. We determined statistical confidence of linear trends as having p-values less than 0.05.

Principal component analysis (PCA) was used to investigate dominant patterns in water chemistry across temporal and spatial scales. All data collected from LSS monitoring were pooled for each individual stream so that PCA could be performed on a stream-by-stream basis. Data from LSS monitoring were standardized by subtracting the mean and dividing by the standard deviation of each parameter (Gelman, 2008). A stopping rule comparable to the Rand-Lamda rule defined by Peres-Neto et al. (2005) was used to determine how many PC modes to interpret. Only principal components that

revealed significantly higher variance than expected due to chance at a p < 0.05 level (Rippy et al., 2017) were retained and interpreted in our analysis. Any missing data values due to sample handling or instrument detection limits were estimated using the minimum value of that parameter. PCA results were displayed in three ways to highlight different factors that might influence dominant patterns in water chemistry; (1) by LSS sampling campaign date (differences by season), (2) by baseflow/stormflow responses (differences by flow condition), and (3) by surrounding land use/land cover (differences by degree of urbanization). PCA calculations were performed in R-studio using FactoMineR (Lê et al., 2008) and factoextra (Kassambara & Mundt, 2017) packages.

#### Results

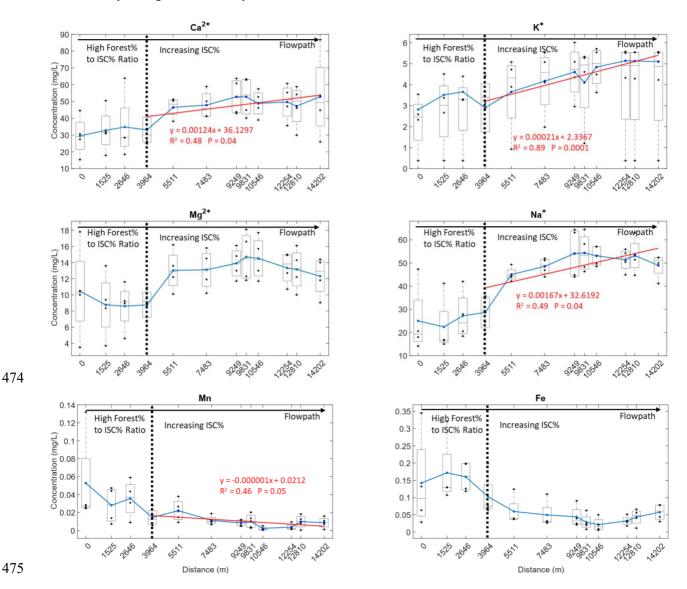
#### Longitudinal Patterns in Streamwater Chemistry Along Watershed Flowpaths

Patterns of salt ion concentrations and redox-sensitive reactions were explored as biogeochemical indicators of hydrologic connectivity. Previous studies have shown that hydrologic connectivity would be linked to longitudinally decreasing salt ion (Ca<sup>2+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>) trends due to dilution and retention on ion exchange sites in soils and sediments (Galella et al., 2023; Kaushal et al., 2022). Following those studies, we also expected Fe, Mn, and sulfate (SO<sub>4</sub><sup>2-</sup>) reduction, suggesting increased redox reactions, and increases in dissolved Fe and Mn concentrations with decreases in elemental S in response to decreased redox potentials. In addition, we expected an inverse relationship between DOC and TDN in some stream reaches, which could suggest denitrification (Forshay et al., 2022; Mayer et al., 2010; Taylor & Townsend 2010) where hydrologic connectivity was greater.

#### Sligo Creek Watershed (Minimal Floodplain Reconnection and High Impervious Surface Cover)

There were distinct patterns in longitudinal water quality along different stream flowpaths that appeared to be influenced by stream restoration features and surrounding land use. For example, there were increasing trends in base cation concentrations from headwaters to confluence at Sligo Creek, likely influenced by surrounding land use (Figure 4). In the reaches of Sligo Creek draining land use with less impervious surface cover, base cations of Ca<sup>2+</sup>, Na<sup>+</sup>, and K<sup>+</sup> increased significantly (p<0.05) at rates of 1.00, 1.14, and 0.04 mg/L per km downstream, respectively. Mg<sup>2+</sup> decreased at a rate of 0.42 mg/L per km at this reach of the flowpath. In the reaches of Sligo Creek draining land use with increasing impervious surface, all base cations increased significantly (p<0.05) at 1.24, 1.67, and 0.21 mg/L per km downstream for Ca<sup>2+</sup>, Na<sup>+</sup>, and K<sup>+</sup>, respectively. Overall, the rates of base cations increased in the two segments of Sligo Creek and were greater where there was more impervious surface cover suggesting low retention in groundwater and therefore poor hydrologic connectivity along the flowpath. Fe and Mn

concentrations decreased along Sligo Creek's entire flowpath (Figure 4), which is tied to decreasing DO levels along the flowpath (Figure 5d) and further indicating changes in surrounding land use and decreased hydrologic connectivity.



**Fig. 4** Longitudinal variations in  $Ca^{2+}$ ,  $K^+$ ,  $Mg^{2+}$ ,  $Na^+$ , and dissolved Mn and Fe at Sligo Creek. The area to the left of the dashed line represents a high forest cover to impervious surface cover ratio; the area to the right represents a lower forest cover to impervious surface cover ratio. The arrow represents the direction of flow at Sligo Creek. Blue lines represent data averages for each stream sampling site. Red lines represent significant patterns in the data

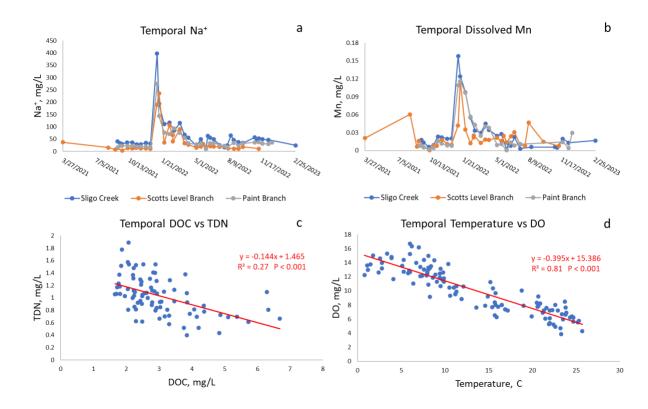
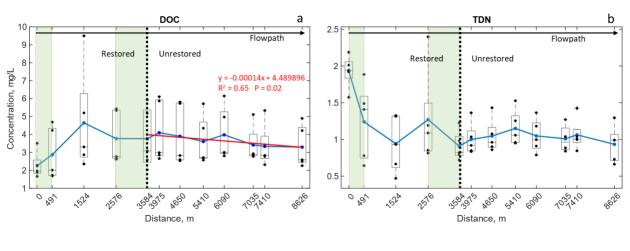


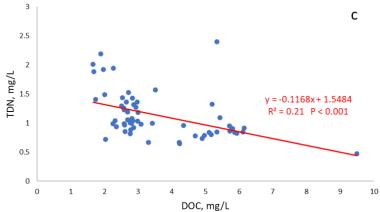
Fig. 5 Biweekly temporal concentrations of Na<sup>+</sup> (a) and dissolved Mn (b) at Sligo Creek, Scotts Level Branch, and Paint Branch. Cumulative biweekly DOC and TDN (c) and temperature and DO (d) relationships at Sligo Creek, Scotts Level Branch, and Paint Branch. Streamwater samples were collected biweekly via grab sample at fixed locations along each flowpath. Fixed sampling locations corresponded with USGS gauges in the Sligo Creek and Scotts Level Branch watersheds. Grab samples collected at Paint Branch were not collected at the USGS site, but they were collected at the same location biweekly

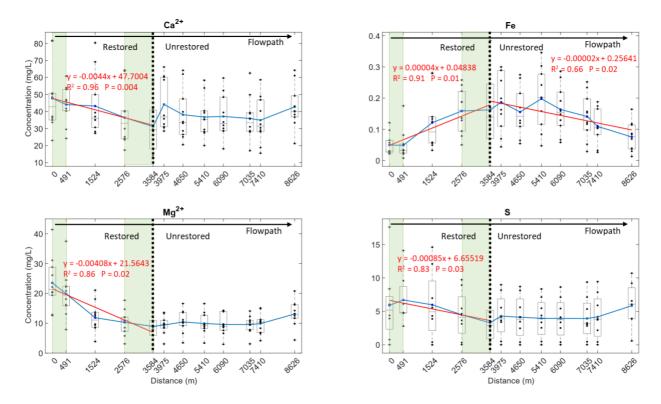
#### Scotts Level Branch Watershed (Floodplain Reconnection Along Headwater Reaches)

 Total dissolved nitrogen (TDN) decreased between both restored reaches at Scotts Level Branch, while dissolved organic carbon increased, but there were few statistically significant trends (Figure 6). Linear regression of dissolved organic carbon (DOC) of the trend along the flow path revealed a significant decrease below the restored reach of the flowpath ( $R^2 = 0.645$ , F(1,6) = 10.9, p<0.05). We observed an inverse relationship between DOC and TDN at Scotts Level Branch (Figure 6c), suggesting increased denitrification in restored reaches and indicating increased hydrologic connectivity. There were significant (p<0.05) decreasing linear trends of 4.40 and 4.41 mg/L per km downstream in base cations  $Ca^{2+}$  and  $Mg^{2+}$ , respectively, in the restored reach (Figure 7a,b). Decreasing linear trends in base cations in restored reaches suggest that there is dilution or retention within the floodplain as water moves through

the restored reach. Conversely, there were no significant linear relationships in base cation concentrations along the unrestored reaches of Scotts Level Branch; there appeared to be a plateau and stabilization in chemical concentrations through these unrestored stream reaches (Figure 7). Stable forest and impervious surface cover percentages after sampling site SLB6 (3975 m), as well as the introduction of Scotts Level Park at site SLB7 (4650 m), appeared to influence steady state concentrations of some chemicals along the unrestored segment of the flowpath. S and Fe are redox-sensitive elements that can reflect the amount of DO in the stream. A significant (p<0.05) decreasing trend in S and a significant (p<0.05) increasing trend in Fe in the restored reach (Figure 7c,d) reflects a lower DO in the stream water from slower flows due to stream restoration. Elemental S concentrations increase below restored reaches while Fe significantly decreases, which potentially reflects less floodplain reconnection along the unrestored flowpath.







**Fig.** 7 Longitudinal variations in  $Ca^{2+}$ ,  $Mg^{2+}$ , and dissolved Fe and S at Scotts Level Branch. The area to the left of the dashed line represents the restored reach of flowpath; the area to the right represents the unrestored reach of flowpath. The arrow represents the direction of flow at Scotts Level Branch

Discharge measurements at Scotts Level Branch were taken once during baseflow conditions three days after a storm event. Linear regressions show that discharge and stream velocity had increasing trends between the restored reaches ( $R^2 = 0.93$ , F(1,3) = 39.2, p < 0.001) and also along the unrestored reaches ( $R^2 = 0.944$ , F(1,5) = 79.6, p < 0.01) (Figure 8a). All four base cations ( $Ca^{2+}$ ,  $K^+$ ,  $Mg^{2+}$ ,  $Na^+$ ) decreased in concentration from headwaters to confluence (Figure 8b).  $Na^+$  peaked at the third sampling site within an unrestored reach and decreased along the flowpath. Using the longitudinal discharge and longitudinal base cation concentrations, the longitudinal base cation mean daily loads were calculated and plotted against the distance downstream (Figure 8c). Mean daily loads increased along the flowpath, with  $Ca^{2+}$  and  $Na^+$  reaching around 380 and 340 kg/day, respectively.  $K^+$  had a comparatively much smaller mean daily load, likely because it is a biologically available nutrient to plants (Tripler et al., 2006). When normalized to basin area and discharge, we observed that export of salt ions did not follow the same

pattern as stream discharge (Figure 8d). Stable export between restoration features suggests that there is retention of salt ions and that the longitudinal patterns in loads are not just hydrologically driven.

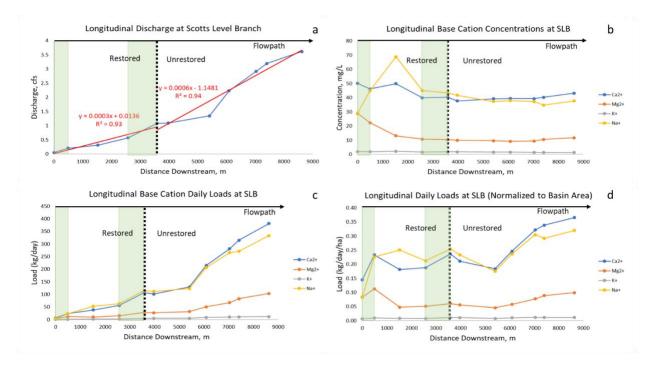


Fig. 8 Longitudinal discharge measurements (a), base cation concentrations (b), daily load of base cations (c), and daily load of base cations normalized to basin area (d) plotted against distance downstream at Scotts Level Branch

# <u>Paint Branch Watershed: Campus Creek Watershed (Floodplain Reconnection with Regenerative Stormwater Conveyance along Headwater Reach)</u>

Along Campus Creek, concentrations of all four base cations plateaued in the stream reach, draining the restoration project with RSCs, but increased (p<0.05) in the degraded, unrestored reach downstream of the restoration area (Figure 9). Ca<sup>2+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, and Na<sup>+</sup> increased by 8.63, 0.95, 3.53, and 22.7 mg/L per km downstream in the degraded, unrestored reach of Campus Creek, respectively. There was also less variability in chemical concentrations along the restored reach than the unrestored reach. Concentrations of base cations were steady within the RSCs of the restored reach, while there was a significant increase in base cations further downstream in the unrestored reach. Fe and Mn concentrations increased throughout the restored reach, followed by a decrease in Fe and a significant (p<0.05) decrease in Mn through the degraded, unrestored reach (Figure 9). Consistent with longitudinal patterns observed at Sligo Creek and Scotts Level Branch, the increasing trends in dissolved Fe and Mn concentrations

suggest increased hydrologic connectivity through Campus Creek's RSCs. Previous work at this same site has shown that concentrations of DO declined through the RSCs at Campus Creek, sometimes to levels undetectable by the instrument, which enhance conditions for Fe and Mn reduction and increased concentrations of Fe and Mn in these restoration features (Kaushal et al., 2023).

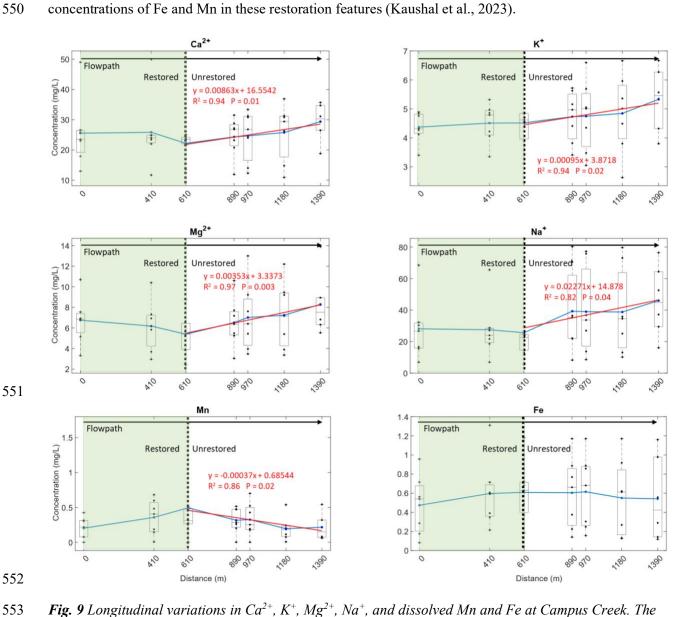


Fig. 9 Longitudinal variations in  $Ca^{2+}$ ,  $K^+$ ,  $Mg^{2+}$ ,  $Na^+$ , and dissolved Mn and Fe at Campus Creek. The area to the left of the dashed line represents the restored reach of flowpath; the area to the right represents the unrestored reach of flowpath. The arrow represents the direction of flow at Campus Creek

#### Paint Branch Watershed: Little Paint Branch (Natural Floodplain Reconnection)

Paint Branch and the Little Paint Branch tributary offer a comparison between a tributary and mainstem chemistry. The mainstem Paint branch shows significantly (p<0.05) increasing Na+ and decreasing Fe. These patterns are not found along the Little Paint Branch tributary (Figure 10a,b). If consistent with other watersheds in this study, the increasing Na+ and decreasing Fe found along Paint Branch may suggest that it has poor hydrologic connectivity with its floodplain, despite being a restored reach. The reach along the Paint Branch mainstem sampled with repeated LSS monitoring was relatively small compared to the watershed-scale length of the Paint Branch flowpath (22 km in length).

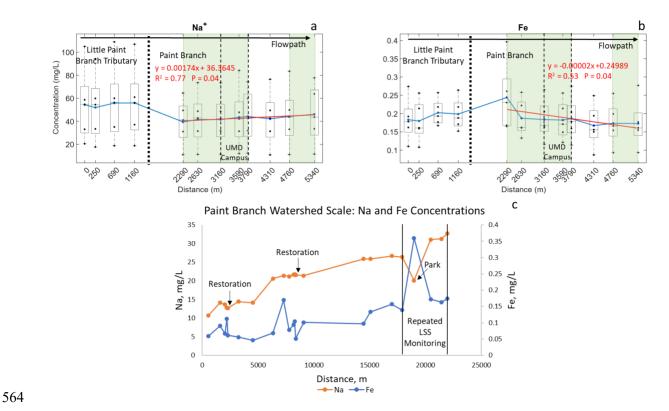


Fig. 10 Longitudinal variations in Na<sup>+</sup> and dissolved Fe at Paint Branch (a). Na<sup>+</sup> and dissolved Fe concentrations at Paint Branch at the full watershed scale (b). The area to the left of the dashed line represents the Little Paint Branch flowpath; the area to the right represents the main Paint Branch flowpath. The arrow represents the direction of flow through these watersheds. Vertical solid black lines represent similar sampling sites between the repeated LSS monitoring sites and the entire watershed-scale sampling sites (c). Parks and restorations along the Paint Branch flowpath are indicated

#### Differences in Chemical Cocktails Across Seasons and Sampling Locations

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PCA biplots allow us to visualize dominant patterns in chemical constituents in various watersheds. Here we can visualize the patterns that exist in the compositions of chemical mixtures of salt, metals, and nutrients and seeing the extent to which they have spatial or temporal signatures that are consistent with changes in land use, storm events, and seasons in urban streams (Figure 11). We do not show the full potential of PCA to analyze all the different analytes possible and how all chemical cocktails shift along longitudinal stream synoptic flowpaths; further examples of this are described in Kaushal et al. (2023b), Maas et al. (2023), and elsewhere (e.g., Byrne et al., 2017). Instead, we explore a few case studies illustrating that the combination of LSS monitoring and PCA can be a useful approach to detect how entire chemical mixtures and groups of elements shift in response to stream restoration and management along flowpaths. For example, the five LSS monitoring events along the Paint Branch flowpath appear as clusters in the PCA biplot (Figure 11a), showing that the average chemical cocktail of the watershed changes depending on the time of year. At Scotts Level Branch, monitoring occurred at least twice during baseflow, stormflow, and road salting events in the watershed. A PCA biplot shows the importance of monitoring a stream during these various weather events, as distinct clusters in chemical cocktails can be seen depending on the flow intensity and introduction of road salts to the watershed (Figure 11b). Finally, there was a difference in stream chemistry at Sligo Creek based on surrounding land use/land cover along the flowpath, emphasizing the importance of sampling at multiple locations along the flowpath (Figure 11c). Along Sligo Creek, sampling sites with a higher ratio of forest cover to impervious surface cover had a stream water chemical composition different from sites draining a lower ratio of forest cover to impervious surface cover.

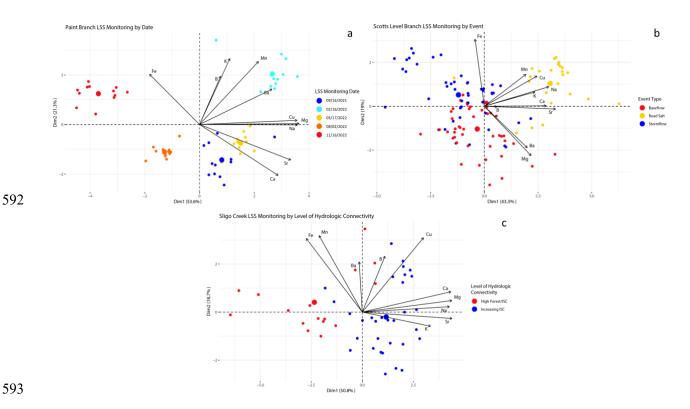


Fig. 11 PCA biplots of LSS monitoring data categorized by monitoring campaign at Paint Branch (a), baseflow, stormflow, and road salt events at Scotts Level Branch (b), and level of hydrologic connectivity at Sligo Creek to show differences in chemical cocktails based on those factors. Larger points on each biplot represent the average data point for each cluster

# Flashy Variations in Chemistry due to Stormflow Conditions at Sligo Creek and Paint Branch

In order to investigate flashiness of streamwater chemistry due to stormflow, Sligo Creek and Paint Branch were sampled hourly over 24 hours (Figure 12). Baseflow conditions were sampled at least three days following a storm event to allow the stream to recover. There was relatively little variation in chemical concentrations during baseflow conditions compared to stormflow conditions. However, stormflow showed large fluctuations, or flashiness, in chemical concentrations. For example, the storm event captured in the headwaters of Sligo Creek showed a dilution in base cations in response to a heavy influx of runoff (Figure 12a). Baseflow concentrations, captured between sampling times 10:00 AM and 2:00 AM, are generally stable until the storm event begins after 2:00 AM. The quick salt ion dilution is followed shortly after by the beginning of a recovery period (Reisinger et al., 2017), where concentrations can be observed rising back to baseflow conditions. Hourly concentrations of base cations at Paint Branch

showed a dilution during a heavy rainstorm during the same evening when the automated stream sampler was deployed but rebounded quickly after the storm (Figure 12b). Diurnal samples collected at Paint Branch were also measured for dissolved inorganic carbon (DIC), DOC, and TDN (Figure 12c). In contrast to the dilution observed in salt ion concentrations due to the storm event, carbon and nitrogen experienced a pulse in concentrations likely due to hydrologic flushing of nonpoint pollution sources within the watershed.

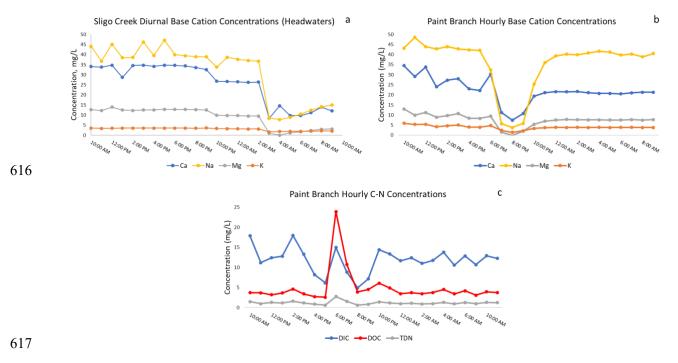


Fig. 12 Base cation concentrations of hourly samples taken after a storm event at Sligo Creek (a) and during a different storm event at Paint Branch (b). Carbon and nitrogen concentrations collected from the same storm event at Paint Branch (c). Dashed black lines depict where the effects due to storms are first observed

#### Discussion

This study investigates longitudinal patterns in the transport of nutrients, salt ions, dissolved organic matter, and metals along restored flowpaths to provide further insights into whether restoration can influence different chemical cocktails. We found that repeated LSS monitoring can be used to detect changes in stream chemistry at varying spatial and temporal scales in response to stream-floodplain connection. Hydrologic connectivity can be linked to longitudinally decreasing salt ion trends, increased

concentrations of redox sensitive elements (dissolved Fe and Mn), and relationships between carbon and nitrogen indicating denitrification. We also found that in general, stream reaches with restored flowpaths by means of stream-floodplain reconnection show more geochemical indicators of hydrologic connectivity (changes in Fe, Mn, S, C, N) than stream reaches with minimal to no restoration strategies. Periods of baseflow and stormflow, as well as seasonal road salting events, can result in different chemical cocktails longitudinally along flowpaths and over time.

There are many considerations and challenges when monitoring and evaluating the effectiveness of stream restoration projects. Each stream restoration project may be unique, and there can be variability in stream restoration responses not only among sites but also variability along stream reaches within the same restoration project (Kaushal et al., 2008, 2023b; Sivirichi et al., 2011). Varying spatial and temporal scales of monitoring can impact perceptions of positive and negative outcomes for both biological and water quality responses (Griffith & McManus, 2020; Kaushal et al., 2023b). Although most work has focused on analyzing changes in urban water quality over time, there is growing work investigating how water quality changes along urban stream flowpaths (*e.g.*, Deemy & Rasmussen, 2017; Duan et al., 2019; Fernald et al., 2006; Kaushal & Belt, 2012; Kaushal et al., 2014b; Lintern et al., 2018; Newcomer Johnson et al., 2014; Pennino et al., 2016b; Smith et al., 2017; Welty et al., 2023). Analysis of spatial patterns in water quality represents a research frontier in hydrological sciences (Lintern et al., 2018).

Similarly, many studies evaluating the effects of stream restoration on water quality have focused on N because of the impacts associated with eutrophication, but more work also needs to holistically consider the fate and transport of salt ions, organic matter, and metals (Galella et al., 2023; Kaushal et al., 2018b, 2022, 2020; Morel et al., 2020). For example, freshwater salinization is increasingly recognized as an urban water quality issue, and major ions in urban streams can be significantly greater than in agricultural and forest streams, with road salt and chemical weathering of impervious surfaces suggested as potential sources (Kaushal et al., 2017). Less work has focused on understanding mechanisms of salt retention along flowpaths (Oswald et al., 2019), but stream restoration involving floodplain reconnection may have the potential to retain salt ions within limits (Cooper et al., 2014; Kaushal et al., 2022; Maas et al., 2021, 2023). Changes in concentrations of redox sensitive elements like Fe, Mn, S, and N may be valuable indicators of localized inputs of subsurface groundwater to streams or the effects of associated wetlands with lower levels of DO (*e.g.*, Kaushal et al., 2023c, 2014b; Lautz & Fanelli, 2008; Sharma et al., 2022).

#### Biogeochemical and Hydrological Processes that Influence Chemical Cocktails

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Our results showed that the base cations (Ca<sup>2+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, and Na<sup>+</sup>) tend to decrease along restored reaches. Recent work shows that stream restoration and stormwater management have the potential to retain different salt ions (Galella et al., 2023; Kaushal et al., 2023c, 2022). Ion exchange and dilution are the two main mechanisms for decreasing salt ions in restored stream reaches which have enhanced hydrologic connectivity with floodplains (Galella et al., 2023; Kaushal et al., 2022; Maas et al., 2023). Engineering floodplains to increase meanders, riffles, and pools can increase hydrologic exchange (Bukaveckas, 2007; Kasahara & Hill, 2006; Kaushal et al., 2008; Klocker et al., 2009). These engineered features can increase the sinuosity and length of the stream channel, leading to enhanced hyporheic exchange and a longer residence time for water within the stream (Bukaveckas, 2007; Kasahara & Hill, 2006). As water moves slowly through the restored stream reach, it has more contact time with the streambed, enhancing opportunities for ion exchange processes to occur between the water and the sediments or biofilms present (Bukaveckas, 2007; Klocker et al., 2009). Stream sediments can also act as a reservoir for salt ions through ion exchange and influence water quality (Kaushal et al., 2023b.c., 2022; Maas et al., 2023). Stream restoration efforts may focus on managing sediment inputs and transport and introduce geologic substrates and expose soils with the capacity for ion exchange. Sediment management strategies, such as stabilizing eroding stream banks or installing sediment traps, may promote ion exchange in streams. Hyporheic exchange may also increase opportunities for ion exchange and retention along flowpaths (Kaushal et al., 2022). Slowing water flow can also increase the opportunity for dilution by allowing additional water to mix with the saline stream water, thereby reducing salt ion concentrations (Kaushal et al., 2022; Maas et al., 2021, 2023).

Stream restoration projects that incorporate floodplain reconnection, wetland creation, or the addition of woody debris can enhance nutrient cycling and biogeochemical processes (Harrison et al., 2012b; Kaushal et al., 2008; Newcomer Johnson et al., 2014, 2016; Passeport et al., 2013). Stream restoration often involves the re-establishment of riparian vegetation, which plays a critical role in ion exchange processes as well as the movement of water throughout the floodplain. Restoration can also involve construction activities that disrupt riparian soils and vegetation leading to pulses of nutrients, major ions, and metals in ground water and streams (Kaushal et al., 2022; Wood et al., 2022). The roots of riparian vegetation can release organic acids and other compounds that alter the chemistry of the surrounding soil and stream water, influencing ion exchange reactions (Dosskey et al., 2010; Gift et al., 2010; Miller et al., 2016). Additionally, organic matter inputs from vegetation and leaf litter contribute to the development of biofilms and microbial communities on streambed surfaces (Romaní et al., 2013). These biofilms can promote denitrification and ion exchange by providing organic surfaces for ion

adsorption and facilitating microbial-mediated transformations (Groffman et al., 2005; Kapoor & Viraraghavan, 1997; Xu et al., 2022). A discussion of whether the cumulative effects of stream restoration on longitudinal biogeochemical patterns and processes can be detected is explored further in our case studies and comparisons below.

#### Restoration Strategies May Influence Longitudinal Patterns of Streamwater Chemistry

Scotts Level Branch and Sligo Creek are two watersheds within 40 miles of each other on Maryland's Piedmont plateau and are comparable in watershed size, land use, and hydrologic characteristics. Thus, differences in longitudinal patterns in chemical concentrations between Sligo Creek and Scotts Level Branch may be strongly influenced by differences in management along the stream valley (a combination of surrounding riparian management, land use, or stream-floodplain restoration activities).

The Sligo Creek and Scotts Level Branch watersheds showed contrasting longitudinal patterns of base salt cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>). Base cation concentrations at Sligo Creek generally increase downstream along the flowpath. Conversely, Scotts Level Branch showed attenuation of base cation concentrations downstream, along with a general decrease in concentrations through the restored areas along the flowpath. There was a significant (p<0.05) inverse relationship between longitudinal concentrations of DOC and TDN along both streams (Online Resource 7) that could be due to denitrification (Mayer et al., 2010; Taylor & Townsend 2010) and/or biological uptake and transformation of N to organic matter (Kaushal et al., 2014a). There were strong, significant (p<0.05) longitudinal increases in dissolved Fe and decreases in S concentrations along restoration features at Scotts Level Branch likely due to floodplain reconnection, decreased DO in groundwater, and Fe and SO<sub>4</sub><sup>2</sup> reduction. In contrast, Sligo Creek showed no patterns in Fe and Mn, suggesting lower degrees of stream-floodplain connection. These differences in streamwater quality may be due to stream-floodplain reconnection at Scotts Level Branch and the lack of a comparable restoration approach at Sligo Creek. The decreased hydrologic connectivity between the floodplain and Sligo Creek due to a narrow and highly urbanized stream corridor and a focus on bank stabilization approaches and armoring could be one factor explaining multiple differences in longitudinal patterns of chemical concentrations along the flowpath.

Detecting Impacts of Engineered Floodplain Reconnection on Longitudinal Water

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Campus Creek has the highest degree of engineered stream-floodplain connection in this study via the RSC construction. There were significant increases in Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, and K<sup>+</sup> in the degraded

reach, but not in the upstream restored reach. Previous work has shown that there can be substantial retention of salt ions in the restored reach of Campus Creek likely due to base cation exchange (Kaushal et al., 2022). There is also likely dilution of salt ions in the RSC systems (Kaushal et al., 2022). The combination of retention and dilution processes may be enhanced by stream-floodplain reconnection in smaller upstream reaches, but there may be a limited capacity for contaminant retention processes in downstream reaches with higher peak flows. Base cation concentrations measured at Campus Creek during longitudinal monitoring were comparable to previous studies (Kaushal et al., 2022; Wood et al., 2022). Previous work at Campus Creek has also shown that there can be a longitudinal increase in dissolved Fe and Mn in the RSCs, as well as a significant relationship between dissolved Fe and Mn concentrations and riparian buffer width along the flowpath (Kaushal et al., 2023a).

#### Effects of Hydrologic Variability and Seasonality on Urban Chemical Cocktails

Fluctuations in streamflow and seasonal pollution events can result in varied chemical cocktails. PCA shows the differences in chemical cocktails during periods of baseflow, stormflow, and in response to road salting events in the Scotts Level Branch watershed (Figure 11). Sudden increases in streamflow due to storm events can dramatically change concentrations of base cations, DOC, and TDN along the flowpath (Figure 12). Under certain conditions, both natural and engineered systems can be overwhelmed by storm and road salting events, potentially resulting in either dilution of ions or pulses of contaminants. Annual wet and dry periods will also impact chemical cocktail concentrations in stream water, as observed at Paint Branch (Figure 11a). In general, less is known about diurnal cycles of water chemistry and the impacts of storms on elemental chemistry along small urban streams; there may be substantial fluctuations in some chemical concentrations throughout the day and night (Kaushal et al., 2020). For example, one study monitored a river in southwest Germany every 15 minutes for 355 days to explore diurnal patterns in nitrate and concluded that diurnal variability was caused by in-stream processes (Greiwe et al., 2021). Another study found significant changes in concentrations of nitrate, base cations, and other major anions at the Montousse catchment at Aurade in southwest France over sampling periods of hours to decades (Ponnou-Delaffon et al., 2020). In this study, there were large diurnal fluctuations in stream chemistry during storm events compared to baseflow, which suggests that pollution events may also have an important impact on longitudinal transport and transformation of chemicals.

There were distinct seasonal patterns in chemical concentrations in the watersheds reflecting the effects of dominant processes such as road salting during winter months, biogeochemical transformations, and changes in seasonal baseflow. For example, there were large seasonal variations in specific conductance during the sampling period with seasonal pulses in specific conductance during winter months when road salts were applied (Figure 3). Mean daily specific conductance also fluctuated during

non-winter months, usually due to changes in streamflow and storm events. There were also peaks in concentrations of Na<sup>+</sup> and Mn in all streams during winter months coinciding with winter road salting events (Figure 5a,b). There were significant inverse relationships between DOC and TDN in all streams over time (Figure 5c), reflecting the importance of biogeochemical reactions such as denitrification, uptake of nitrogen, and primary production of organic carbon (Kaushal et al., 2014b). Similarly, there were significant inverse relationships between water temperature and DO in all streams over time (Figure 5d). Peaks in Na<sup>+</sup> and Mn can be indicative of road salts entering the stream in all three watersheds (Galella et al., 2021). Mn and other metals can be mobilized by road salt events due to ion exchange, sodium dispersion of organic matter and release of sorbed and complexed metals, and other biogeochemical processes (Galella et al., 2021; Kaushal et al., 2019). Overall, seasonal cycles appeared to be consistent across sites, although the peaks and persistence of chemical concentrations varied.

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Influence of Natural Floodplain Reconnection on Longitudinal Patterns in Streamwater Chemistry and Redox Sensitive Elements as Indicators of Hydrologic Connectivity

Redox-sensitive elements have been used as indicators of hyporheic exchange in wetlands (Briggs et al., 2013; Hoagland et al., 2020; Soils, 2002). In saturated soils under low DO conditions, Fe, Mn, S, and N are reduced to forms available for anaerobic microbial respiration (Mayer et al., 2010), whereas redox-sensitive metals form particulates in unsaturated soils (D'Amore et al., 2004; Ou et al., 2019). In restored streams, redox conditions influence the oxidation and reduction of redox-sensitive metals. For example, under aerobic conditions, Fe and Mn tend to be present in their oxidized forms (Fe<sup>3+</sup> and Mn<sup>4+</sup>), which are less soluble and tend to precipitate as solid particles. In hydrologically connected systems, as oxic surface water flows into hypoxic and anoxic groundwater, redox-sensitive elements, such as Fe and Mn, become electron acceptors and reduce to more soluble forms. This in turn increases the concentrations of redox-sensitive Fe and Mn in the surface water. Conversely, under hypoxic and anoxic conditions, these metals are reduced to more soluble forms (Fe<sup>2+</sup> and Mn<sup>2+</sup>), which can stay dissolved in the water column and increase dissolved Fe and Mn concentrations. Therefore, a stream that is hydrologically connected with its floodplain allows for greater surface water-groundwater interactions and potentially higher subsurface DO. Restoring a hydrologic connection is a goal of many stream restoration efforts (Feng et al., 2022), but evaluating whether hydrologic connectivity is actually achieved may be complex and challenging. Results from this study suggest measurements of redox-sensitive elements may serve as geochemical indicators of hydrologic connectivity that improve our ability to understand groundwater-surface water interactions along restored streams.

### Effects of Watershed Spatial Scales on Detecting Longitudinal Patterns in Chemical Concentrations

Unlike the other stream reaches, longitudinal patterns in chemical concentrations were difficult to detect along Paint Branch when conducting repeated LSS monitoring over relatively smaller spatial scales. Interestingly, the smaller scale restoration project along Paint Branch near the University of Maryland campus actually showed that there was minimal hydrologic connectivity when analyzing geochemical indicators. For example, there was a longitudinal increase in Na<sup>+</sup> and decrease in dissolved Fe concentrations. These longitudinal trends in geochemical indicators underscore the notion that not all stream restoration projects will show positive signs of hydrologic connectivity. However, there were clear increases in Na<sup>+</sup> and dissolved Fe concentrations in restoration projects and conservation areas along the entire Paint Branch at the watershed scale (Figure 10c). This discrepancy between smaller reach- and whole watershed-scales points to the need to conduct LSS monitoring at spatial scales sufficiently long enough to detect potential "hot spots" of hydrologic connectivity. The rapid increases in Fe near restoration sites and conservation areas in parks further support the idea that dissolved Fe can be an indicator of local redox conditions. However, the significant decrease in Fe measured with repeated LSS monitoring at the reach scale did not significantly impact longitudinal patterns at the watershed scale. This suggests that reach-scale engineered stream restoration projects, such as the one on the mainstem of Paint Branch, will show localized but not necessarily watershed scale impacts (Figure 10c).

#### Potential Benefits of Incorporating LSS Monitoring Approaches in Assessing Restoration

The LSS monitoring approach described in this study can be used to monitor other streams and rivers with their own unique forms of restoration, whether natural or engineered. By considering both temporal and spatial scales, we can gain a more well-rounded assessment of management activities within a watershed context. In addition, there is value in incorporating a watershed chemical cocktail approach considering multiple chemicals holistically (Galella et al., 2023; Kaushal et al., 2018a, 2020; Maas et al., 2023; Morel et al., 2020). Stream monitoring can focus purely on physical changes, chemical changes, biological changes, or any combination of these. Evaluating these parameters together will provide the most information regarding cumulative changes along flowpaths or over time (Kaushal et al. 2023b). Diurnal sampling of baseflow, storms, and road salting events can reveal important information regarding limitations and context for our interpretations of successes and failures in restoration (Kaushal et al., 2023b). Spatial and temporal resolution of sampling should be planned according to individual

watersheds. Physical, chemical, and biological characteristics of a stream can change along a flowpath, and disentangling the drivers can be difficult. Changes in erosion and depositional patterns can change the physical flow of a stream; point and nonpoint sources of pollution into the channel can alter the chemistry; the amount of canopy cover and direct sunlight can affect biota processes (Yoshimura & Kubota, 2022). Therefore, sampling at only one location or the top and bottom of a stream reach may not be adequate. Exploring stream sampling locations around tributaries, roadways, new construction, and natural and engineered stream restorations can sometimes help to explain where and how the physical, chemical, and biological characteristics of a watershed are behaving along its flowpath (Cooper et al., 2014; Kaushal et al., 2014, 2023a; Maas et al., 2023; Newcomer-Johnson et al., 2014; Pennino et al. 2016a: Sivirichi et al., 2011).

### Longitudinal Stream Synoptic Monitoring Can Help Evaluate Trade-Offs Associated with Restoration

Typically, stream restoration approaches are used for habitat rehabilitation, flow velocity control, and streambank and substrate stability (Palmer et al., 2014; Smith and Prestegaard, 2005). Floodplain reconnection has been shown to enhance N and P retention (Bukaveckas, 2007; Duan et al., 2019; Forshay et al., 2022; Newcomer-Johnson et al., 2016; Williams & Filoso, 2023). However, it is unclear whether stream-floodplain reconnection approaches have the potential to retain multiple contaminants (Kaushal et al., 2022; Wood et al., 2022). For example, recent work suggests there may be water quality tradeoffs during and after stream restoration, such as (1) increases in multiple contaminants mobilized due to removal of trees and disturbance of soils during the construction process (Kaushal et al., 2022; Wood et al., 2022); (2) retention and release of chemical cocktails in restored streams due to road salt (Kaushal et al., 2022); (3) weathering of chemical cocktails from geological substrates used during the restoration process (Williams et al., 2016); and (4) low dissolved oxygen (DO) impacts on aquatic organisms induced by reconnecting streams to wetland and ponded features (Fanelli et al., 2019).

Stream restoration projects may need to consider complex trade-offs in water quality. While these projects aim to restore natural processes and enhance ecosystem services, they often involve trade-offs due to various factors (Wood et al., 2022). Large-scale stream restoration projects can offer the greatest potential for watershed rehabilitation (Shields et al. 2003), but they can be expensive, requiring significant financial resources (Kenney et al., 2012). Restoration projects can also take a long time to implement and achieve desired outcomes and delays can occur due to permitting requirements, stakeholder consultations, and the natural time needed for ecosystems to recover (Mayer et al., 2022). Balancing the urgency of restoration goals with the time required for project completion is a trade-off. Another potential trade-off relates to impacts due to weather. A large storm during implementation could

completely destroy a project before it has time to establish or uproot all riparian buffer restoration efforts. If this happens and there are no additional funds to replant or repair the work that was done the project could be discontinued or fail again in the future. Finally, stream restoration usually includes significant disturbance to implement the project, such as removing large trees and compacting the streambed, and could degrade water quality for some time before improvements are seen.

Streams are complex ecosystems with interconnected components, including physical, chemical, and biological factors. Disturbing an ecosystem to restore its flowpath can disrupt existing ecological relationships, leading to unintended consequences and increases in contaminant concentrations (Kaushal et al., 2022; Mayer et al., 2022; Wood et al., 2022). There may be trade-offs between the desired scope of restoration activities and negative impacts (Kaushal et al., 2023b, Wood et al., 2022). We observed that prioritization of restoration goals and careful planning is necessary to balance cost considerations with ecological benefits. LSS monitoring approaches can reveal tradeoffs. For example, we observed decreases in DO in RSCs at Campus Creek (Online Resource 5), and this has been documented elsewhere (Kaushal et al., 2023a). LSS monitoring also revealed local changes in pH associated with restoration features (Online Resource 5). Changes in DO and pH associated with restoration may influence habitat for aquatic organisms, although not a focus of this study. Future work incorporating more metrics in LSS monitoring could help identify whether modifying stream channels may alter the habitat for certain species or change sediment transport patterns. Balancing the restoration objectives with potential ecological impacts and tradeoffs is crucial. Implementing adaptive management approaches that allow for learning and adjustment based on LSS monitoring results can help mitigate these trade-offs.

#### Management Implications and Conclusions

This study shows that there can be longitudinal patterns in water chemistry with distance downstream, and these relationships can be different among different stream reaches experiencing variations in land use, restoration, and management. Results from this study show that, depending on where we sample along an urban stream, we can get completely different answers and insights regarding investigating patterns and processes of water quality. Results from longitudinal monitoring in this study also suggest that there may be differences in the impacts of restoration in headwater systems *versus* further downstream. For example, in Scotts Level Branch and Campus Creek, it was possible to detect longitudinal patterns influenced by stream restoration. However, these patterns were not as evident along the restored stream reaches of Paint Branch, which were much further downstream and larger in size. We see restoration activities and parks buffering Na<sup>+</sup> and Fe concentrations, yet overall increases in both Na<sup>+</sup> and Fe along the entire Paint Branch flowpath (Figure 10c). Restoration projects along headwater reaches may have more of an impact than restorations on downstream reaches or with minimal floodplain

reconnection (Filoso and Palmer, 2011; Newcomer-Johnson et al., 2014). For smaller watersheds, headwater restoration projects may be more useful for improving overall water quality along a shorter flowpath. For larger watersheds, headwater restoration projects may be impractical, if there are many first-order streams at the top of the flowpath. In this case, fewer but larger restoration projects downstream may be less expensive to complete. If the upstream sources of pollution are not controlled, the constant flow of lesser-quality water may overwhelm ecosystem contaminant retention functions in a restoration project.

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LSS monitoring has the potential to detect hydrologic connectivity, localized disturbances along stream flowpaths, and help prioritize reaches for stream restoration impacted by wastewater leaks and other disturbances. One potentially promising indicator of hydrologic connectivity may be dissolved Fe and Mn concentrations along flowpaths. Our results at the reach scale and entire watershed scale of Paint Branch suggested that increases in dissolved Fe and Mn can occur in restoration and conservation areas with increased potential for groundwater-surface water interactions. LSS monitoring can also identify areas along streams receiving pollution. Sewage leaks represent a major nonpoint source of pollution in urban streams of our study region (Kaushal et al., 2011). Many public sewage drain pipes are commonly buried near streams in urban developments (Kaushal & Belt, 2012) as the pipes need to run downhill for gravitational flow. As baseflow stream velocity throughout the stream network slows and discharge from urban areas increases, stream channels are subject to erosion. If sewage drain pipes are placed too close to the stream, they can become exposed through weathering and erosion, which contributes to rusting and cracking of the pipes and eventually leads to sewage leaks. This would heavily pollute the stream network and may require expensive rehabilitation efforts (Bonneau et al., 2017; Kaushal & Belt, 2012). This can have a great impact on the quality of its water and surrounding environment (Roy & Bickerton, 2012). Most stream restoration projects in and around Maryland strive to improve water quality (Newcomer-Johnson et al., 2016), as many streams ultimately empty into the Chesapeake Bay (Chang et al., 2021). A stream-floodplain reconnection approach would need to work to protect and maintain, if not relocate, nearby sewage drain pipes in surrounding stream watersheds to prevent groundwater from the incursion of excess pollutants. This approach reverses hydrologic degradation and brings polluted water to hot spots of contaminant retention in floodplains.

Overall, the longitudinal data collected from each of the five watersheds in this study show the importance of monitoring streams at various spatial and temporal scales. Changes in stream chemistry can occur along a flowpath, so sampling one location along a flowpath over time will not provide an accurate overview of the watershed as a whole. Local natural and anthropogenic inputs such as tributaries or new construction can change the chemistry of a stream and the rest of the downstream flowpath. Future stream

restoration projects should be monitored over both spatial and temporal scales. Multidimensional monitoring approaches including lateral, longitudinal, or surface-groundwater sampling should be considered when assessing the effectiveness of a stream restoration. In addition, more longitudinal sampling locations throughout a watershed allows for more accurate conclusions about local changes in water chemistry along flowpaths.

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## 1326 Tables

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Table 1. Stream characteristics. Stream length and stream elevation drop were calculated using Google
 Earth measuring tools. Basin area, impervious surface cover (ISC), and forest cover data retrieved from
 USGS StreamStats.

Watershed	Basin Area, km²	Stream Length, km	Stream Sinuosity	ISC %	Forest Cover %	Restoration Approach
Sligo Creek	29.0 km <sup>2</sup>	14.2 km	1.33	41%	12%	Scattered stormwater ponds, bioretention zones, and minimal in-stream projects
Scotts Level Branch	10.4 km <sup>2</sup>	8.7 km	1.22	41%	14%	Floodplain Reconnection with riprap, J-hooks
Paint Branch	80.5 km <sup>2</sup>	5.35 km (22.5 km)	1.24	33%	24%	Floodplain Reconnection with riprap, J-hooks
Campus Creek	1.8 km <sup>2</sup>	1.4 km	1.13	24%	23%	Regenerative Stormwater Conveyance system

Table 2. Table defining all longitudinal synoptic and diurnal sampling dates. Synoptic date column defines the date of longitudinal sampling and either the start or end date of diurnal sampling. The two synoptic dates marked with "N/A" did not include longitudinal sampling, but automated samplers were placed starting on the dates listed in parentheses. "Road Salting" events are characterized by sampling dates within a week after road salting in the watershed. Average daily discharge and average daily specific conductance were collected from USGS stream gauge data; "--" was shown for streams without a USGS gauge along the sampled flowpath.

Watershed	Synoptic Date	Diurnal Sampling Site(s)	Event	Avg Daily Discharge, m <sup>3</sup> /s	Avg Daily Specific Conductance, µS/cm at 25 °C
Sligo Creek	06/08/2022	SC2, SC7, SC12	Stormflow	0.124	612
Sligo Creek	08/17/2022	SC2, SC7, SC12	Stormflow	0.063	N/a
Sligo Creek	11/04/2022	SC7	Baseflow	0.059	670
Sligo Creek	03/01/2023	N/A	Baseflow	0.111	600
Scotts Level Branch	03/27/2021	N/A	Baseflow	0.072	520
Scotts Level Branch	08/12/2021	N/A	Stormflow	0.012	359
Scotts Level Branch	09/02/2021	N/A	Stormflow	0.060	202
Scotts Level Branch	11/02/2021	SLB10	Baseflow	0.046	394
Scotts Level Branch	01/05/2022	N/A	Road Salting	0.029	1820
Scotts Level Branch	01/12/2022	N/A	Road Salting	0.028	2120
Scotts Level Branch	02/22/2022	SLB1, SLB7, SLB10	Baseflow	0.051	731
Scotts Level Branch	05/25/2022	SLB1, SLB7, SLB10	Stormflow	0.037	378
Scotts Level Branch	08/09/2022	SLB1, SLB7, SLB10	Stormflow	0.031	329
Scotts Level Branch	11/09/2022	N/A	Baseflow	0.017	420
Paint Branch	09/16/2021	PB8	Stormflow		
Paint Branch	N/A	PB8 (10/20/2021)	Baseflow		
Paint Branch	02/16/2022	PB1, PB6, PB9	Baseflow		
Paint Branch	05/17/2022	PB1, PB6, PB9	Stormflow		
Paint Branch	08/02/2022	PB1, PB6, PB9	Stormflow		
Paint Branch	11/16/2022	N/A	Stormflow		

Campus Creek	09/02/2021	CC0	Stormflow	 
Campus Creek	10/06/2021	N/A	Baseflow	 
Campus Creek	N/a	CC0	Baseflow	 
_		(10/20/2021)		
Campus Creek	02/09/2022	CC6, CC4, CC0	Stormflow	 
Campus Creek	05/10/2022	CC6, CC4, CC0	Stormflow	 
Campus Creek	07/15/2022	N/a	Baseflow	 
Campus Creek	07/26/2022	CC6, CC4, CC1	Baseflow	 
Campus Creek	10/28/2022	N/A	Baseflow	 