

ABSTRACT

Title of Thesis: **TREE TRADE-OFFS IN STREAM
RESTORATION: IMPACTS ON RIPARIAN
GROUNDWATER QUALITY**

Kelsey Wood, Master of Science, 2020

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Restoring urban degraded stream channels in efforts to improve water quality often includes substantial alteration of the riparian zone which can require the removal of mature trees. This study assessed the impact of tree removal on riparian groundwater quality over time and space using a chronosequence of restored site ages 5-20 years and well transects along groundwater flow paths. The response of multiple elements through various hydrologic conditions were evaluated by monitoring dissolved concentrations of inorganic carbon, organic carbon, total nitrogen, boron, calcium, copper, iron, potassium, magnesium, manganese, sodium, and sulfur over a 2-year period. Results revealed that concentrations of most bioreactive and organically derived elements were significantly elevated and increase along flowpaths at recently restored sites.

**TREE TRADE-OFFS IN STREAM RESTORATION: IMPACTS ON RIPARIAN
GROUNDWATER QUALITY**

by

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INTRODUCTION

Riparian zones are a vital interface between land and stream and are often the focus of stream restoration efforts in urban areas to reduce nutrient pollution in waterways. Restoring degraded stream channels often includes major physical alteration of the riparian zone to reshape streambank topography leading to the removal of mature trees. This study assessed the impact of tree removal on riparian groundwater quality over space and time. Twenty-nine wells were installed across 5 sites in watersheds of the Washington D.C. and Baltimore metropolitan areas in Maryland. Study sites encompassed a range in restoration ages (5, 10 and 20 years) as well as unrestored comparisons. Groundwater wells were installed as transects of 3 perpendicular to the stream channel to estimate nutrient uptake along groundwater flow paths. Well and stream water samples collected over a 2-year period (2018-2019) were analyzed for concentrations of dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), total dissolved nitrogen (TDN), and dissolved components of boron (B), calcium (Ca), copper (Cu), iron (Fe), potassium (K), magnesium (Mg), manganese (Mn), sodium (Na), and sulfur (S). Results showed some interesting patterns such as: (1) significantly increased mean concentrations of some nutrients and carbon in riparian groundwater for at least 5 years following tree removal then subsequent decline with recovery; (2) maximum TDN, DOC, and S concentrations at 5-year cut sites (20.5, 51.92, and 43.8 mg/L respectively) were higher than maximum TDN, DOC, and S concentrations at nearby comparison uncut sites (2.65, 18.53, and 14.1 mg/L respectively); (3) decreasing linear trends in concentrations of TDN, K and S during a 2 year shift from wet to dry conditions (p -value < 0.0001); (4) strong linear relationships between DOC (organic matter) and plant nutrients across sites suggesting the importance of plant uptake

and biomass as sources and sinks of nutrients ($p < 0.05$); (5) increasing concentrations along hydrologic flow paths from uplands to streams in riparian zones where trees were recently cut, and opposite patterns where trees were not cut. Riparian zones appeared to act as sources or sinks of bioreactive elements based on tree removal. Mean TDN, DOC, and S, concentrations decreased by 78.6%, 12.3%, and 19.3% respectively through uncut riparian zones, but increased by 516.9%, 199.7%, and 34.5% respectively through the 5-year cut transects. In contrast, concentrations of elements that are nonessential plant nutrients (*e.g.*, Na and trace metals) did not share similar spatial or temporal patterns with the most bioreactive elements. Like other studies, results from this study showed that riparian tree removal can disturb multiple chemical constituents for the first few years after construction leading to significant groundwater quality impacts. However, this study also observed ecosystem recovery and an improvement in groundwater quality by 10-20 years after restoration. These effects of tree removal should be considered in cost-benefit analyses of restoration projects and where possible mature trees and soil profiles should be conserved. Overall, a more holistic understanding of the effects of riparian tree removal on groundwater quality can inform strategies for minimizing unintended negative consequences of stream restoration.

MOTIVATION

Widespread degradation of surface waters due to changing land use, non-point source pollution, and channel erosion has driven an increase in stream restoration practices to improve water quality (T. Newcomer Johnson et al. 2016). In efforts to reduce nutrient pollution in waterways, billions of dollars are spent in the United States each year on stream restoration projects (Newcomer Johnson et al. 2016; Bernhardt et al. 2005). Excess nutrients, such as nitrogen (N) and phosphorus (P), are introduced to urban waterways through a variety of point and nonpoint sources such as agricultural fertilizers, industrial discharges, urban runoff, septic systems and sewage leaks (Pennino et al. 2016; Duan et al. 2012; Kaushal et al. 2011). The nutrient retention capacity of urban wetlands, floodplains, and hyporheic zones can often be overwhelmed or compromised by flashy hydrology, reduced hydrologic residence times, and decreased hydrologic connectivity between streams and ‘hot spots’ of nutrient retention in floodplain and riparian soils (Vidon 2010; Kaushal et al. 2014). Water quality regulations and total maximum daily loads (TMDLs) set by federal and state agencies mandate municipalities and landowners to invest in reducing their nutrient loads to streams. Stream restoration strategies are growing in popularity, particularly in urbanized areas developed prior to widespread implementation of modern stormwater management practices (Bernhardt et al. 2005; Newcomer Johnson et al. 2016). In some cases, riparian trees are removed during the construction phase of stream restoration, and this may produce a variety of unintended water quality consequences, which has been less studied. This study investigates potential trade-offs in groundwater quality in response to riparian tree removal before, during, and after

construction activities associated with urban stream restoration. Results from this study can be used to guide and improve future restoration activities by documenting the critical role of trees on regulating groundwater quality in urban riparian zones and anticipating timeframes of ecosystem recovery after disturbance.

Urbanization has degraded streams and floodplains for decades contributing to urban water quality issues (Leopold et al. 2005; Walsh et al. 2005; Kaushal 2012) and stimulated interest in riparian buffers as a management strategy (Lowrance et al. 1997; Sweeney et al. 2004; Vidon et al. 2018). A large increase in impervious surface coverage within urban watersheds leads to scouring of stream beds, stream channel incision, hydrologic disconnection between streams and floodplain soils, and an overall degradation of stream morphology and function (e.g. Wolman 1967; Walsh et al. 2005; Angier et al. 2005; Fanelli 2017). This degradation of headwater streams often amplifies the transport of nutrient pollution because it inhibits hydrological and biogeochemical retention processes and accelerates the delivery of water and pollutants further downstream (Sweeney et al. 2004; Vidon 2012; Kaushal et al. 2014). Ultimately, the combination of increased nonpoint source pollution and hydrologic degradation has led to widespread efforts attempting to restore the health of urban headwater streams.

One of the most widely accepted best management practices (BMP) for reducing N and P loads from uplands to waterways are riparian zones (Lowrance et al. 1997; Sweeney et al. 2004; Vidon et al. 2018). Riparian zones are areas bordering bodies of surface water such as rivers and streams and are known to be ‘hot spots’ of nutrient retention *via* plant uptake and microbial transformations (Lowrance et al. 1997, Sweeney et al. 2004, Vidon et al. 2010). Shallow groundwater environments provide a redox gradient which fosters

microbial nutrient transformations (Hedin et al. 1998; Duncan et al. 2015) and promotes growth of vegetation, boosting nutrient uptake and retention. Shallow groundwater flow paths interact with vegetation creating an opportunity for either nutrient retention by plants and microbes or nutrient release through mineralization of soil organic matter, which is influenced by water table depth or wetting and drying events (Groffman et al. 2002; Duncan et al. 2015). Often in degraded streams in which the channel has been scoured down into the landscape, the water table lowers and loses hydrologic connectivity with riparian vegetation and organic rich soils, contributing to a decrease in nutrient retention (Mayer et al. 2010; Groffman et al. 2002). In other cases, stream channels are disconnected from hydrologic exchange with the riparian zone by levees or walls engineered to prevent flooding, which reduces nutrient retention capacity (*e.g.*, Elmore and Kaushal 2008; Pennino 2014).

Efforts to hydrologically reconnect streams to riparian zones often require streambank reshaping and major construction activities, which can affect the ecosystem structure, plant communities, and the water quality functions of riparian zones. There are many types of stream restoration projects which require extensive construction and major disturbance of plants and soils such as: legacy sediment removal, natural channel design, wet channel regenerative stormwater conveyance, and floodplain reconnection. For instance, a stream floodplain reconnection project may require extensive excavation of streambanks that have become disconnected through channel scouring (Laub et al. 2013). Unsurprisingly, herbaceous and woody vegetation growing in the excavated landscape are cut from the riparian zone and mature soil profiles are removed. Herbaceous vegetation is relatively fast-growing and can recover quickly but woody vegetation does not recover as

quickly, especially trees (Tabacchi et al. 1998). Differences in vegetation can influence nutrient retention and riparian water quality functions based on factors such as nutrient content of biomass, aboveground-belowground plant-microbiome dynamics, and differences in plant nutrient uptake and retention capacity (Sabater et al. 2000; Dosskey et al. 2010; Reisinger et al. 2019).

Overall, trees provide many ecological and biogeochemical functions and are immensely valuable to riparian and riverine ecosystems (Sweeney et al. 2004). All riparian zones are not equal in their ability to retain nutrients (Mayer et al. 2007; Dosskey et al. 2010) and the groundwater chemistry of a riparian zone is significantly impacted by uptake, storage or release of nutrients by vegetation (Osborne and Kovacic 1993; Dosskey et al. 2010). Many chemical constituents can be affected by plant growth. Some elements necessary for plant growth in order of most to least abundant in plant tissues are carbon (C), oxygen (O), hydrogen (H), nitrogen (N), potassium (K), calcium (Ca), phosphorus (P), magnesium (Mg), sulfur (S), chlorine (Cl), iron (Fe), manganese (Mn), zinc (Zn), boron (B), copper (Cu), and molybdenum (Mo) (Berner and Berner 2012, sourced from Zinke 1997). Nutrient uptake, which can influence riparian groundwater quality, is strongly correlated with biomass production (Dosskey et al. 2010) and the magnitude of nutrient uptake by plant biomass depends on the stage of tree maturity (McMillan et al. 2014). Studies on riparian vegetation have also observed greater nutrient accumulation by trees than by grasses (Tufekcioglu et al. 2003). In addition, riparian zones with trees can be more efficient at retaining nitrogen across seasons than riparian zones with grass (Haycock and Pinay 1993). Vegetation also greatly influences the physical form of a stream channel; the removal of vegetation from riparian zones and floodplains has been shown to decrease

channel stability and increase erosion potential (Smith and Prestegard 2005). Increased erosion influences mobilization of nutrients when particulates and sediment wash into streams from streambanks (*e.g.*, Noe 2013; Ostojic et al. 2013; Wolf 2013).

There is a substantial body of research on the effect of deforestation and clear-cutting on surface water quality; showing that concentrations of plant nutrients (N, Ca, Mg, and K) increase in streams following deforestation (Likens et al. 1970; Martin, Noel, and Federer 1985; Burns and Murdoch 2005). Studies of tree removal in riparian zones have shown that it can take several years for elevated groundwater nutrient concentrations to decrease after planting trees (Rusanen et al. 2004; Yamada et al. 2007; Löfgren et al. 2009). However, the potential unintended consequences of tree removal on groundwater quality during construction activities associated with stream restoration has received very little attention, particularly studies encompassing multiple elemental cycles. An understanding of groundwater chemistry following tree removal is imperative in improving our restoration practices.

The goal of this study was to evaluate the impact of tree removal on shallow riparian groundwater quality with an emphasis on numerous elements that can be influenced as an unintended consequence of stream restoration. Major hypotheses tested were: (1) shallow groundwater quality will exhibit elevated concentrations of common plant nutrients in sites where trees were removed compared to sites with mature undisturbed trees, and (2) concentrations of common plant nutrients in shallow groundwater will be most elevated immediately following tree removal and will decrease over time as regrowth progresses. Groundwater chemistry responses to hydrologic conditions and patterns along well transects were also explored. Further study into the effects of tree removal during stream

restoration projects is necessary to guide future urban water quality best management practices and to predict time frames of ecosystem recovery. In addition, observations of a greater number and diversity of elements can improve our holistic understanding of biogeochemical processes in riparian zones.

STUDY DESIGN

The goal of this study was to assess the effects of stream restoration efforts that involve tree removal on riparian groundwater elemental concentrations and to gauge subsequent recovery timescales. To achieve this, restored sites were selected to span a range in restoration ages from 5 to 20 years. Each of the 5-year cut sites had a direct uncut comparison in an attempt to isolate the effect of restoration age from any inherent site specific differences. This study design allows us to compare unrestored and recently restored sites to sites as old as 20 years over a span of only 3 years. Groundwater wells were installed in transects through the riparian zones perpendicular to the stream edge and sampled on a 1-3-month basis. Transects from uplands to streams provide a view of spatial variations in chemical concentrations along groundwater flow paths. Routine year-round sampling allows for insight into seasonal or flow condition controls on groundwater chemistry. Previous research has been conducted at these sites to characterize hydrology and biogeochemistry, which included investigating nutrient uptake in restored streams (Klockner et al. 2009; Reisinger et al. 2019) and oxbow wetlands (Harrison et al. 2011), measuring denitrification rates in riparian zones and floodplain soils (Kaushal et al. 2008; Newcomer et al. 2012), and characterizing changes in ground and surface water chemistry along drainage networks and riparian zones (Mayer et al. 2010; Svirichni et al. 2011).

However, our previous work has not investigated the potential unintended impacts of riparian tree removal on groundwater quality.

Given that many urban riparian studies only focus on one or a few elements, a valuable aspect of this study is the breadth of elements observed. Elemental analyses in this study included concentrations of dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), total dissolved nitrogen (TDN), and dissolved components of boron (B), calcium (Ca), copper (Cu), iron (Fe), potassium (K), magnesium (Mg), manganese (Mn), sodium (Na), and sulfur (S). Most exhaustive analyses were focused on the major plant nutrients and cations (DIC, DOC, TDN, Ca, K, Mg, Na, and S) to address the question of tree removal effects on water quality.

STUDY SITES

All 5 study sites are within urban-degraded watersheds of Maryland (**Figure 1**) and are tributaries of the greater Chesapeake Bay watershed. Previous research has been conducted at these sites assessing nitrogen uptake in streams, riparian denitrification, groundwater studies of nutrient dynamics, and other hydrologic biogeochemical processes (e.g., Svirichni et al. 2011; Newcomer et al. 2012; Harrison et al. 2011; Kaushal et al. 2008; Mayer et al. 2010; Klocker et al. 2009). All sites have been the subject of a stream restoration project that involved tree removal and encompass a range in restoration project age of 5-20 years. Sites are in the Piedmont and Coastal Plain physiographic provinces spanning the Washington, D.C. and Baltimore, Maryland metropolitan areas. The area of tree removal and other site attributes such as riparian zone (RZ) slope and width, and

channel width were estimated using satellite imagery through ArcGIS or Google Earth (**Figure 2**). For all sites, soil classifications and textures were obtained from the U.S. Department of Agriculture (USDA) Web Soil Survey. Wetland classifications were acquired from the U.S. Fish & Wildlife Service's National Wetland Inventory (NWI). (**Table 1**).

Campus Creek and Paint Branch are located near the University of Maryland in College Park, just north of Washington, D.C. Campus Creek and Paint Branch are on the inner Coastal Plain which has a characteristic flow regime consisting of unconfined surficial aquifers resulting from year-round precipitation, low topographic relief, and relatively high infiltration rates (Lowrance et al. 1997). Campus Creek is a tributary of Paint Branch which flows through the University of Maryland College Park campus. Due to increased impervious surface cover in the watershed, the channel had become severely incised. Campus Creek (age group: uncut) was unrestored during the sampling period of this study and used as a control comparison for Paint Branch. However, in 2019 Campus Creek underwent a stream restoration in which an extensive Regenerative Stormwater Conveyance (RSC) system was constructed. Trees were removed to re-grade streambanks, widen the stream channel, and allow for access to large construction machinery near the end of this study.

Paint Branch (age group: 5-year cut) is a major tributary in the Anacostia watershed. The Anacostia watershed has a long history of degradation and poor water quality associated with early and sustained urbanization of the Washington D.C. area. Paint Branch's increasingly erosive force began to threaten nearby structures and so it underwent restoration from 2012 to 2014. This was a very large project, covering

approximately a one-mile reach, conducted by the US Army Corps of Engineers with support from Prince George's County Department of Environmental Resources, Maryland-National Capital Park and Planning Commission, and the University of Maryland. Stream bank reformation/ armoring and the addition of cross vanes resulted in the removal of many riparian trees (**Table 1; Figure 2**).

Scotts Level and Minebank Run are located just outside Baltimore City in Randallstown and Towson, respectively, Stony Run is in Baltimore City (**Figure 1**). Scotts Level Branch, Stony Run, and Minebank Run are all located in the Piedmont geologic province underlying Baltimore and much of central Maryland. Scotts Level Branch (age group: 5-year cut) flows through suburban areas west of Baltimore city. In efforts to improve water quality approximately a 2,000ft reach was restored in 2014 by Baltimore County. Trees were removed to restructure banks and create a wetland to support nutrient retention. The areal extent of tree removal extended well into the floodplain at some locations. One transect at Scotts Level was installed in an undisturbed reach just upstream as a control (age group: uncut).

Stony Run (age group: 10-year cut), located in north central Baltimore city, is part of the Jones Falls watershed. Widespread impervious surface cover in the watershed caused erosive storm flows and led to extensive channel incision and bank degradation (Harrison et al. 2011). Stream restoration efforts were completed in 2009 on a reach of the stream and involved tree removal for bank regrading and hydrologic reconnection.

Minebank Run (age group: 20-year cut) is part of the Gunpowder Falls Watershed that also experienced urbanization driven degradation (e.g., Kaushal et al. 2008; Mayer et al. 2010; Sivorichi et al. 2011). About 700 m of Minebank Run was restored in 1998-1999

by the Baltimore County Department of Environmental Protection and Resource Management. In order to remediate channel incision and increase channel stability, geomorphic reconstruction techniques were implemented and some riparian trees were lost. Meanders, riffles, step-pool sequences point bars and channel filling were some of the features constructed. Trees planted following construction included sugar maple, beech, tulip poplar, white and red oaks.

METHODS

Groundwater Well Installation and Sampling

Methods for groundwater well installation and groundwater sampling were modeled after the simplified three-well method introduced and tested by Vidon and Dosskey (2008). The three-well system, simplified from large networks of wells and piezometers, has shown relatively good precision and accuracy in assessing nitrate fluxes (Vidon and Dosskey 2008). Groundwater well locations within the site were chosen based on topography, accessibility, and vegetation. Wells were installed in transects of three in line perpendicular to the stream, two transects per site. Well positions were categorized as “lower” (closest to the stream edge), “middle”, and “upper” (farthest from the stream edge). Vertical 3-inch diameter holes were dug using a hand auger to the depth of the water table and as far below as possible. Wells were made of 2-inch diameter polyvinyl-chloride (pvc) pipe with alternating slots cut into the bottom portion of the pipe within the saturated zone. The slotted portions were sheathed in a well sock, to prevent sediment from clogging the well. Extra space surrounding the pipe was backfilled with quartz sand, and the top foot

with bentonite clay to prevent surface flow infiltration. All wells were capped with airtight rubber pvc caps and metal brackets.

Once well installation was complete groundwater sampling began. All wells were sampled every few months. Groundwater was retrieved from wells using a syringe and plastic tubing attached to a stake, which was lowered into the wells to about the middle of the water column. The top end of the tubing was attached to a 150 mL syringe with a 3-way valve stopcock allowing the negative pressure pulling water into the syringe to persist through multiple pulls of the syringe. Measured depths to the top of the water table on any given sampling date varied based on precipitation and evapotranspiration. In general, water tables were lower in the warm growing season due to increased evapotranspiration, especially in riparian zones with trees. It was not unusual for wells in fully forested (uncut) sites to dry out during the growing season, barring sampling. Wells were purged after installation but due to low volumes and slow recovery of groundwater at these sites, a purging method was not implemented on every sampling date. A lack of purging may have introduced some error, but the importance of purging has been debated in literature for sites where groundwater is difficult to pump and sediments can be disturbed (e.g., Robin and Gillham 1987; Puls and Barcelona 1996). In some cases, there have been no major differences in groundwater chemistry between purged and unpurged samples based on hydrogeology and well construction (Robin and Gillham 1987; Puls and Barcelona 1996). In this study, we focused on many elements that are not redox sensitive, and a direct comparison of N and C concentrations of purged and unpurged samples showed no major differences. We acknowledge the possibility of some variability, but it was likely small relative to the large statistically significant variations observed across years and among

sites. Approximately 200 mL of water from each well, and the open stream channel in line with each transect (denoted as position “channel”), were collected in bottles and transported to the laboratory for chemical analyses.

Chemical Analyses

Samples were first filtered through a 0.7-micrometer glass fiber filter, removing particulates. All analyses in this study were done on dissolved constituents only. An aliquot (60 mL) of each filtered sample was acidified to 0.5% with ultra-pure nitric acid, and the remaining sample left unacidified. Acidification keeps chemical constituents in suspension by preventing flocculation and inhibiting any biological activity. Acidified samples were stored at room temperature, and unacidified samples were refrigerated prior to analyses.

Filtered and unacidified samples were analyzed with a Shimadzu TOC-L for dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), and total dissolved nitrogen (TDN). All quantities detected are calculated based on a concurrently measured 5-point calibration curve, auto diluted by the instrument from stock solutions of known concentration. Carbon was measured in the form of dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC). DIC includes carbon contained in carbonates or in dissolved carbon dioxide. By introducing enough hydrochloric acid to each sample to achieve a pH less than 3 all carbonates are converted to carbon dioxide which is sparged from the sample via bubbling and detected by the non-dispersive infrared (NDIR) gas analyzer. DOC was obtained following DIC elimination because carbon not volatilized by

acidification is considered non-purgeable and thus organic. This remaining portion of carbon was obtained by combustion in an oxidation catalyst, converting all organic carbon to carbon dioxide which is then dehumidified, scrubbed of halogens, and measured by the NDIR gas analyzer. Nitrogen was measured in the form of TDN which includes nitrates, nitrites, ammonia, and most other organic nitrogen compounds. Combustion of samples in the furnace column decomposes all forms of nitrogen to nitrogen monoxide which was then transported through a dehumidifier and measured by a chemiluminescence gas analyzer.

The acidified portions of liquid samples were analyzed using a Shimadzu Ion Coupled Plasma Optical Emission Spectrometer (ICP-OES) ICPE-9800. Common plant nutrients measured with the ICP-OES for this study included boron (B), calcium (Ca), copper (Cu), iron (Fe), potassium (K), magnesium (Mg), manganese (Mn), sodium (Na), and sulfur (S). Stock solution used for trace element calibration contained 10 μ g/mL of each element (B, Ca, Cu, Fe, K, Mg, Mn, Na, S) and 3% nitric acid (HNO₃). Stock was diluted to eight standard concentrations ranging 2.5-500 ppb using a multi-branch serial dilution method. Stock solution used for major cation calibration contained 1000 μ g/mL of Ca, K, Na, Mg, and 2% nitric acid (HNO₃), and was diluted to seven standard concentrations ranging 1,000- 250,000 ppb. Stock solutions were certified accurate to about \pm 1% error or less in concentrations of each element. Acidified blanks and the standard series total a 19-point calibration curve measured at the start of each run of no more than 50 samples. Samples and standards were excited in a torch of argon plasma and apertures view the intensities and wavelengths of photons emitted. Axial and radial view directions were utilized to capture all emissions large (major cations) and small (trace elements). Best wavelengths for each element were chosen and used consistently based on

emission intensity range and minimal interferences. Linear concentration-intensity relationships were calculated using known concentrations of the calibration standards and unknown concentrations were determined by the peak intensity emitted at the chosen best wavelength for any given element. All emission peaks were corrected for background noise and triplicate measurements were averaged to the values recorded for each sample.

Statistical Analyses

Statistical methods used to address hypotheses investigated the following questions: 1) Does groundwater chemistry differ significantly based on age of riparian trees and stream restoration? 2) Does groundwater chemistry differ significantly based on position along transects from uplands to the stream channel? 3) How do wet and dry years and hydrologic conditions influence questions 1 and 2?

The precision and accuracy of concentrations of all elements recorded for any given sample were ensured by reporting an average of at least three consecutive measurements from analytical instrumentation calculated based on a contemporaneously measured calibration curve. Statistical methods used to address the questions above included descriptive statistics, correlation matrices, and covariance matrices calculated for the entire dataset as well as for groundwater and surface water separately (Supporting Information). ANOVAs were used to determine if elemental concentrations differed significantly spatially (along transects) and/or temporally (among sites of the restoration chronosequence). Linear regressions were used to investigate chemical relationships and trends in concentrations over time.

For ANOVA analyses, data were divided into restoration age groups “uncut” (CC & SLb), “5-year cut” (PB & SLa), “10-year cut” (SR) and “20-year cut” (MR) as well as position groups “channel” (stream water), “lower” (closest to the stream), “middle”, and “upper” (furthest from the stream). Two-way ANOVA’s with independent variables restoration age and position were performed for each of the chemical constituents (DIC, DOC, TDN, B, Ca, Cu, Fe, K, Mg, Mn, Na, and S) as the dependent variable. ANOVAs were performed on all data combined (groundwater and surface water), groundwater only, and surface water only. Two-way ANOVAs with independent variables of restoration age, well position, and interactions between the two, were performed for all elements analyzed in this study. A p-value of 0.05 or less was considered statistically significant.

RESULTS

Water Chemistry Variations along a Riparian Chronosequence

Across the riparian chronosequence there were significant differences in groundwater chemistry. Analysis of variance revealed interesting and significant differences among restoration age groups for each of the major plant nutrients (**Table 2**). Particularly, concentrations of DOC, TDN, K and S in groundwater were elevated (means) and/or more variable (ranges) at Paint Branch and Scotts Level, which were the two youngest restoration sites (5-year cut). Concentrations of plant macronutrients DIC, DOC, TDN, Ca, K, Mg, and S showed statistically significant differences in means among restoration ages for groundwater, surface water and for groundwater and surface water combined (**Table 2**). Mn, a plant micronutrient, did as well despite being less affected by

tree uptake. Tukey's analyses of elemental mean concentrations in groundwater based on restoration age revealed among which restoration age groups significant differences were observed (**Table 3**).

The most recently restored (5-year cut) riparian zones showed significantly elevated concentrations of TDN, DOC and S compared to uncut riparian zones (**Figure 4**). Paint branch was more consistently elevated than Scott's Level which may be due to more extreme hydrologic conditions at Paint Branch which drains a larger and very urbanized watershed. Uncut sites had groundwater TDN concentrations averaging 0.75 mg/L and ranging only 0-2.62 mg/L. In contrast, the 5-year cut sites averaged 2.54 mg/L TDN and showed much more variability ranging 0- 20.5 mg/L. That represents an increase in range of 682% and an increase in mean of 239% in TDN concentrations 5 years after disturbance. Mean DOC concentrations showed significant differences between 5-year cut and all other age groups. Groundwater at uncut sites had DOC concentrations averaging 4.74 mg/L and ranging only 0.74-18.53 mg/L; while DOC concentrations at the 5-year cut sites averaged 9.13 mg/L and ranged 1.47- 51.92 mg/L. Mean DOC concentrations were lower at the 10 and 20 year cut sites than at the uncut sites averaging 3.58 and 2.66 mg/L respectively. Similarly, sulfur concentrations were lowest at the uncut and 20-year cut sites and most elevated at the 5-year cut sites. The uncut sites showed a mean S concentration of 4.17 mg/L and ranged 0.16-14.1 mg/L. The 5-year cut sites showed a mean S concentration of 7.14 mg/L S and ranged 0.14-43.8 mg/L. The 20-year cut site had the lowest concentrations of S with an average of 1.63 mg/L and a range of 0.21-9.28 mg/L. Similarly, ranges in K concentrations at 5-year cut sites were greater but means did not vary largely

through age groups. Uncut sites showed a range in K concentrations of 0.24-7.12 mg/L, whereas 5-year cut sites showed a range 0.01-15.4 mg/L.

DIC, Ca, and Mg concentrations showed similar patterns along the chronosequence likely influenced by lithology in addition to biological factors, but Na showed a slightly different pattern. DIC concentrations showed significant differences among sites of all ages except for 10- and 20-year cut which were similar and the highest with mean concentrations of 68.24 and 64.38 mg/L. DIC concentrations were lowest in the uncut age group with a mean concentration of 14.93 mg/L whereas 5-year cut concentrations averaged 42.19 mg/L. Patterns in mean calcium concentrations across the chronosequence were very similar to patterns and mean concentrations of DIC (**Table 3**). Mean Ca concentrations for uncut, 5-year cut, 10-year cut, and 20-year cut were 14.48, 48.12, 70.39, and 65.28 mg/L respectively. This is likely indicative of a relationship between Ca and DIC (**Figure 5**), perhaps in the form of calcium carbonate. Chemical constituents which may be linked to geologic province include calcium (Ca), inorganic carbon (DIC) and magnesium (Mg). Observed groundwater Ca, DIC, and Mg concentrations were greater at the riparian sites located in the piedmont province, which consists of various types of metamorphic lithologies that contain mafic minerals (Mg-rich) and marble (Ca and DIC). Mean Mg concentrations differed significantly among all sites except for between 10-year cut and 5-year cut sites. Although influenced partially by underlying lithology, Na was likely influenced by other sources along the chronosequence. Na concentrations were significantly higher at the 5-year cut than the 20-year cut sites, but patterns across other sites were likely obscured by anthropogenic sources like road salts.

Relationships between Carbon and Nutrients along a Riparian Chronosequence

In addition to significant changes in concentrations of plant nutrients along the chronosequence, significant elemental correlations with carbon were also observed; this potentially suggests the importance of storage and release of plant nutrients in organic matter or similarities in sources and transport (**Figure 5**). The correlation between DOC and DIC was stronger at each of the 5-year cut sites than at their uncut paired comparison sites [CC uncut (p-value=0.00645) vs. PB 5-year cut (p-value=0.000154) and SL uncut (p-value=0.1599) vs. SL 5-year cut (p-value=0.0014)]. All sites except the 10-year cut site have statistically significant (p-value < 0.005) correlations between K and DOC. Only Paint Branch (5-year cut) and Stony Run (10-year cut) have statistically significant correlations between Ca and DOC; the weakest and nonsignificant correlations were at both the uncut (CC: p=0.7176, SL: p=0.793) and 20-year cut (MR: p=0.5929) sites, while correlations at both 5-year cut (PB: p=0.000546, SL: p=0.2599) and the 10-year cut (SR: p=0.000901) sites were significant and stronger.

Nutrient Concentrations Peak after Disturbance and Decline with Recovery

Overall, there were shifts in mean and maximum values of DOC, TDN, K, and S with consistent peaks at 5-year cut sites and declines to pre-disturbance concentrations over longer time scales (**Figure 6**). Significant differences in concentrations of carbon and nutrients along the entire chronosequence (details described previously in text and Tables 2-4) and especially large differences between the paired uncut and 5-year cut sites were likely due to a combination of factors. These factors include changes in uptake and storage

of nutrients in organic matter, differences in chemical weathering rates influenced by underlying lithology, soil disturbance and/or construction materials, and complex hydrologic interactions.

Nutrient Response to Hydrologic Conditions

The sampling period of this study covered significant changes in hydrologic conditions as illustrated by variations in mean daily discharge in Paint Branch, Minebank Run, and Scotts Level (**Figure 3**). Sampling began in 2018, which happened to be a very wet year. In 2018 there was a total of 1,824.7 mm of precipitation, which was about twice as much as the year prior (2017 totaled 972.9 mm of precipitation) and the year following (2019 totaled 969.1 mm of precipitation). This variation in wet and dry years provided a unique opportunity to assess the effect of wet-dry cycles on groundwater chemistry of restored riparian zones. All sites, regardless of restoration age, showed a decline in dissolved concentrations of some chemical constituents through the sampling period which shifted from wet to dry conditions. TDN, K, and S in groundwater show statistically significant (p -value < 0.0001) declining linear trends (**Figure 7**). In contrast, Na, which is not a plant macronutrient and may be considered a conservative tracer, did not show any statistically significant trend (p -value = 0.6045), as could be expected as it is not under as much plant biological demand. There were some exceptionally high values of concentrations of N and K during the wet year at the 5-year cut sites (**Figure 7**), where there could have been flushing of nutrients due to lack of tree uptake.

There were also statistically significant relationships between carbon and a few plant nutrients with water table depth at the uncut sites (**Figure 8**). Concentrations of nutrients which were most strongly related to carbon (*e.g.*, K, N, and Ca) and most concentrated in plant biomass increased in concentrations towards the soil surface at some uncut sites; statistically significant relationships were not consistent across all sites. Further analysis of groundwater table topography showed that hydrologic flow paths can be complex and vary seasonally in sites across the chronosequence (Supporting Information), which may have contributed to variability in relationships between water table depth and nutrients across sites, particularly riparian zones where trees had been cut.

Spatial Variations in Water Chemistry along Cut and Uncut Riparian Transects

Dissolved concentrations of DIC, Ca, K, Mg, and Na varied significantly based on position (all restoration ages combined) when surface water is considered; when considering just groundwater only Mg and Na varied significantly (**Table 2**). However, there were significant differences in groundwater concentrations of nutrients by position when restoration ages were viewed separately. Where these concentration differences lie was determined through a Tukey's post-hoc analysis for each ANOVA (**Table 4**). Uncut sites did not show significant variation by position for elements DIC, DOC, TDN, Mg, Na, or S. However, Ca was about twice as concentrated in the stream (33.19 mg/L) and in the lower position (28.4 mg/L) relative to the middle and upper positions. K was more concentrated in the channel with a mean concentration of 4.32 mg/L. The 5-year cut category showed more spatial variations, coinciding with the elevated and more variable nutrient concentrations. DOC and K concentrations were significantly elevated in the

lower position well with mean concentrations of 13.11 mg/L and 6.04 mg/L respectively. Mean S concentrations were elevated in the lower (7.4 mg/L) and middle (8.52 mg/L) positions and lowest in the channel (2.93 mg/L). TDN was most elevated in the lower position (4.24 mg/L) and second most in the middle position (2.68 mg/L). DIC and Ca concentrations were concentrated in all groundwater positions relative to the uncut comparisons but showed similar concentrations in stream water. Na was more concentrated in surface water than in groundwater at all sites regardless of restoration age. This could be due to high concentrations of Na in urban runoff due to road salts. The 10- and 20-year sites showed less spatial variation similar to the uncut sites (**Figure 10**).

Concentrations along groundwater well transects showed different spatial trends for uncut sites than for recently restored sites (trees removed 5 years ago) (**Figure 9**). Based on topographic surveys and water table measurements, generally, water tables slope toward the stream channel (Supporting Information). If we assume groundwater flow direction to be from upland toward the stream, mean concentrations by position show distinct trends at uncut and recently cut sites. Mean TDN concentrations decreased by 78.6% through the uncut riparian zones but increased by 516.9% through the recently cut riparian zones. DOC decreased by 12.3% through the uncut transects and increased by 199.7% through the 5-year cut transects. K concentrations increased by only 4.1% through the uncut transects but increased by 157.5% through the 5-year cut transects. S concentrations decreased by 19.3% through the uncut transects and increased by 34.5% through the 5-year cut transects. Based on these variations in concentrations by position, some plant macronutrients are likely assimilated into biomass at the uncut sites with mature trees but concentrated along flowpaths at the recently cut sites.

DISCUSSION

Overall, results suggest that tree removal during stream restoration projects can disrupt multiple elemental cycles and shift the nutrient source or sink dynamics of riparian zones. This study also shows that there is an ecosystem recovery period following tree removal that lasts at least 5 years. In particular, the most bioreactive elements and organic carbon showed clear and interesting patterns such as: (1) significantly increased concentrations in riparian groundwater for at least 5 years following tree removal then subsequent recovery; (2) increased concentrations during wet periods and decreased concentrations during dry periods; (3) strong relationships with DOC (organic matter) across sites suggesting the importance of plant uptake and biomass as sources and sinks of nutrients; (4) significant increases in concentrations along hydrologic flow paths from uplands to streams in riparian zones where trees were recently cut, and opposite patterns where trees were not cut. While there are many ecosystem functions and biogeochemical interactions that could result in these chemical patterns, consistent and similar patterns in concentrations of carbon and plant macronutrients across space and time suggest the importance of trees in water quality functions of riparian zones. Results from this study are consistent with many other studies around the world documenting the impacts of tree cutting on water quality (**Table 5**). Patterns and processes related to observations during this study and implications for stream restoration are discussed below.

Removing Trees Can Increase Nutrient Concentrations: Disturbance and Recovery

In riparian zones where trees were removed most recently (5 years ago) nutrient concentrations were significantly elevated relative to the uncut sites and other similar groundwater studies in this region including forest, suburban, and urban watersheds

monitored by the Baltimore Ecosystem Study Long-Term Ecological Research (BES-LTER) (*e.g.*, comparison in Supporting Information, Kaushal et al. 2008; Mayer et al. 2010; Sviridchi et al. 2011; Newcomer et al. 2012) and others). Uncut riparian zones showed a range of carbon and nitrogen concentrations 0.74-14.44 mg/L DOC and 0.53-2.62 mg/L TDN. 5 year cut riparian zones showed concentrations of nitrogen and carbon in groundwater up to 51.92 mg/L DOC and 20.5 mg/L TDN. That is a 260% increase in DOC and a 682% increase in TDN maximum concentrations relative to uncut site maximums. There are many possible causes for elevated concentrations of nitrogen and carbon in recently deforested areas. After a disturbance where trees are removed and soils are altered there is likely decreased uptake of nutrients by trees, plants and soil microbes (*e.g.*, Williams, Fisher, and Melack 1997; Kubin 1998; Rusanen et al. 2004). Decomposing cut trees could add a substantial amount of organic carbon to riparian groundwater. Also, trees planted after restoration are small and most vegetation is herbaceous, which does not have as large a nutrient uptake capacity as mature trees (Haycock and Pinay 1993; Lowrance and Sheridan 2005). Temperature is a driving force of carbon and nutrient transformation in watersheds and removing riparian trees decreases stream shading potentially raising water temperatures 4-5 °C above shaded streams influencing water quality (*e.g.* Sabater et al. 2000; Kaushal et al. 2014). Disturbance of the soil profile through soil removal, mixing, or burial can disrupt microbial communities impeding their ecosystem function (Laub et al. 2013). Nitrogen input to a riparian system comes from precipitation and upland/ upstream runoff (Kaushal et al. 2011). In a cut riparian zone with little or no canopy cover, low interception potential and low evapotranspiration rates could result in higher atmospheric N inputs (Klopatek et al. 2006). Organic debris from tree

cutting produces ammonium during decomposition; ammonium, which is a preferred form of N for trees, is taken up less because of the absence of trees (Likens et al. 1970). This excess ammonium can then be nitrified to nitrite, and then nitrate through nitrifying bacteria *Nitrosomonas* and *Nitrobacter*; a previous study found increased populations of these two microbial species 18-fold and 34-fold respectively in the soil of a deforested watershed relative to a undisturbed forested watershed (Smith et al. 1968; Likens et al. 1970). The increased nitrate and H^+ concentrations lower the pH of the soil and groundwater accelerating ion exchange and mobilizing cations that would otherwise remain as complexes on clay particles of the soil (Likens et al. 1970). The decrease in pH can also increase the solubility of common minerals (Berner and Berner 2012). All these factors could explain significant and consistent increases in carbon, nutrients, and base cations which were observed following tree removal in riparian zones with largest increases in concentrations at most recently cut sites (Likens et al. 1970). Previous work has also shown increased concentrations of chemical constituents in riparian groundwater in response to tree removal (e.g., Williams, Fisher, and Melack 1997; Kubin 1998; Rusanen et al. 2004) (**Table 5**).

Concentrations of Ca were highest in 5-year cut sites similar to DOC and TDN; however, concentration means were generally elevated in the restored riparian zones of greater age (10-20 years). Concentrations of Ca were also more normally distributed in this 10 to 20 year range, which could suggest greater background concentrations due to geologic province and dilution with hydrologic conditions (Kaushal et al. 2011; Likens et al. 1998). Although vegetation disturbances likely impact Ca concentrations in water as noted in other studies of deforestation (e.g., Likens et al. 1970); mixing, exposing, or

importing geologic materials during construction provides for more interaction between water and fresh weatherable surfaces (Kaushal et al. 2020). Calcium could easily be weathered from geologic materials and soil if excess nitrogen lowers the pH in urban riparian zones (Kaushal et al. 2013; 2017).

Many previous studies around the world have shown that deforestation can increase concentrations of plant nutrients in groundwater similar to this study (**Table 5**). While this study is observational using a restoration chronosequence as a natural experiment, many other studies have observed similar patterns. This study was designed to isolate effects of tree disturbance at paired riparian sites in a subset of watersheds. We analyzed the data using multiple approaches and documenting significant changes in carbon and nutrient concentrations over space and hydrologic changes along the chronosequence and especially with paired cut and uncut sites showing the largest differences. Previous work in the literature has shown, similar to this study, there were elevated concentrations of N (41 to 56-fold higher), Ca (417% increase), Mg (408% increase), K (1558% increase), and Na (177% increase) in a stream following clearcutting of its watershed (G. E. Likens et al. 1970). In addition, Burns and Murdoch (2005) observed tree removal increased nitrate up to eight-fold in stream water within five months. A study in New England found that clearcutting a watershed increases concentrations of nitrate, calcium and potassium in stream water (Martin, Noel, and Federer 1985). Another study observed clearcutting and slash burning in British Columbia increased nitrate, K, Mg, and Na concentrations in stream water for a couple of years (Feller and Kimmins 1984). In contrast, Hewlett et al. (1984) found short term increases in N, P, K, Ca, Mg, Na, TKN and argue that there are no lasting effects on water chemistry. Overall, many studies from different regions around

the world have shown that cutting trees can elevate concentrations of plant nutrients in surface water and groundwater similar to this study (**Table 5**).

Results from this study suggest that recovery of riparian zones seems to take more than 5 years but less than 10 years for most plant nutrients. Before stream restoration or at unrestored urban degraded sites, there is typically low hydrologic connectivity between streams and floodplains (Groffman et al. 2002; Kaushal et al. 2008; Mayer et al. 2010). The mature trees at these sites can draw down the water table through evapotranspiration and take up dissolved nutrients in the groundwater (Satchithanatham et. al. 2017). Soil microbial communities may be long-established and mineral weathering surfaces may be more depleted at some riparian sites based on disturbance history (*e.g.*, Brantley et al. 2011; Lavy et al. 2019). Increases in dissolved nutrient concentrations likely increase immediately following disturbance and tree removal and recovery lasts more than 5 years. Observed concentrations at the 5 year cut sites were the most elevated in this study, however no sites younger than 5 years were studied. It is possible concentrations were higher in the first 3 years, as has been observed in other studies of surface water (Likens et al. 1970). Results of this study suggest full recovery can be reached by 10 years after disturbance and tree cutting. This could be due to the reestablishment of soil microbial communities and a young growing forest (Holmes and Likens 2016). Young growing forests have high uptake rates of nutrients including TDN, K, and S as suggested by site age comparisons and the significant relationships that were observed between DOC and K (*sensu* Tripler et al. 2006). Substrate originated dissolved constituents such as Ca and Mg could take longer to reach pre-restoration concentrations due to continued weathering of

newly exposed surfaces and/or introduced construction materials at stream restoration sites leading to a more sustained source of Ca and Mg, and DIC (Kaushal et al. 2020; 2017).

Plant Nutrient Concentrations Decline with a Shift from Wet to Dry Conditions

Natural systems are dynamic and complex, so hydrological context (**Figure 3**) is useful in interpreting chemical data. If biogeochemical processes were not a significant factor in controlling water chemistry, we would expect to see a simple dilution effect during wet periods and a concentration effect during dry periods. The amount of water, frequency of wetting, or wet-dry cycles greatly effect concentrations of dissolved nutrients and carbon in water (Wolf et. al. 2013). Most biologically reactive elements (TDN, K, S, DOC, DIC) declined from the wet year to the dry year (**Figure 7**). This suggests the potential importance of biological uptake and transformation during low flow conditions and flushing of excess carbon during wet conditions (*e.g.*, Kaushal et al. 2008; 2014; Vazquez et al 2007; McMillan et al. 2018; Vidon, Marchese, and Rook 2017). A significant decline in nitrate concentrations in riparian zones in this region of Maryland, USA can occur with increased nutrient demand by vegetation and denitrification based on riparian hydrologic conditions (Duncan et al. 2015). Na showed a weak increase in concentrations during the dry year in contrast to all the other plant nutrients, likely because it is less affected by biological activity and shows a dilution effect. The cations Ca and Mg may show intermediate patterns because they are not as essential in plant biomass as N, K, S, and C, but they are still needed for growth (Likens et al. 1998). Likens (1970) found relationships between discharge volume and concentration of nitrate to have a slope -1.63, and discharge

volume and concentration of sodium to have a slope 0.66; so, with increased discharge nitrate concentrations increased and Na concentrations decreased (in stream water).

During a wet year, there could be increased ion exchange driven by atmospheric dissolved ion deposition, mobilizing ions from soils to groundwater and streams (Huntington et al. 1994; Kaushal et al. 2018). If there are no trees, there is less interception by the canopy and potentially more influence by atmospheric deposition (Klopatek, et al. 2006). Wet/ dry cycles are associated with carbon and plant nutrient flushing from the watershed and concentration pulses in floodplains and streams (Vazquez et al. 2007.; Wolf et al. 2013; Kaushal et al. 2018; Huntington et al. 1994). Organic matter from decaying biomass can be mineralized and store nutrients temporarily (Mayer et al. 2005), which can then be flushed out during wet years. Urban watersheds are known to show strong pulses of DOC export during storms (Kaushal et al. 2014; 2018). In recently cut sites, where microflora oxidize excess ammonium to nitrate, nitrate can be rapidly flushed away (Bormann et al. 1968; G. E. Likens, Bormann, and Johnson 1969).

A higher water table could result in more dissolved nutrients as well due to the interaction of groundwater with higher profiles and greater volumes of soil (Duncan et al. 2015). Likewise, topography can interact with wetting/drying cycles to amplify pulses in nutrients (Noe et al. 2013; Duncan et al. 2015). When streambanks are reshaped and hydrologic connectivity increased, the lower bank is more frequently inundated potentially contributing to more flushing (Wolf et al. 2013; Noe et al. 2013). Nitrification in the soil of restored riparian zones could be accelerated as they are no longer limited by infrequent inundation and upper soil horizons are now wetted after being long dry. In undisturbed

systems there are still pulses, but pulses can be counteracted or dampened by plant uptake and less weathering of exposed and reactive surfaces in soils and bedrock.

Further work is necessary to holistically study all the potential impacts of tree removal above and below ground in urban ecosystems. However previous studies on stream water have found that pulses of nitrate increased during a wet year following a drought, and concentrations remained high even as runoff declined suggesting a hydrologic flushing of watershed nitrate (Kaushal et al. 2008; 2014). Vidon et al. (2014) found strong N₂O pulses with storms and rewetting events in a restored riparian wetland, which could suggest accelerated denitrification. Groffman et al. (2002) found that urban riparian zones of Maryland had high potential for denitrification but were limited by infrequent wetting. This limitation to denitrification may decrease following a restoration with increased hydrologic connectivity, and we could expect to see an increase in denitrification (Newcomer Johnson et al. 2014).

Plant Nutrient Interactions with Organic Matter

Biogeochemical cycles of multiple elements are influenced by removal of trees because there are large shifts in plant leaf litter sources, root decomposition, decomposers, and other factors. Carbon showed some interesting relationships with nutrients that could indicate various biogeochemical processes. For example, relationships between DIC and DOC were stronger at each of the 5-year cut sites relative to their uncut comparisons. This could suggest more decomposition, and/or tighter coupling between microbial respiration and organic carbon cycling (*e.g.*, Buckau 2000) is occurring in the riparian soils of the 5

year cut sites. This relationship could suggest these processes because respiration of organic matter can produce CO₂ and DIC (Buckau 2000). This relationship was strong at the 10-year cut site also, which could be a continuation of tree removal effects as well as soil respiration driven by microbes and growing tree roots. In addition, N can be bound up and accumulate in plant leaf litter and organic matter, thereby potentially influencing the movement of N to groundwater and streams (Mayer 2005; Heffernan and Sponseller 2004) and effects can vary across a successional gradient of forest ages and with differences in decomposer community (Mayer et al. 2008). Overall, microbial communities and decomposers can have a significant influence on carbon and many of the nutrients studied including TDN, Ca, Na, and K, which can be influenced by removal of trees and above-ground organic matter sources (Mayer 2005; Mayer et al. 2008; Zhou et al. 2020).

Ca and DOC relationships were highly significant at recently cut sites which may suggest a larger proportion of Ca at these sites originates from dead biomass (Likens et al. 1998). However, Ca is not typically a limiting plant nutrient in soils and showed weak or no relationships with DOC among most sites suggesting a majority of Ca originates from geological and anthropogenic sources like weathering of impervious surfaces, rocks, and soils in some of these same urban watersheds (Kaushal et al. 2017; 2020). This is also supported by the strong relationships found between Ca, Mg and DIC at most sites, particularly at the 10- and 20- year sites. This could indicate a calcium carbonate (Cockeysville marble) or mafic bedrock origin; geological sources and processes may be more or equally as important as biological sources and processes in determining Ca concentrations in riparian groundwater (*e.g.*, Sivirichi et al. 2011; Cooper, Mayer, and Faulkner 2014). Strong relationships between a commonly limiting plant nutrient such as

K and DOC (organic matter) across sites suggests the importance of plant uptake and biomass as sources and sinks of nutrients (Tripler et al. 2006); In fact, the slope in K and DOC was lowest at the oldest and most mature tree sites probably due to either less demand for K in older trees or greater fluctuations or pulses in carbon following tree removal at 5-year cut sites. There is more DOC in the groundwater relative to K at the 5-year cut sites potentially because K is being rapidly taken up and there is an excess of DOC. When trees are alive and growing, carbon and limiting nutrients are stored in their biomass. When trees are cut down and left to decompose, they can release carbon and limiting nutrients into the soil-groundwater ecosystem. The decomposition and mineralization of organic matter can be important in releasing N as it fuels denitrification and can even be a control on soil pH and ion exchange (Likens et al. 1970; Mayer et al. 2008; Mayer 2005; Newcomer et al. 2012; Zhou et al. 2020). Overall, results from this study suggest that organic matter may have different water quality roles in riparian zones contingent on if trees are cut or not.

Tree Removal Can Determine if Riparian Zones are Nutrient Sources or Sinks

Spatial patterns differ significantly at recently restored riparian zones relative to uncut or recovered sites (**Figure 10**). DOC and most reactive plant nutrients (N, K, S) show decreasing trends along flow paths from uplands to streams at uncut sites and increase significantly from uplands to streams at cut sites. At uncut sites decreasing trends are likely a result of nutrient uptake by existing biomass, and at recovering sites the result of a growing forest (*e.g.*, Yamada et al. 2007; Hedin et al. 1998; Dosskey et al. 2010). A decreasing trend from upland to stream could also be the result of dilution as groundwater

begins to assimilate with stream water in the hyporheic zone as observed for conservative tracers (Hedin et al. 1998). Recently cut sites showed a significant increase in nutrients and carbon from upland to the stream. Possible explanations for this increasing trend could be accumulation along the groundwater flow path as water comes into contact with decaying roots and organic matter, excess nitrogen, and fresh weatherable surfaces (Heffernan and Sponseller 2004; Svirichni et al. 2011). Hydrologic flowpaths can influence whether riparian buffers act as N sinks or sources (Mayer et al. 2007). There could also be decreased uptake by mature vegetation and microbes following restoration, leading to excess nutrients and nitrate as mentioned above. Easy flushing of nitrate and carbon could make the cut riparian zone a source of nitrogen and carbon to the stream during wet events similar to observations of riparian zones and streams in other regions (Heffernan and Sponseller 2004; Ostojić et al. 2013). Some have found in urban areas that riparian zones can contribute up to 75% of the DOC flushed into streams during storms (Hook and Yeakley 2005). Nutrient concentrations were also most concentrated in the lower position well closest to the stream channel suggesting that this may be a riparian “hot spot” of biogeochemical transformation (Vidon 2010). Analogous to wet/ dry cycle effects, there could be accelerated organic matter decomposition and nitrogen mineralization due to drying and re-wetting cycles with fluctuating water levels and inundation (Ostojić et al. 2013; Wolf 2013; Heffernan and Sponseller 2004; Noe 2013). Increased hydrologic connectivity could be promoting nitrogen uptake from stream water into the floodplains or deposition of particulate nitrogen during high flow events (Noe 2013; Wolf 2013).

Na was concentrated in the stream channel at all sites, this could be due to Na sources from road salts and sewage leaks along the stream (Cooper, Mayer, and Faulkner

2014; Kaushal et al. 2017; 2014). At uncut sites Ca and K are concentrated in the stream channel. High runoff in these urban watersheds and disconnected riparian zones at the unrestored sites could explain higher concentrations of Ca which can come from weathering of impervious surfaces, and K as it can also come from sewage leaks (*e.g.*, Sivirichi et al. 2011; Kaushal et al. 2018). Given that multiple chemical constituents or ‘chemical cocktails’ vary across space and time in urban waters, future work should consider analyzing stream restoration impacts on multiple elements similar to this study and others in degraded urban streams (*sensu* Kaushal et al. 2020; Morel et al. 2020; Galella et al. In Review).

Conclusions and Management Implications

This study has significant management implications. An improved understanding that dissolved nutrient concentrations are likely to increase directly after tree removal during some forms of stream restoration and remain elevated for at least 5 years will be helpful in predicting nutrient concentrations and fluxes post-restoration. Results from this study show that there may be a successional progression in nutrient release and uptake along riparian zones of different ages and there can be a recovery and return to pre-disturbance conditions; thus, there are opportunities for ecosystem recovery, but the outcome may take years to get back to pre-disturbance conditions after construction.

In the future, a detailed cost-benefit analysis of a restoration project can be used to determine if a project will be truly beneficial to water quality overall and an effective use of funds over all time scales. Soils are likely just as important as vegetation as it is the

combination of their ecosystem functions that control water quality, and they are interdependent as vegetation stabilizes the soils and soils feed vegetation. So, strategies of the trade-offs on water quality should consider the conservation of coupled soil and plant ecosystems. Some have explored passive restoration approaches that use less disruptive approaches. However, floodplain reconnection and inundation and rising groundwater tables may also kill trees, which suggests the need for a detailed cost-benefit analysis for each project.

Results from this study show that tree removal disturbs multiple chemical constituents for the first few years after construction leading to significant water quality impacts. This study was unique in its observation of multiple elements in riparian groundwater, and this showed a wide range of unintended water quality impacts that have been poorly documented at restoration sites. More work should focus on stream restoration impacts on multiple chemical constituents to ensure restoration efforts are optimized. For the first time to our knowledge, patterns in nutrient increases in restored riparian zones experiencing tree removal were shown to be similar to many other watershed and riparian groundwater studies on tree removal and water quality around the world. Empirical results from this study can lead to new conceptual models of riparian disturbance and recovery in urban ecosystems and help guide, improve, and better anticipate effects of the restoration process on water quality over time and space in the future.

TABLES

	Campus Creek (Uncut)	Paint Branch (5-year Cut)	Scotts Level (Uncut & 5-year Cut)	Stony Run (10-year Cut)	Minebank Run (20-year Cut)
Year restored	2019	2014	2014	2009	1999
Area of Tree Canopy Removed (km²)	TBD	13.958	9.703	6.089	NA
Geologic Province	Coastal plain (quaternary sediments)	Coastal plain (quaternary sediments)	Piedmont (quartz feldspar schist and granulite)	Piedmont (gabbro and norite)	Piedmont (schist and gneiss)
USDA Soil Classification	ZS—Zekiah and Issue soils, frequently flooded	CF- Codorus and Hatboro soils, frequently flooded	hbA- Hatboro silt loams	50A- Hatboro- Codorus complex, frequently flooded	MmA- Melvin silt loam
Soil Texture	Loam, silt loam, mucky silt loam, fine sandy loam, sandy loam	Silt loam, loam	Silt loam, silty clay loam, sandy loam	Silt loam, Gravelly silt loam, very gravelly silt loam	Silt loam, silty clay loam
Riparian Zone Slope	0.05	0.12	0.07	0.09	0.1
Riparian Zone Width (m)	32-35	40+	5-25	10-18	20-25
Channel Width (m)	2-3	10-12	2-4	2-4	1-2
NWI Wetland Classification	PFO1A Freshwater forested/ shrub wetland	PFO1A Freshwater forested/ shrub wetland	PEM5Ax- Freshwater emergent wetland PFO1Ax-Freshwater forested/ shrub wetland	R3UBH- Riverine	PFO1/EM5A- Freshwater forested/ shrub wetland
Vegetation	Mature Trees (Maple, Holly, Beech)	Herbaceous near river, Mature trees upland (Tulip Magnolia, Maple)	Transect A: Herbaceous Transect B: Mature trees (Hickory, Oak)	Young/relatively smaller trees (Redbud, Beech)	Mature trees (Sycamore, Beech, Oak) & herbaceous
Drainage Basin Area (mi²)	0.59	29.3	1.19	0.64	0.41
Impervious Surface Cover in Watershed	22.8 %	31.6 %	37.7%	39.6%	40.8
Forest Cover in Watershed	24.9 %	25.6 %	19.9 %	12 %	25 %

Table 1: Site Attributes.

	Groundwater & Surface Water									Groundwater									Surface Water		
	Restoration Age			Position			Restoration Age x Position			Restoration Age			Position			Restoration Age x Position			Restoration Age		
	n	F	p-value	n	F	p-value	n	F	p-value	n	F	p-value	n	F	p-value	n	F	p-value	n	F	p-value
DIC*	259	24.212	<0.001	259	5.724	<0.001	259	2.723	0.005	186	22.27	<0.001	186	1.284	0.28	186	1.316	0.253	73	17.977	<0.001
DOC*	259	7.75	<0.001	259	1.216	0.305	259	2.331	0.016	186	7.822	<0.001	186	0.79	0.456	186	1.706	0.123	73	4.572	0.006
TDN*	259	3.731	0.012	259	0.89	0.447	259	3.08	0.002	186	3.45	0.01	186	2.466	0.088	186	1.662	0.112	73	19.359	<0.001
B	263	0.726	0.537	263	0.865	0.46	263	0.639	0.763	187	0.489	0.691	187	1.039	0.356	187	1.149	0.337	75	0.261	0.853
Ca*	263	44.524	<0.001	263	2.857	0.038	263	3.965	<0.001	187	35.952	<0.001	187	2.669	0.072	187	0.86	0.526	75	13.752	<0.001
Cu	263	2.536	0.058	263	0.495	0.686	263	0.462	0.899	187	2.79	0.042	187	0.119	0.888	187	0.388	0.886	75	0.854	0.471
Fe	263	1.885	0.133	263	0.638	0.592	263	1.179	0.309	187	1.962	0.122	187	0.667	0.515	187	0.845	0.537	75	15.736	<0.001
K*	263	2.849	0.038	263	2.942	0.034	263	5.159	<0.001	187	3.083	0.029	187	2.654	0.074	187	6.094	<0.001	75	0.269	0.848
Mg*	263	58.203	<0.001	263	4.967	0.002	263	10.67	<0.001	187	45.538	<0.001	187	6.482	0.002	187	16.965	<0.001	75	16.622	<0.001
Mn	263	5.885	<0.001	263	2.136	0.097	263	4.632	<0.001	187	6.612	<0.001	187	1.564	0.212	187	3.463	0.003	75	7.556	<0.001
Na	263	1.456	0.228	263	5.804	<0.001	263	1.328	0.223	187	2.566	0.057	187	11.37	<0.001	187	2.489	0.025	75	1.99	0.126
S*	263	4.618	0.004	263	0.32	0.811	263	2.238	0.021	187	6.366	<0.001	187	0.205	0.815	187	0.622	0.713	75	4.216	0.009

Table 2: Two-way Analysis of Variance (ANOVA) results for each chemical constituent with independent variables set as site restoration age (Uncut, 5-yr Cut, 10-yr Cut, or 20-yr Cut) and sampling position (Channel, Lower, Middle or Upper) as well as interactions. ANOVA performed on groundwater (Lower, Middle and Upper) and surface water (Channel) combined and separately. (*) Indicates a major plant nutrient.

	DIC			DOC			TDN			Ca		
	Mean	SE	post-hoc*	Mean	SE	post-hoc*	Mean	SE	post-hoc*	Mean	SE	post-hoc*
Uncut	14.931	4.155	a	4.742	0.831	a	0.752	0.326	a	14.483	3.409	a
5-yr cut	42.186	4.753	b	9.126	0.95	b	2.535	0.373	b	48.118	3.926	b
10-yr cut	68.235	8.913	c	3.576	1.782	a	0.867	0.699	a,b	70.389	7.465	c
20-yr cut	64.384	5.406	c	2.657	1.081	a	1.5	0.424	a,b	65.281	4.539	c
	K			Mg			Na			S		
	Mean	SE	post-hoc*	Mean	SE	post-hoc*	Mean	SE	post-hoc*	Mean	SE	post-hoc*
Uncut	2.746	0.253	a	4.625	1.028	a	6.283	0.855	a,b	4.166	0.732	a
5-yr cut	3.777	0.291	a	8.691	1.184	b	8.435	0.985	a	7.143	0.843	b
10-yr cut	3.958	0.553	a	11.554	2.252	b	7.468	1.873	a,b	5.534	1.602	a,b
20-yr cut	3.5	0.336	a	24.751	1.414	c	4.357	1.139	b	1.63	0.974	a

Table 3: Tukey's (*post-hoc) results from restoration age-based ANOVA. For each chemical constituent, restoration ages that share a letter (a, b, etc), mean concentrations are not significantly different. Those that do not share a letter are significantly different.

		DIC			DOC			TDN			Ca		
		Mean	SE	post-hoc*	Mean	SE	post-hoc*	Mean	SE	post-hoc*	Mean	SE	post-hoc*
Uncut	Channel	17.982	5.599	a	6.073	1.164	a	0.931	0.437	a	33.185	4.687	a
	Lower	24.395	5.848	a	4.176	1.216	a	0.574	0.456	a	28.399	4.87	a,b
	Middle	10.091	5.486	a	5.29	1.141	a	0.656	0.428	a	12.722	4.602	b
	Upper	10.308	7.082	a	4.76	1.473	a	1.025	0.552	a	10.607	5.192	b
5-yr cut	Channel	15.932	5.379	a	4.842	1.119	a	0.99	0.419	a,c	31.128	4.87	a
	Lower	46.066	6.465	b	13.114	1.345	b	4.238	0.504	b	56.274	5.587	b
	Middle	39.417	5.719	a,b	9.887	1.189	a	2.681	0.446	b,c	41.771	5.078	a,b
	Upper	41.075	8.674	a,b	4.376	1.804	a	0.687	0.676	c	68.729	9.204	b
10-yr cut	Channel	22.904	12.267	a	1.581	2.551	a	3.377	0.956	a	41.3	17.219	a
	Lower	75.798	12.267	b	2.98	2.551	a	0.707	0.956	a	78.85	17.219	a
	Middle	61.817	11.198	b	3.996	2.329	a	0.855	0.873	a	82.25	12.176	a
	Upper	67.09	15.836	b	3.752	3.293	a	1.037	1.235	a	74.367	14.06	a
20-yr cut	Channel	43.499	7.918	a	1.849	1.647	a	1.96	0.617	a	63.992	7.03	a,b
	Lower	55.644	7.918	a	1.858	1.647	a	1.907	0.617	a	70.658	7.03	a,b
	Middle	52.475	8.27	a	3.551	1.72	a	0.972	0.645	a	48.769	7.03	a
	Upper	85.033	7.918	b	2.562	1.647	a	1.622	0.617	a	76.417	7.03	b
		K			Mg			Na			S		
		Mean	SE	Post-hoc*	Mean	SE	post-hoc*	Mean	SE	post-hoc*	Mean	SE	post-hoc*
Uncut	Channel	4.323	0.354	a	8.299	1.663	a	25.837	10.959	a	4.358	1.084	a
	Lower	2.597	0.368	b	8.508	1.728	a	7.222	11.206	a	4.136	1.108	a
	Middle	3.043	0.348	b	3.871	1.633	a	4.922	10.512	a	3.24	1.04	a
	Upper	2.496	0.392	b	3.825	1.842	a	6.704	12.388	a	5.122	1.225	a
5-yr cut	Channel	4.019	0.368	a	9.103	1.728	a	92.972	10.512	a	2.925	1.04	a
	Lower	6.04	0.422	b	10.66	1.982	a	13.865	12.058	b	7.404	1.193	b
	Middle	3.272	0.384	a	8.273	1.802	a	6.276	10.959	b	8.52	1.084	b
	Upper	2.109	0.695	a	9.533	3.266	a	5.164	15.847	b	5.506	1.568	a,b
10-yr cut	Channel	4.325	1.301	a	11.34	6.11	a	57.583	21.457	a	7.302	2.122	a
	Lower	3.985	1.301	a	13.47	6.11	a	16.57	23.505	a	7.236	2.325	a
	Middle	3.373	0.92	a	9.383	4.321	a	3.854	19.866	a	4.442	1.965	a
	Upper	5.33	1.062	a	7.203	4.989	a	1.98	30.345	a	4.923	3.002	a
20-yr cut	Channel	4.032	0.531	a	30.458	2.494	a	46.45	15.173	a	3.36	1.501	a
	Lower	4.169	0.531	a	13.089	2.494	b	5.132	15.173	a	1.623	1.501	a
	Middle	4.793	0.531	a	14.443	2.494	b	2.045	15.173	a	1.499	1.501	a
	Upper	1.536	0.531	b	46.72	2.733	c	5.895	15.173	a	1.767	1.501	a

Table 4: Tukey's (*post-hoc) test results of 2-way ANOVAs (see Table 2) by position for each restoration age. For each chemical constituent and restoration age, positions that share a letter (a, b, etc.) have similar mean concentrations/ are not significantly different. Those that do not share a letter do have significantly different mean concentrations.

Study	Water Chemistry Response after Tree Removal	Location
Löfgren et al. (2009)	Increased concentrations of Na, K, N, Cl, etc. in streams	Sweden
Martin and Pierce (1980)	Increased concentrations of Ca and N in streams	Northeastern U.S. /New England
Likens et al. (1970)	Increased concentrations of N, Ca, K, Na, Mg, etc. in streams	New Hampshire, USA
Aubertin and Patric (1974)	Increased concentrations of nitrate and phosphate in streams	West Virginia, USA
Hewlett, Post, and Doss (1984)	Increased concentrations of N, K, Na, Ca, Mg, etc. in streams	Georgia, USA
Burns and Murdoch (2004)	Increased concentrations of nitrate in streams	Catskills, New York, USA
Swank, Vose, and Elliott (2001)	Increased concentrations of nitrate, K, Na, Ca, Mg, S, and Cl in streams	Southern Appalachian Mountains, North Carolina, USA
Feller and Kimmins (1984)	Increased concentrations of N, K, Mg, Ca, etc. in streams	Vancouver, British Columbia
Rusanen et al. (2004)	Increased concentrations of nitrate in groundwater	Finland aquifers
Kubin (1998)	Increased concentrations of nitrate in groundwater	Finland aquifers
Williams, Fisher, and Melack (1997)	Increased concentrations of nitrate, potassium, sodium, and chloride in groundwater	Amazonian rainforest in Brazil

Table 5: Previous studies showing similar water quality responses to tree removal and biogeochemical patterns in ecosystem disturbance and recovery.

FIGURES

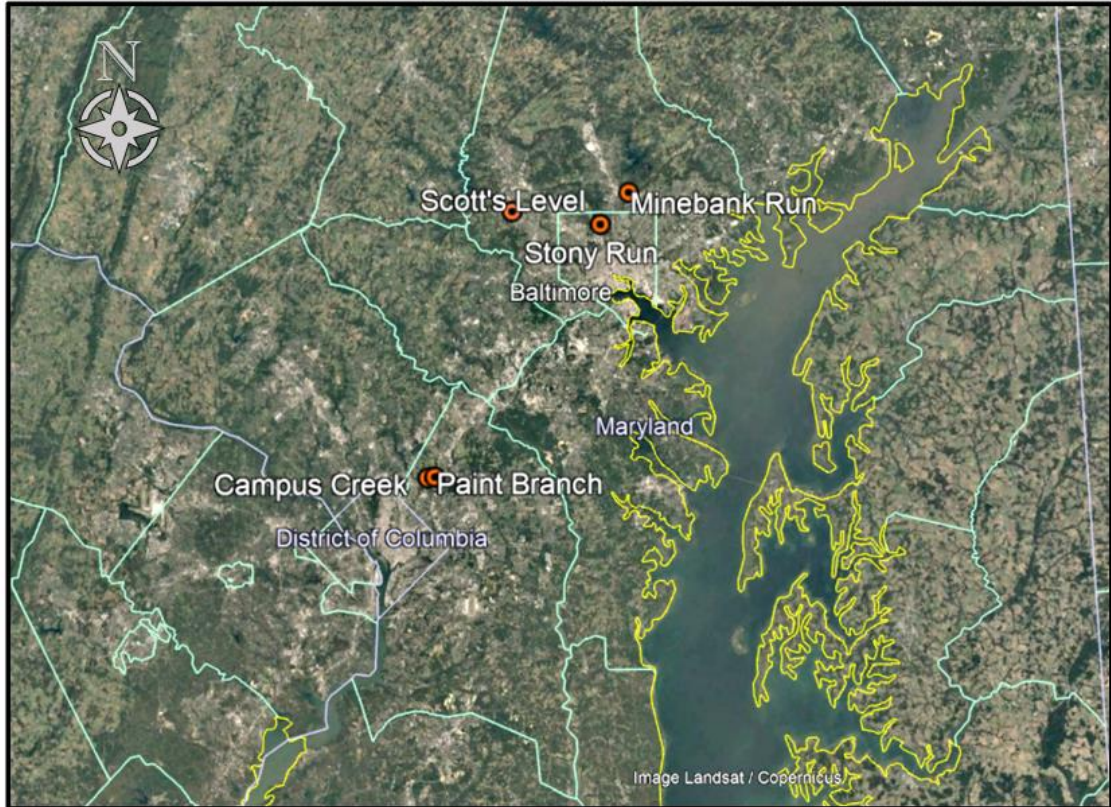


Figure 1: Site Map showing the locations of all 5 study sites in Maryland.



Figure 2: Tree removal at Paint Branch during stream restoration. Before (2012) After (2014)

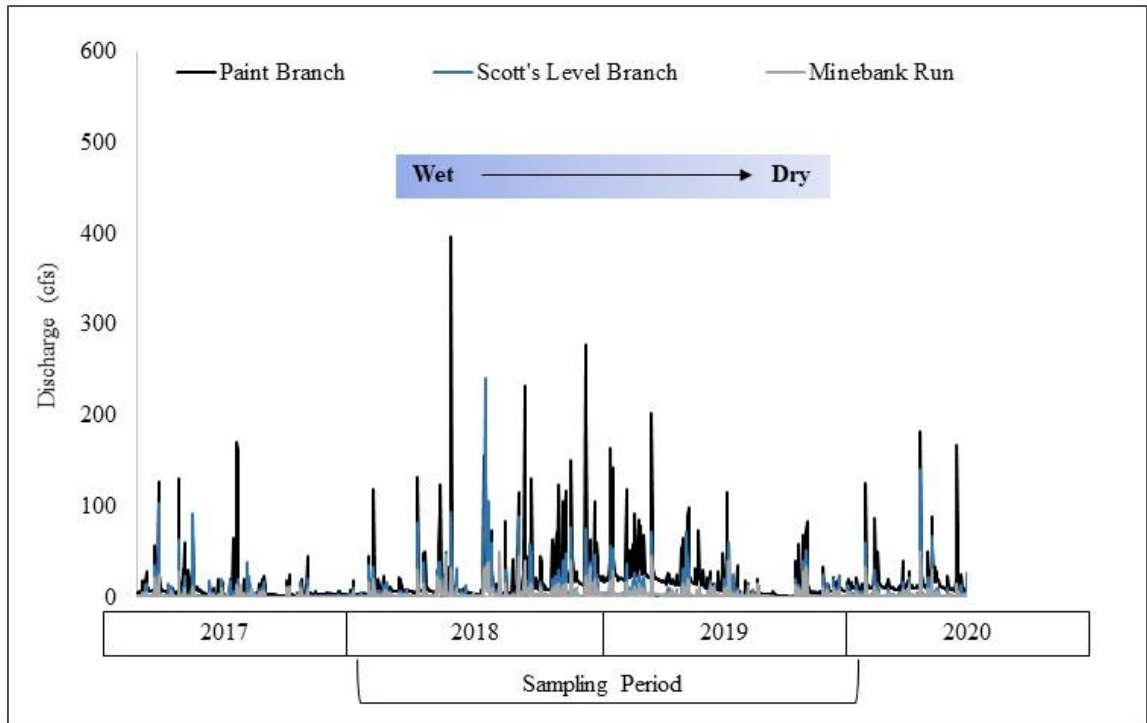


Figure 3: Hydrograph showing daily discharge (cubic feet per second, cfs) as measured by USGS stream gauges located in Paint Branch (upstream of site), Scotts Level (downstream of site), and Minebank Run (downstream of site). Publicly available data obtained via waterdata.usgs.gov.

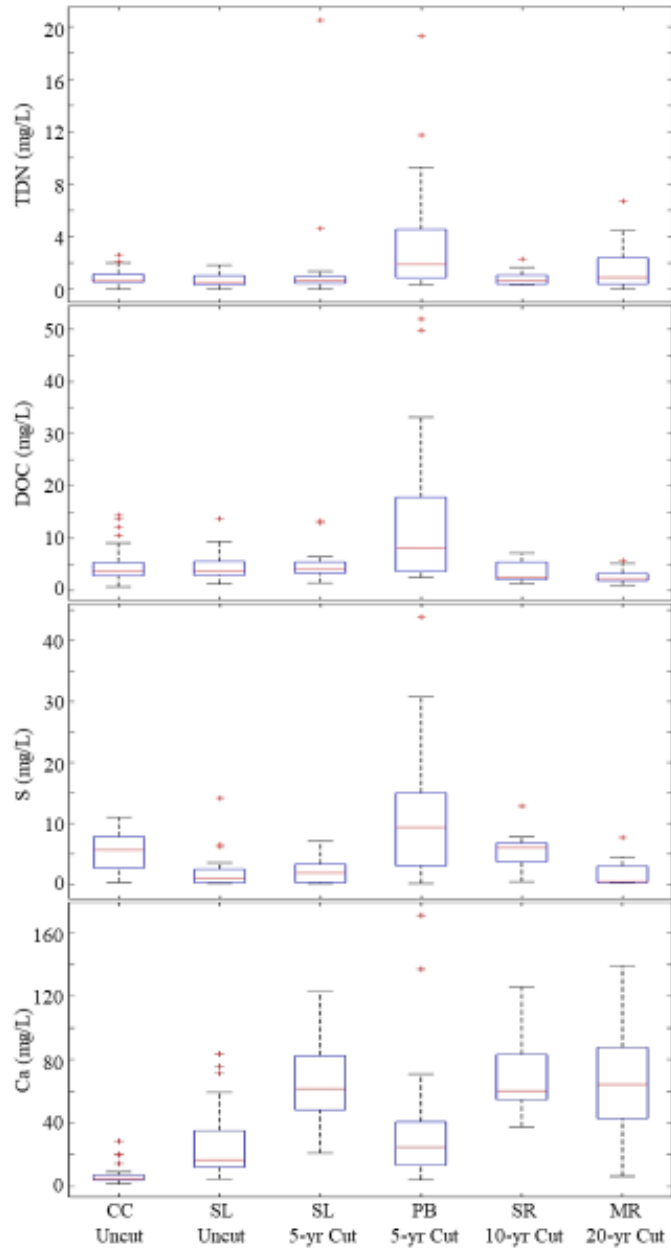


Figure 4: Box and whisker plots showing groundwater concentrations of TDN, DOC, S, and Ca by site and restoration age.

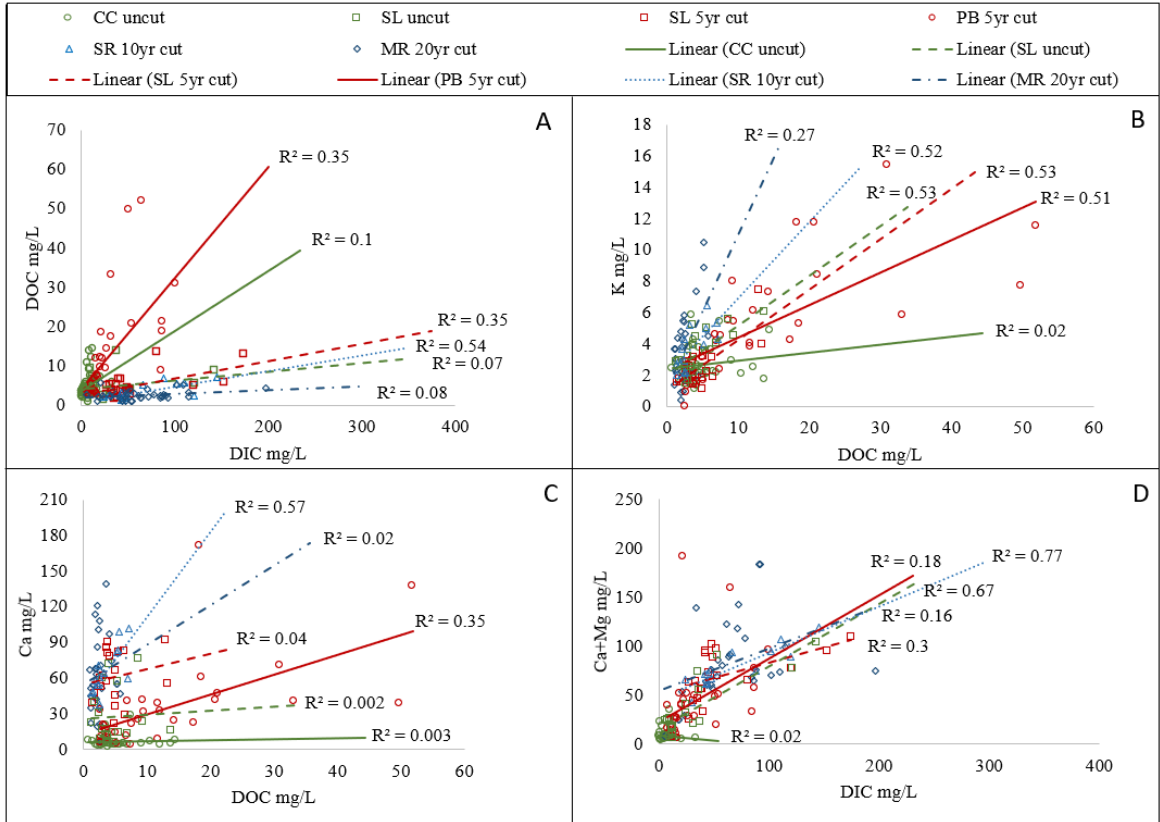


Figure 5: Chemical interactions indicative of biogeochemical processes. Scatter plot by site and restoration age with linear regressions. Regression statistics: A) DOC vs DIC [CC uncut $r=0.38$ / p -value=0.006; SL uncut $r=0.3$ / p -value=0.16 ; SL 5yr cut $r=0.64$ / p -value=0.001 ; PB 5yr cut $r=0.62$ / p -value=0.0001 ; SR 10yr cut $r=0.79$ / p -value=0.001 ; MR 20yr cut $r=0.33$ / p -value=0.033]. B) K vs DOC [CC uncut $r=0.43$ / p -value=0.002; SL uncut $r=0.73$ / p -value=0.0001 ; SL 5yr cut $r=0.6$ / p -value=0.003 ; PB 5yr cut $r=0.65$ / p -value=0.0001 ; SR 10yr cut $r=0.5$ / p -value=0.08 ; MR 20yr cut $r=0.47$ / p -value=0.002]. C) Ca vs DOC [CC uncut $r=0.05$ / p -value=0.72; SL uncut $r=0.06$ / p -value=0.79 ; SL 5yr cut $r=0.25$ / p -value=0.26 ; PB 5yr cut $r=0.58$ / p -value=0.001 ; SR 10yr cut $r=0.81$ / p -value=0.001 ; MR 20yr cut $r=0.09$ / p -value=0.59]. D) Ca + Mg vs DIC [CC uncut $r=0.39$ / p -value=0.005; SL uncut $r=0.71$ / p -value=0.0002 ; SL 5yr cut $r=0.56$ / p -value=0.006 ; PB 5yr cut $r=0.41$ / p -value=0.02 ; SR 10yr cut $r=0.91$ / p -value=0.00002 ; MR 20yr cut $r=0.34$ / p -value=0.03]

Water Quality Recovery along a Restoration Chronosequence

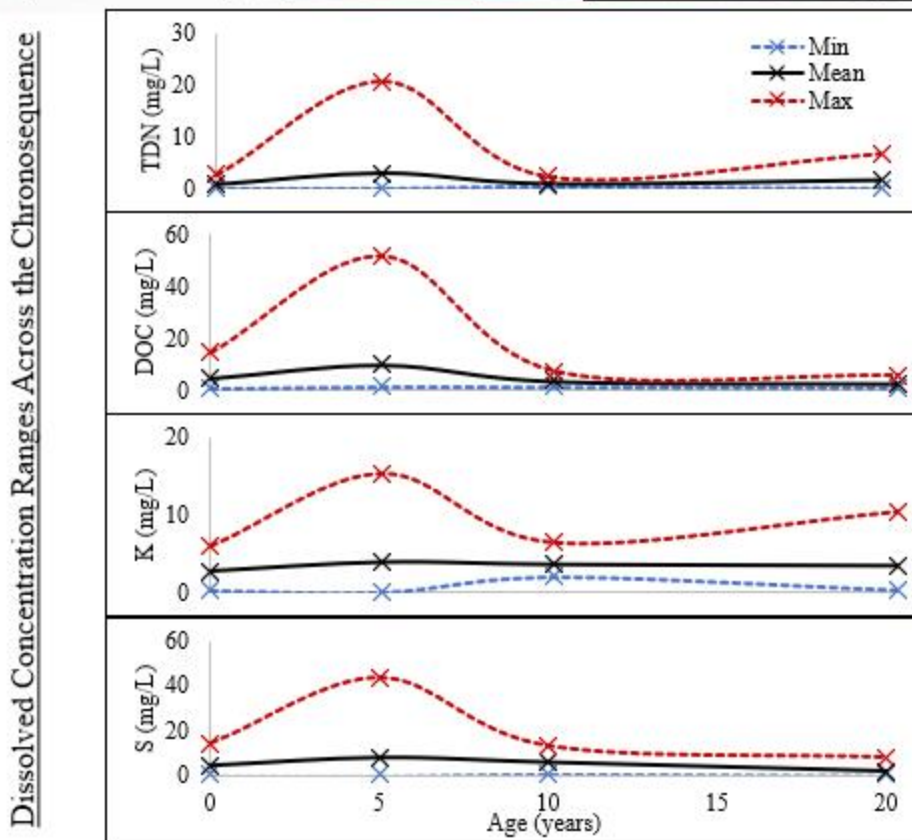
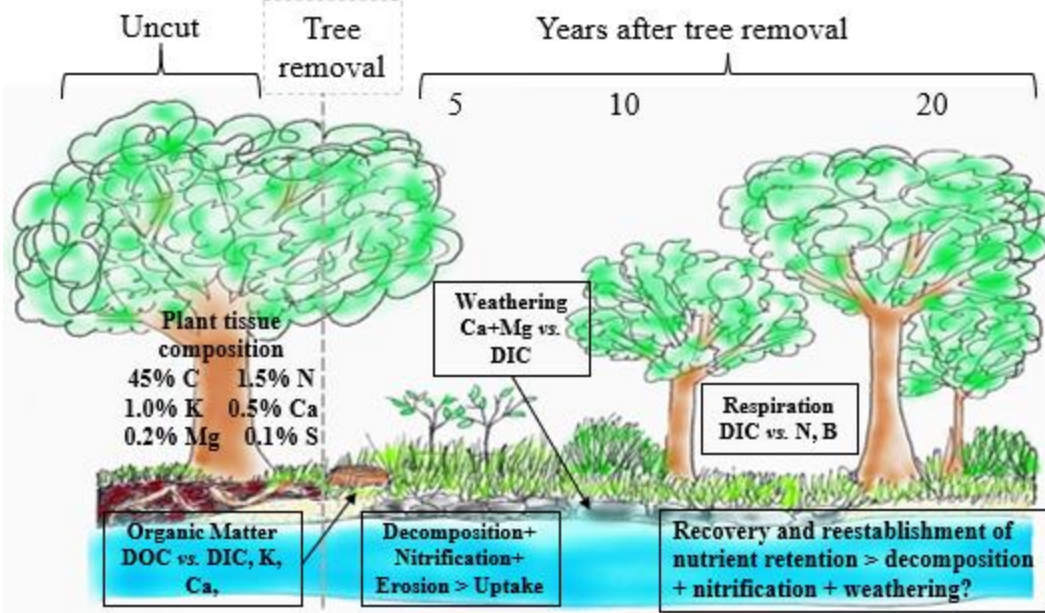


Figure 6: Conceptual model of the restoration chronosequence; from pre-restoration to tree removal to subsequent recovery. Mean concentrations of nutrients by restoration age 0 (uncut), 5 (5-year cut), 10 (10-year cut), and 20 (20-year cut).

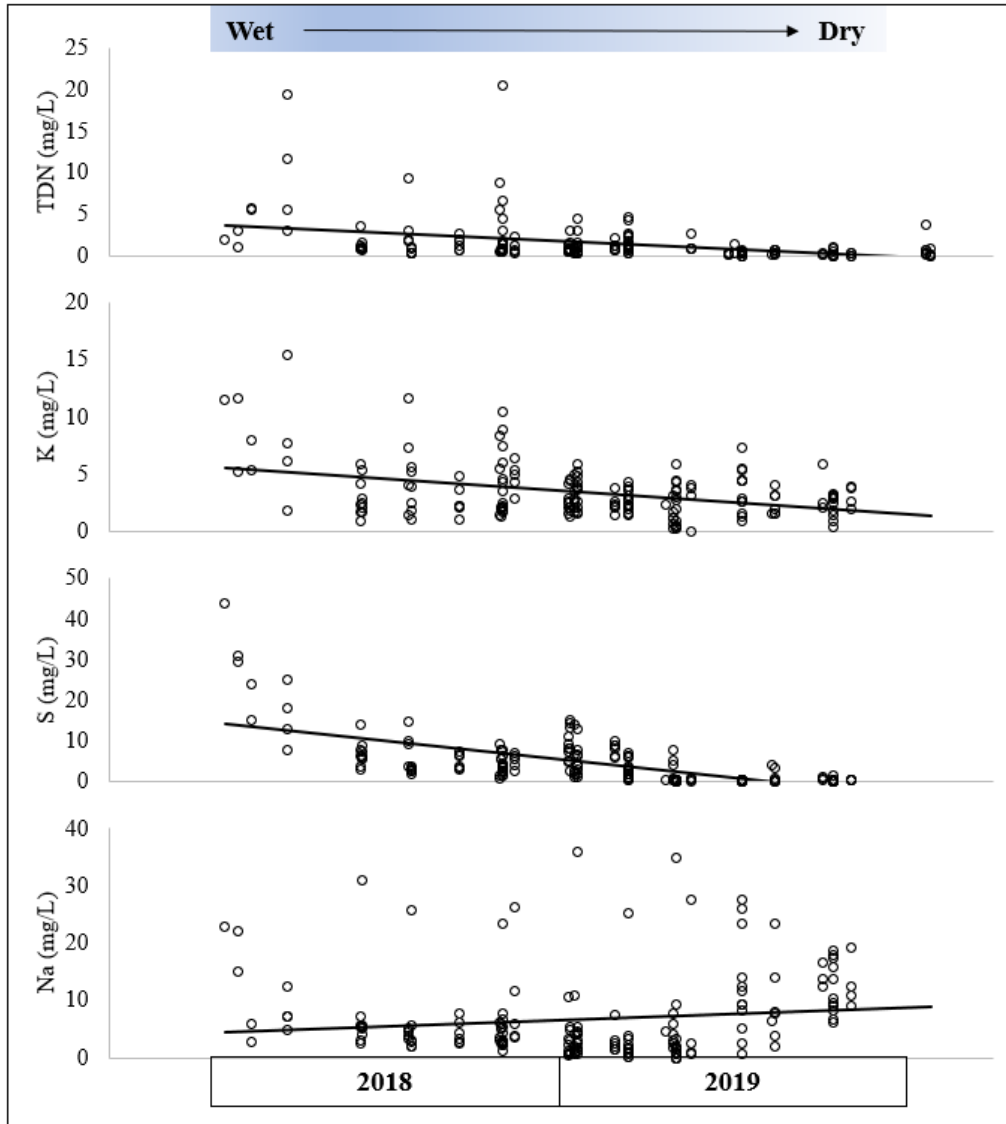


Figure 7: Timeseries of all groundwater data (all sites combined) trends from wet to dry conditions (refer to Figure 2). Regression statistics: [TDN $r=-0.37$ / $p\text{-value} < 0.00001$; K $r=-0.38$ / $p\text{-value} < 0.00001$; S $r=-0.65$ / $p\text{-value} < 0.00001$; Na $r=0.04$ / $p\text{-value} = 0.6045$].

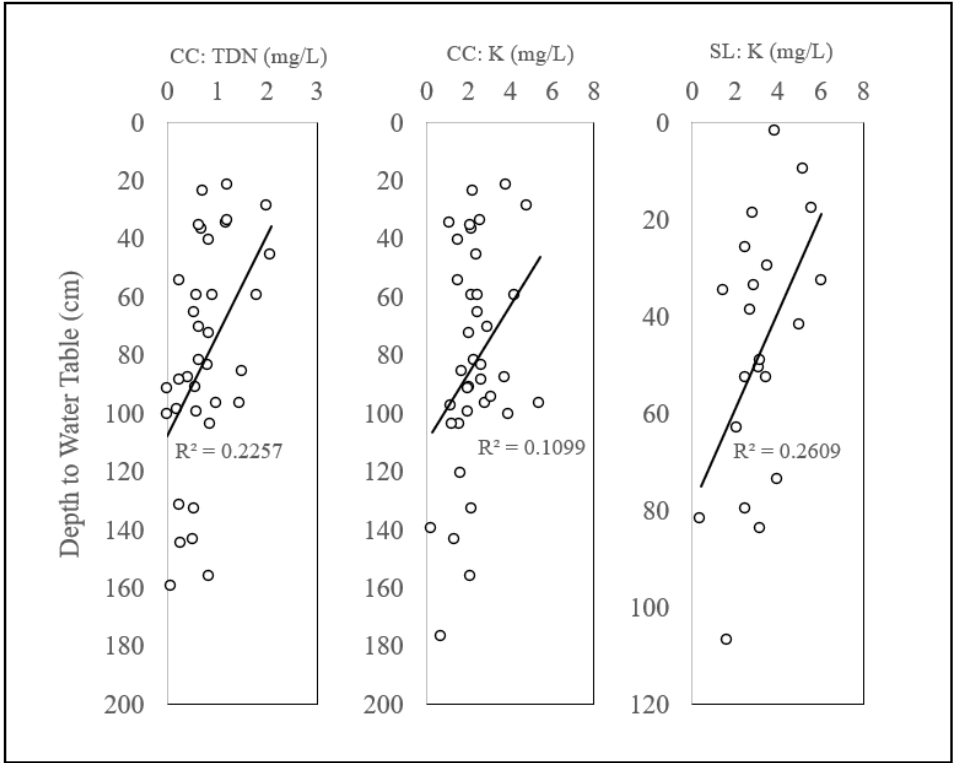


Figure 8: Relationships between nutrients and water table height at uncut sites Campus Creek (CC) and Scott's Level (SL).

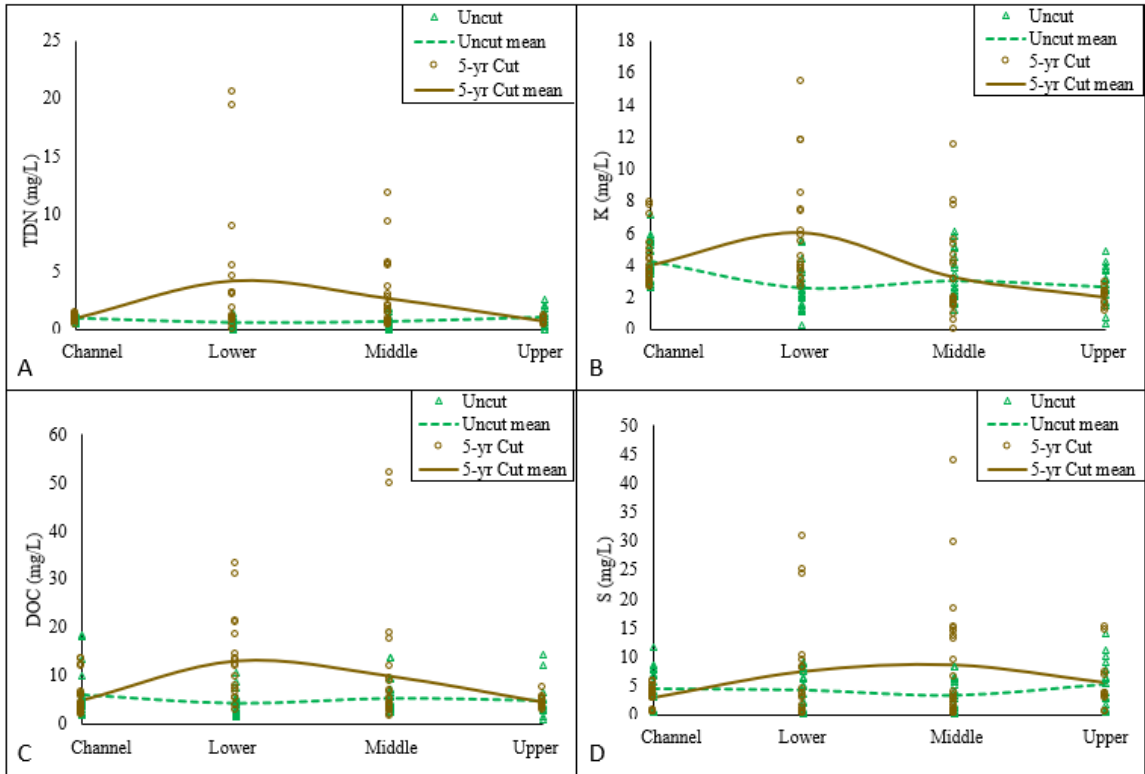


Figure 9: Plots of dissolved concentrations by position of A) TDN, B) K, C) DOC, and D) S; comparing uncut sites and 5-yr cut sites (mean concentration by position connected by curved line).

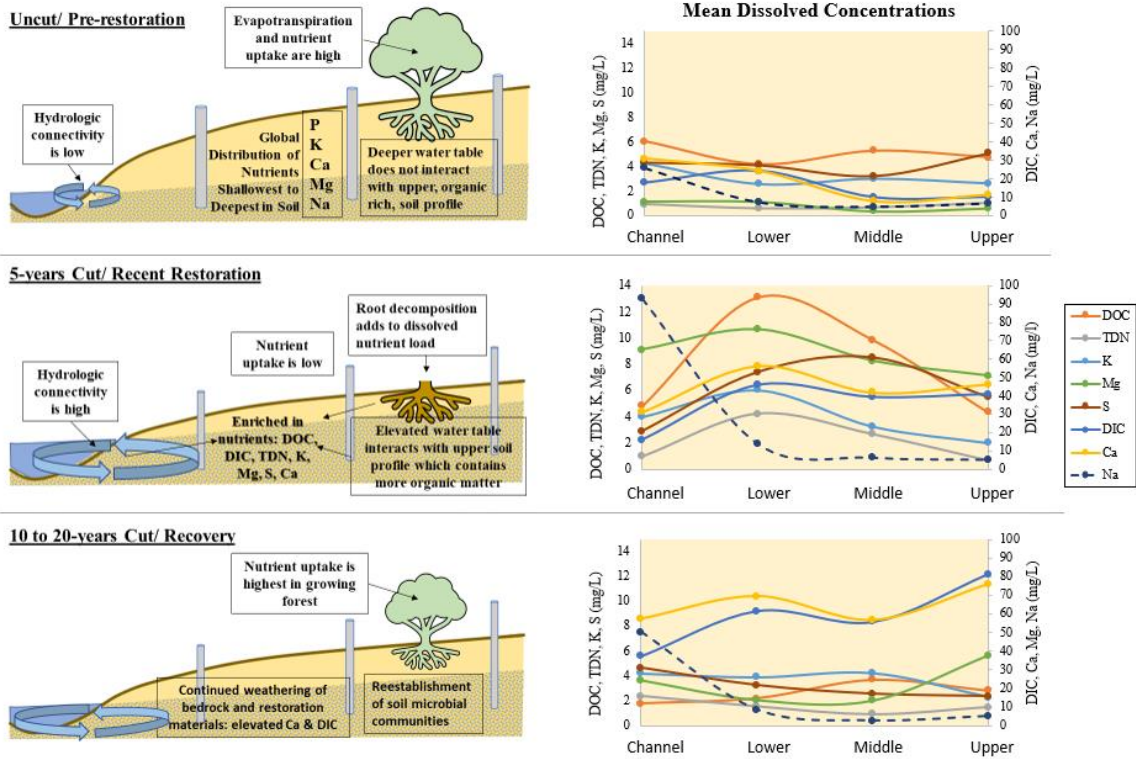


Figure 10: Left: Conceptual model of spatial differences between sites in different ages of recovery after tree removal. Right: mean concentrations by position (connected by curved lines) for each condition (Uncut, 5-yr Cut, and 10-20yr Cut (combined)). Global distribution of nutrients along vertical soil profiles from Jobbagy and Jackson (2001).

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