Chapter 1
Effects of Human Activity on the Processing of Nitrogen in Riparian Wetlands: Implications for Watershed Water Quality

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Abstract Wetlands are critical ecosystems that make substantial contributions to ecosystem services. In this study, we asked how the delivery of an ecosystem service of interest (N processing such as denitrification and mineralization) is impacted by anthropogenic activity (as evidenced by land cover change). We identify relevant factors (hydrology, nitrogen, and carbon variables), select headwater wetland sites in Ohio and Pennsylvania USA to represent a gradient of anthropogenic disturbance as indicated by land cover characteristics (represented by the Land Development Index, or LDI), and determine if there are differences in the selected variables as a function of this gradient by categorizing sites into two groups representing high and low disturbance. We utilized Classification and Regression Trees (CART) to determine which variables best separated high from low disturbance sites, for each spatial scale at which land cover patterns were determined (100 m, 200 m, 1 km radius circles surrounding a site), and within each category of water quality variable (hydrology, nitrogen and carbon). Thresholds of LDI were determined via the CART analyses that separated sites into two general classes of high and low disturbance wetlands, with associated differences in Total Nitrogen, NH_4^+, Soil Accretion, C:N, Maximum Water Level, Minimum Water Level, and %Time in Upper 30 cm. Low Disturbance Sites represented forested settings, and exhibit relatively higher TN, lower NH_4^+, lower Soil Accretion, higher C:N, higher Maximum Water Level, shallower Minimum Water Level, and higher %Time in Upper 30 cm than the remaining sites. LDIs at 100 m and 200 m were best separated into groups of high and low disturbance sites by factors expected to be proximal or local in nature, while LDIs at 1000 m predicted factors that could be related to larger scale land cover patterns that are more distal in nature. We would expect a water quality

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process such as denitrification to be relatively lower in forested settings, due to the low available nitrogen (associated with high C:N) and constant and saturated conditions; conditions for maximum denitrification may be found in agricultural settings, where high nitrate groundwater can interact with surface soils through a wetting and drying pattern. The use of land cover patterns, as expressed by LDI, provided useful proxies for nitrogen, carbon, and hydrology characteristics related to provision of water quality services, and should be taken into account when creating, restoring, or managing these systems on a watershed scale.

Keywords Headwater wetlands • Denitrification • Nitrogen processing • Disturbance • Land cover • Land Development Index (LDI)

1.1 Introduction

The need to manage landscapes for ecosystem services is essential if we are to find solutions to issues that are critical for humanity, including energy policy, food security, and water supply (Holdren 2008; Robertson et al. 2008). Wetlands are critical ecosystems that make substantial contributions to the most valued of these ecosystem services (Millennium Ecosystem Assessment 2003), and their common location between human activities (e.g., agriculture, development) and critical water resources (e.g., aquifers and rivers used as water supplies, streams for recreational use) adds to their importance. The recognition that wetlands provide valuable ecosystem services has led to the development of assessment protocols to estimate service levels across wetland types in a landscape, evaluate services in relation to the impact that human activities have on these systems, and provide guidelines for wetland restoration in terms of these services (e.g., Zedler 2003).

Human activities are known to alter the benefits that ecosystems provide (MEA 2003). However, human activities often occur within the wider surrounding landscape and may be spatially disconnected from the ecosystem services they impact. For example, activities such as agriculture, expressed on the landscape as land cover in row crops or pasture, create stressors/drivers such as sedimentation and modification of hydrological patterns, which may influence ecosystem processes and condition indicators such as soil biogeochemistry and plant community, thus influencing an ecosystem service such as denitrification. This complicates our ability to determine linkages between land use change and subsequent impacts on the ecosystems that are part of that landscape. Assessing impacts requires understanding how human activities generate stressors that alter wetland ecological condition, and ultimately affect the flow of these services. The many system connections between activities, stressors, condition, and the ultimate delivery of services render simple landscape predictions to ecosystem service impossible (Xiong et al. 2015). For example, to inform our understanding of biogeochemical processes in wetlands we must necessarily look at linkages at several intermediate scales, including landscape to wetland scale linkages (e.g. how land use affects conditions within a site, such as water levels); and landscape to process scale linkages (how land use affects the delivery of materials that drive ecosystem processes, e.g. nitrogen inflow).

While all ecosystem services are important, some of the most valued ecosystem services that wetlands provide, and are managed for, are those associated with water quality improvement due to the biogeochemical processing and storage of nutrients and sediment. For example, denitrification is the primary process by which nitrate is transformed in wetlands, thereby removing a key waterborne pollutant. In the U.S., nitrate runoff is a significant problem, enriching surface waters (Carpenter et al. 1998; Verhoeven et al. 2006) and contributing to hypoxia in the Gulf of Mexico (Turner and Rabalais 1991; Rabalais et al. 2002). Because of their connectivity to lotic ecosystems, high C availability, and inflows of nitrate, denitrification tends to be greatest in riparian and floodplain wetlands (Fennessy and Cronk 1997; Hill 1996).

The ecosystem services related to nitrogen processing are potentially controlled by a number of factors that occur at a range of spatial and temporal scales (Fig. 1.1). For example, denitrification is a microbial process that is most directly affected by factors at the process scale (Groffman et al. 1988) such as the availability of nitrate (Seitzinger 1994), dissolved organic carbon (DOC) (Sirivedhin and Gray 2006), temperature (Sirivedhin and Gray 2006), pH (Simek and Cooper 2002), and levels of dissolved oxygen (Hochstein et al. 1984). These process scale factors are affected by the wetland-scale structures of vegetation and hydrology; vegetation can affect carbon availability and temperature while hydrology can affect nitrate loading and redox conditions (Prescott 2010;

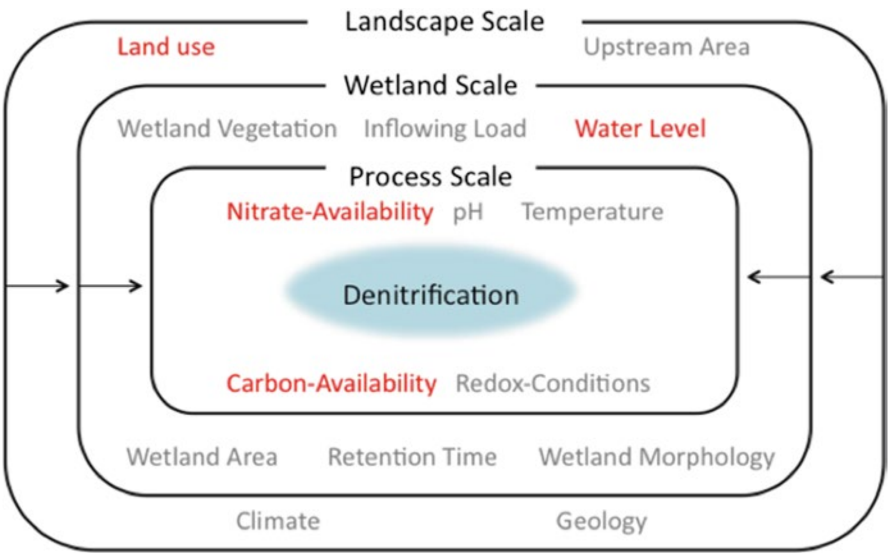

Fig. 1.1 Factors working at different spatial scales that affect the process of denitrification in wetlands. Factors shown in *red* were a focus of this study (Modified from Trepel and Palmeri 2002)

Adamus and Brandt 1990; Mitsch and Gosselink 2007). The wetland scale factors can also be affected by the landscape scale factors of land use, geology, and climate. Agricultural activities have been known to affect wetland hydrology, nitrate loading, and vegetative community, while climate and geology can affect wetland size and vegetation (Xiong et al. 2015; Groffman et al. 2002; Wardrop and Brooks 1998; Adamus and Brandt 1990; Mitsch and Gosselink 2007). This same dependence on both landscape- and wetland scale factors can be postulated for nitrogen mineralization, which is also affected by the process-scale factors of carbon and nitrogen availability, as well as temperature and pH.

Understanding the complexity of the interactions between an ecosystem and its landscape requires that the variables that drive ecosystem processes (shown in Fig. 1.1) be tested as a function of landscape characteristics, such as land cover pattern. Some variables serve dual roles; for example, hydrology can respond to land cover changes, but may also be a driver, affecting the microbial community present at a site, which is related to the denitrification potential. In this study, we asked how the delivery of ecosystem services is impacted by anthropogenic activity (as evidenced by land cover change), as described by the proposed conceptual model (Fig. 1.1). To investigate this we used the following approach: (1) identified the factors (variables) that affect the delivery of the ecosystem services of interest, in this case the soil characteristics that affect N processing (such as denitrification and mineralization); (2) selected sites to represent a gradient of anthropogenic disturbance as indicated by land cover characteristics, ranging from least impacted to heavily impacted land use conditions; and (3) determined if there are differences in the selected soil characteristics as a function of this gradient by categorizing sites into two groups representing high and low disturbance.

1.2 Methods

1.2.1 Wetland Study Sites

For this study, we selected 20 wetland sites in the Mid Atlantic Region, with 10 located in the Ridge and Valley region of Pennsylvania and 10 located in the Appalachian Plataea and Central Lowland of Ohio (Fig. 1.2). Riverine and depressional wetland sites were selected within these regions to represent a range of surrounding land-uses and land covers (LULC) (Table 1.1), while keeping wetland Hydrogeomorphic Classification, climate, and geology similar. Floodplain and Headwater Floodplain designations represent similar wetland types (wetlands along headwater streams), located in Ohio and Pennsylvania, respectively. Depression and Riparian Depression represent similar wetland types (closed depressions in a floodplain setting of a headwater stream), located in Ohio and Pennsylvania, respectively.

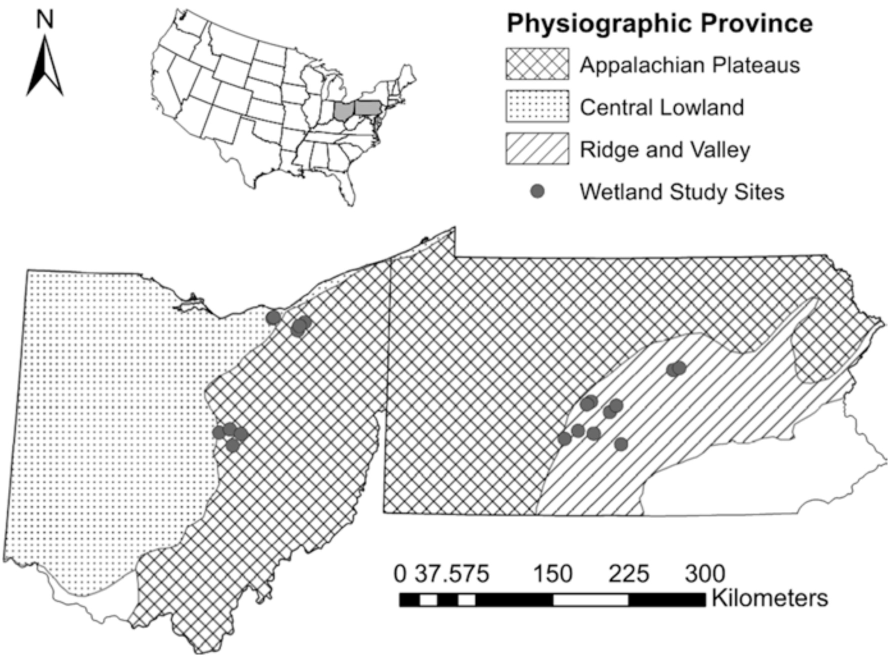

Fig. 1.2 Map of the study sites and the physiographic provinces in which they occur in Ohio and Pennsylvania

1.2.2 Quantifying Anthropogenic Activity Surrounding Wetland Study Sites

We used the Landscape Development Intensity (LDI) index, originally proposed by Brown and Vivas (2005), to assess the level of anthropogenic/human activity on wetland study sites. The LDI index estimates potential human impact to a study location by taking a weighted average of the intensity of land use (by LULC classifications) in a defined area surrounding the location. LDI index scores can range from 1 to 8.97, with a score of 1 indicating 100 % natural land cover (e.g. forest, open water) and higher scores indicating increasingly more intensive land uses (e.g. agriculture, urban). The LDI scores are calculated based on assignment of land-use coefficients (Table 1.2). Coefficients were calculated as the normalized natural log of energy (embodied energy) per area per time (Brown and Vivas 2005), and defined as the non-renewable energy needed to sustain a given land use type. The LDI is calculated as a weighted average, such that:

$$\mathrm{LDI} = \sum \%\mathrm{LUi} * \mathrm{LDIi}.$$

where, LDI = the LDI score, %LUi = percent of total area in that land use i, and LDIi = landscape development intensity coefficient for land use i (Brown and Vivas

Table 1.1 Information on study site locations, soil series and the data for each site that was available for use in the CART analyses

Wetland study site information						Data available for CART analyses				
Site name	State	Latitude	Longitude	HGM class[a]	Soil series[b]	N (n =14)[c]	C/S (n = 20)[d]	Hyd. (n = 16)[e]	Hydrology data range (M-Y)[f]	No. wells
Laurel Run	PA	40.70264	−77.84851	HF	Atkins silt loam	Yes	Yes	Yes	6-2011 to 5-2013	3
Clarks Trail	PA	41.03170	−77.10830	RD	Udifluvents and fluvaquents, gravelly	Yes	Yes	Yes	7-2010 to 8-2011	2
McCall Dam	PA	41.01590	−77.18160	RD	Philo and atikns, Very stony soils	Yes	Yes	No	N/A	N/A
Secret Marsh	OH	41.31295	−81.58878	D	Sebring silt loam	No	Yes	Yes	7-2010 to 7-2011	2
Shavers Creek	PA	40.64521	−77.92506	HF	Atkins silt loam	Yes	Yes	Yes	7-2010 to 5-2013	3
Tuscarora	PA	40.35920	−77.79330	HF	Atkins silt loam	No	Yes	No	N/A	N/A
Mustang Sally	PA	40.73650	−78.14303	SP/HF	Holly silt loam	Yes	Yes	Yes	9-2011 to 05-2013	3
Kokosing	OH	40.37599	−82.44648	RD	Tioga fine sandy loam	Yes	Yes	Yes	7-2010 to 7-2012	4
Got Milk	PA	40.45390	−78.11040	HF/RD	Atkins silt loam	No	Yes	No	N/A	N/A
Cauldron	PA	40.47810	−78.28917	HF	Holly silt loam	Yes	Yes	Yes	7-2010 to 3-2012	3
Ballfield	OH	40.26875	−82.28320	D	Linwood much	No	Yes	Yes	7-2010 to 3-2012	3
Bat Nest	OH	40.37542	−82.19557	F	Shoals silt loam	Yes	Yes	No	N/A	N/A
Hellbender	OH	40.40971	−82.32442	F	Tioga fine sandy loam	Yes	Yes	Yes	7-2010 to 11-2012	4

Cambaris	PA	40.40646	−78.44539	HF	Udifluvent-Dystrorchepts complex	Yes	Yes	Yes	7-2011 to 5-2013	3
Skunk Forest	OH	41.38366	−81.50924	F	Tioga loam	No	Yes	Yes	7-2010 to 6-2011	3
R & R	PA	40.71338	−78.18883	HF	Udifluvent-Dystrorchepts complex	Yes	Yes	Yes	9-2011 to 05-2013	3
Bee Rescue	OH	41.40832	−81.89191	D	Chagrin silt loam	Yes	Yes	Yes	7-2010 to 6-2011	3
Blackout	OH	41.35251	−81.56918	D	Mitiwanga silt loam	No	Yes	Yes	7-2010 to 7-2011	3
Lizard Tail	OH	41.41611	−81.87608	RD	Chagrin silt loam	Yes	Yes	Yes	7-2010 to 6-2011	2
Vernal Pool	OH	41.41833	−81.87273	RD	Chagrin silt loam	Yes	Yes	Yes	7-2010 to 6-2011	1

[a]Hydrogeomorphic (HGM) classifications include: *HF* headwater floodplain, *RD* riparian depression, *SP* slope, *F* floodplain, *D* depression
[b]Soil series come from the SSURGO Web Soil Survey (accessed 10/15/2013)
[c]Sites used for categorical regression tree (CART) analyses based on nitrogen pools
[d]Sites used for CART analyses based on carbon pools and soil accretion rates
[e]Sites used for CART analyses based on hydrology metrics
[f]The ranges describe the temporal extents (Month-Year) of data collected across all wells at a wetland study site. Thus, all wells at a site might not have spanned the ranges denoted here

Table 1.2 Landscape development intensity coefficients used to calculate the LDI index scores (Brown and Vivas 2005). Land cover categories come from the National Land Cover Database (Homer et al., 2015)

Land cover categories	LDI weights
Water	1
Deciduous Forest	1
Evergreen Forest	1
Mixed Forest	1
Shrub/Scrub	1
Woody Wetlands	1
Emergent Herbaceous Wetlands	1
Grassland/Herbaceous	3.31
Pasture/Hay	3.31
Cultivated Crops	5.77
Developed, Open Spaces	7.18
Developed, Low Intensity	7.18
Barren Land	7.81
Developed, Medium Intensity	8.97
Developed, High Intensity	8.97

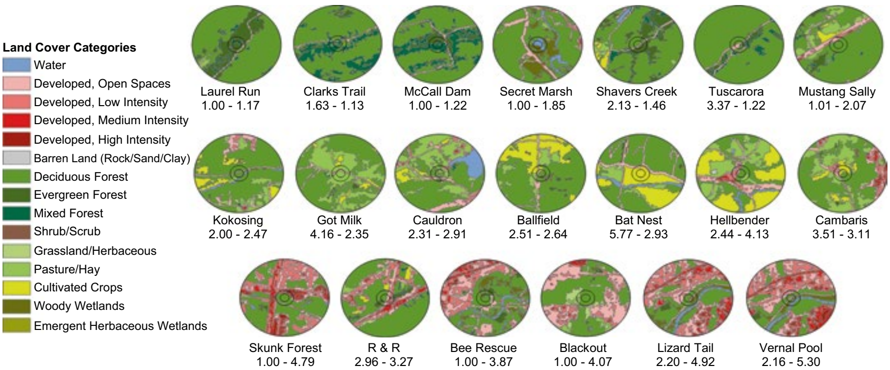

Fig. 1.3 Land cover in the 1000 m radius circles around each site included in this study. Sites are organized into rows according to their dominant land cover setting arranged, from *top* to *bottom*, by natural, agricultural, and urban/developed land use. Land Development Intensity Index (LDI) values at 100 m and 1000 m, respectively, are shown below each land cover *circle*

2005). This provides an integrative measure of land-use for a defined area around a site in a single score rather than looking at each land-use class separately.

The LDI was calculated using the 2011 National Land Cover dataset (NLCD) (Homer et al. 2015) for three landscape scale assessment areas in 100-m, 200-m and 1-km radius circles around the center of the wetland assessment area (Fig. 1.3). Percent area of LULC classifications for each wetland assessment area was extracted from the NLCD using ArcGIS (version 10.3, Esri, Inc.).

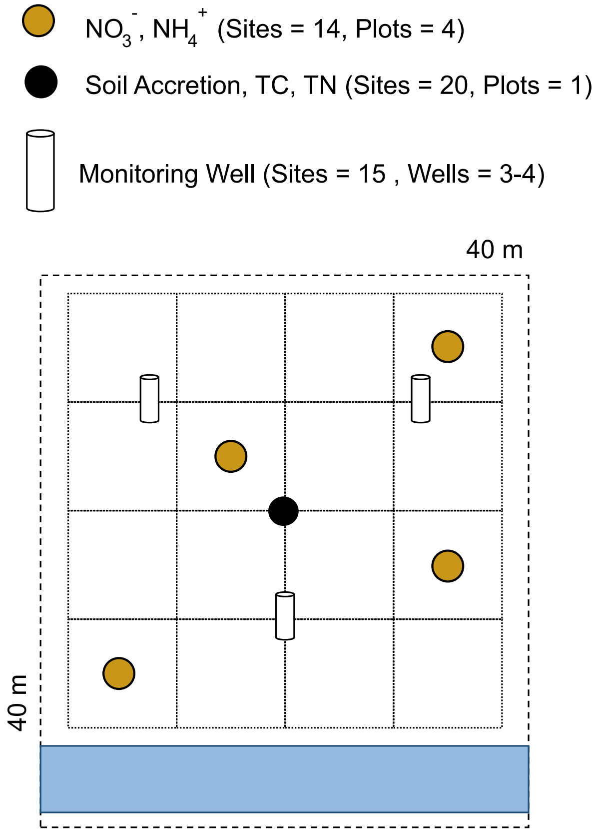

Fig. 1.4 Schematic of the sampling design used at each site

1.2.3 Field and Laboratory Measurements

Data were collected on ecosystem service measurements related to nitrogen cycling (e.g., denitrification and nitrogen mineralization), including related measures of soil carbon, and hydrologic variability. The generalized sampling design for each site is presented in Fig. 1.4.

1.2.3.1 Nitrogen Pools

Nitrogen processing in wetland ecosystems is spatially dynamic. As such, we implemented a spatial sampling regime to measure average site-level nitrogen pools in the fall of 2011 in 14 of our wetland study sites. Ten m by 10 m plots were established in a grid over a 40 m by 40 m wetland assessment area at each study site (Fig. 1.4), resulting in 16 plots. Four sampling plots were randomly selected from this pool of 16 plots for nitrogen pool analysis.

In each sampling plot, a soil core was collected at each of the four subplots using an 8-cm diameter PVC tube to a depth of 5 cm, placed into a re-sealable plastic bag and stored on ice for transport to the laboratory. The core was used to measure extractable pools of ammonium (NH_4^+) and nitrate (NO_3^-). All samples were stored at 4 °C until processing, which occurred within 48 h of field collection. Soils were weighed and subsequently homogenized by pushing through a 2-mm sieve. Approximately 20.0 g of wet mass soil was sampled in duplicate or triplicate for gravimetric water content. Samples were dried at 60 °C until a constant mass was reached.

A second subsample, consisting of 20.0 g of wet mass soil was weighed out in duplicate or triplicate for extraction of N species (i.e., NH_4^+, NO_3^-), following Keeney and Bremner (1966). Samples were extracted using 2 M KCl, agitated for 1 h on an orbital shaker and left to settle for > 12 h, before the extractant was filtered through 1.5 μm binder-free glass fiber filters to remove any remaining soil particles. Filtrate was stored at −20 °C in polypropylene test tubes until colorimetric measurement were made using a Lachat QuikChem® 8500 Series 2 Flow Injection Analysis. Final soil extractable NH_4^+ and NO_3^- concentrations were calculated on a dry weight basis and corrections were made for small concentrations NH_4^+ and NO_3^- found on filters.

Approximately 1 month later (i.e., 24–29 days later), a second core, encapsulated by resin bags, was taken ~0.25 m away from the first core as part of a nitrogen mineralization incubation (methods based on Noe 2011). Soil extractable NH_4^+ and NO_3^- were significantly related at the site-level across sampling periods (extractable NH_4^+ adj. $R^2 = 0.65$, p-value < 0.001, extractable NO_3^- adj. $R^2 = 0.77$, p-value < 0.001) and as such, only initial soil core samples are used in the subsequent analyses.

1.2.3.2 Soil Accretion and Carbon Pools

A soil core, measuring 8.5 cm in diameter and 40–50 cm in depth (depending on site conditions), was collected from the center of each wetland assessment area in the summer of 2011 (Fig. 1.4). Cores were collected using a hand-operated stainless steel corer designed for use in freshwater wetland soils. Each core was extruded and sectioned into 2-cm increments for analysis. Increments were stored in re-sealable plastic bags and placed on ice while being transported to the laboratory for analysis. Increments were dried at 60 °C until a constant mass was reached.

Cesium-137 was measured on each increment by gamma spectroscopy of the 661.62 keV photopeak (Craft and Richardson 1998). The depth of the ^{137}Cs maximum in each core corresponds to the 1964 period of maximum deposition of radioactivity from aboveground nuclear weapons testing (Reddy and DeLaune 2008). This peak was used to calculate the medium- term (47-year) rate of vertical soil accretion. Only cores that contained interpretable ^{37Cs} profiles were used. Soil accretion rates (mm · year^{-1}) were calculated as follows (Moshiri 1993):

$$\text{Soil accretion rate}\left(\text{mm year}^{-1}\right) = \frac{\text{Depth the}^{137}\text{Cs peak}}{2011 - 1964}$$

Each core section was also analyzed for total carbon (TC %) and TN. A dried subsample was ground passed through a 0.25 mm sieve for analysis by dry combustion using a Perkin-Elmer 2400 Series CHNS/O elemental analyzer. TC and TN was averaged for the top 10 cm of soil and TC:TN ratios were calculated.

1.2.3.3 Hydrologic Metrics

Three to four Ecotone WM-1-m automatic water level monitoring wells (Remote Data Systems, Inc. Model #: WM16k1015) were established at 16 of the wetland study sites. When possible we positioned 3 of the wells in an equilateral triangle with the base of the triangle towards adjacent hillslopes. Water level recordings were collected at 3-h intervals between 2010 and 2013, with each site-well varying in its collection period.

Hydrology metrics were selected to provide insight into groundwater variation, biogeochemical processes, and environmental stress. To quantify these dynamics 11 hydrology metrics were calculated: average water level, relative to ground surface (cm), maximum water level, relative to ground surface (cm), minimum water level, relative to ground surface (cm), the 25th, 50th, and 75th percentile water level, relative to ground surface (cm) of all recorded water levels over the sampling period for an individual well, percent time the water level was above ground (%), percent time the water level was in the upper 10 cm of the soil profile (%), percent time water level was in the upper 30 cm of the soil profile, percent time the water level was between 10 and 30 cm (%), the mean water level difference over a 24-h period, and mean water level difference over a 7-day period.

Average water level provides a general measure of a site's hydroperiod during a given year. The metrics 'percent time the water level is in the upper 30 cm of the soil profile' and 'percent time above ground' provide information specifically relevant to water availability to vegetation and biogeochemical processes. The "percent time" metrics were calculated as the number of data points equal to or above the depths (i.e., ground level, 10 cm, and 30 cm) with respect to the total number of data points. Mean 7-day and 24-h differences provide insights into water level stability and temporal reaction rates. These two metrics were calculated once per day on a rolling basis. These hydrology metrics were calculated for individual wells, where duration was unique to each well. Final metrics were calculated as the average metrics across wells within a site; spatial variability of hydrology metrics within a given site was relatively low.

1.2.3.4 Data Analysis

We utilized classification and regression tree (CART) analysis to explore thresholds between LDI metrics at the three landscape assessment scales utilizing drivers of nitrogen processes (nitrogen, carbon, and hydrology metrics) as explanatory variables. CART is suited for this because it takes into account non-linear and high-order interactions that might be missed in simple linear regression analyses. CART uses binary cluster trees to explain variation in a single response variable by one or more explanatory variable (De'ath and Fabricius 2000). For each landscape assessment scale, CARTs were further broken into three predictor groups, including predictors related to soil carbon (i.e., soil accretion, TC, and C:N ratios), those related to soil nitrogen (i.e., TN, extractable NH_4^+, and extractable NO_3^-), and hydrology predictors (i.e., 10 metrics listed above in *Hydrologic Metrics*). CART analyses were performed in JMP ® Pro (Version 12.0.1, SAS Institute, Inc.) Only the first split (i.e., strongest predictor) in each CART was used for discussion. CARTs were also used to examine threshold LDIs with the three landcover classes (forested, agriculture, and urban).

1.3 Results

Our collection of sites provided a diversity of land cover settings (Fig. 1.3); sites varied in their LDIs at our specified spatial scales of assessment (100 m, 200 m, and 1000 m), and in the change in LDI values with increasing distances from the site (i.e., the shape of the curves across this distance; Fig. 1.5). Sites basically fell into three groups based on the shape of the LDI curves: those that are in primarily low-LDI land cover settings from 100 to 1000 m (Clark's Trail, Shaver's Reference, Tuscarora, Laurel Run, McCall Dam in PA; Kokosing and Secret Marsh in OH); those that begin in moderate LDI settings and whose LDI decreases as one proceeds outward from the site (Got Milk, Cambaris, R&R, Cauldron, and Mustang Sally in

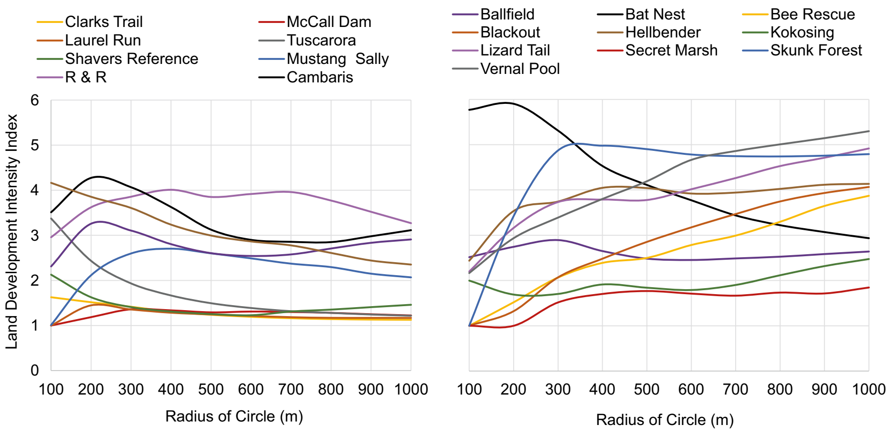

Fig. 1.5 Plots of LDI scores with increasing distance around each site. LDI scores were calculated at 100 m intervals across the distance from 100 to 1000 m. Pennsylvania sites are shown on the *left* and Ohio sites on the *right*

PA; Ballfield in OH); and those that begin in relatively high LDI settings and whose LDI increases as one proceeds outward from the site (Hellbender, Lizard Tail, Vernal Pool, Skunk Forest, Bee Rescue, Blackout in OH). One outlier (Bat Nest in OH) begins at the highest LDI and decreases to moderate LDI levels. These groups roughly correlate with the three groups of sites characterized as Forested, Agricultural, and Developed in Fig. 1.3, due to the direct relationship between predominant land cover (forested, agriculture, and urban) and the LDI weights (Table 1.2). There is also a difference in LDI pattern between the Pennsylvania and Ohio sites, which may be related to the two physiographic provinces in which the sites are located. The Pennsylvania sites are in the Ridge & Valley Physiographic province, characterized by long, unbroken forested ridges with limestone or shale valleys. A 1000 m radius circle will often just fit into the valley bottoms, and may trend toward the bottoms of the forested ridges at the far extent of the circle in which the LDI is calculated. In contrast, the Ohio sites are generally located in the Glaciated Allegheny Plateau, with a rolling hill topography and lacking the strict topographic constraints on land cover of the Ridge & Valley (i.e., activities such as agriculture and urban development are not constrained by the high slopes of ridges).

Our investigation of linkages between land cover patterns and wetland and process scale variables that are relevant for the provision of water quality services is initially organized by the spatial scale at which the land cover patterns are determined. For example, land cover patterns within a 1 km buffer around the wetland site may be predictive of soil accretion rates because of the increase in potentially erodible areas and the accumulation of the runoff volumes needed to transport it from the contributing watershed. In contrast, land cover patterns within a 100 m buffer around the wetland may be predictive of hydrologic characteristics such as median depth to groundwater, due to the importance of local variability in topography, soil, and vegetation characteristics. We utilized CART to determine which variables best separated high from low disturbance sites, for each spatial scale at which land cover patterns were determined (100 m, 200 m, 1 km), and within each category of water quality variable (hydrology, nitrogen and carbon). Results for 100 m, 200 m, and 1000 m are shown in Fig. 1.6. The results are described by each variable category, as follows.

1.3.1 Nitrogen and Carbon (Soil Properties Important to N Cycling)

We looked at several measures of soil carbon (C) and nitrogen (N) that are important to N cycling and relevant for the provision of water quality services in order to determine how they varied with antrhropogenic activity, as represented by the LDI (Table 1.3). CART analysis identified high and low disturbance sites (Fig. 1.6), and indicated thresholds for the soil measures related to soil N and C. At the scale of 1000 m, the LDI index split the sites into two groups based on ammonium (N-related

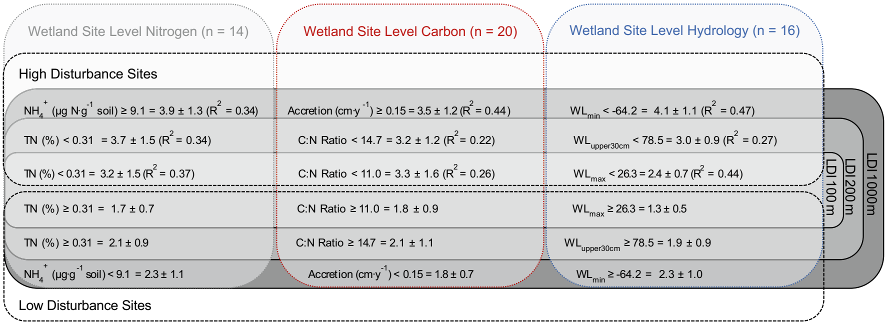

Fig. 1.6 Results of the classification and regression trees (CARTs) showing the relationship between the response variable of anthropogenic disturbance (LDI index scores at 100 m, 200 m, and 1000 m) and explanatory variables of nitrogen processing (soil nitrogen, soil carbon and hydrology). Based on the thresholds identified in the LDI index scores, sites were separated into High and Low Disturbance groups. Values are shown for the factors identified in the first split along with the LDI thresholds and R^2 values for relationships that are significant. LDI thresholds were consistent across scales with mean LDIs at High Disturbance Sites greater than 3 for all parameters except Maximum Water Level (Average LDI = 2.4). Mean LDIs in Low Disturbance Sites ranged from 1.7 to 2.3

measures) and soil accretion rates (C-related measures) such that high disturbance sites were characterized by relatively high levels of extractable ammonium (≥9.1 μg g^{-1} soil) and higher soil accretion rates (≥0.15 cm y^{-1}). The high disturbance sites were defined as those with LDI values above 3.9, indicating that land use around the sites was, at minimum, as intensive as agricultural land. The strong links between high LDI scores and ammonium are illustrative of the excessive anthropogenic loading of nitrogen sources onto our landscapes.

Higher LDI scores in the 1000 m area around a site were also predictive of higher sediment accretion rates due to anthropogenic disturbance in the local watershed such as agricultural or construction activities. This is correlated with the flashy hydrology of the High Disturbance sites (see below) that increases the transport and deposition of sediment and organic matter as materials from upstream/up gradient accumulate over longer flow distances and are transported into the wetlands. Over the past 25–50 years, elevated sediment deposition rates have been observed in riparian wetlands with significant anthropogenic disturbances (Johnston et al. 1984; Hupp et al. 1993; Hupp and Bazemore 1993; Kleiss 1996; Wardrop and Brooks 1998). Studies have documented rates of sedimentation ranging from 0.07 to 5 cm $year^{-1}$ in forested riparian wetlands affected by land use disturbance (Hupp et al. 1993; Hupp and Bazemore 1993; Kleiss 1996). In Central Pennsylvania, Wardrop and Brooks (1998) showed that sediment deposition ranged from 0 to 8 cm $year^{-1}$ across four freshwater hydrogeomorphic subclasses with varying levels of land use disturbance. It is thought that this accelerated sedimentation overloads the assimilative capacity of these wetlands (Jurik et al. 1994; Wardrop and Brooks 1998; Freeland et al. 1999) and interferes with other ecosystem services wetlands provide.

Table 1.3 Mean values for measures of soil nitrogen, soil carbon, and hydrology by land cover category. Sites were categorized by dominant land cover in the 1000 m radius area surrounding each as shown in Fig. 1.3

Study parameters	Units	Surrounding landscape			All sites (n=20)
		Forested (n=7)	Agricultural (n=7)	Urban (n=6)	
Soil properties					
TC	%	9.27±7.74	6.96±6.98	12.28±15.29	9.36±10.03
TN	%	0.47±0.33	0.62±0.62	0.66±0.43	0.58±0.46
TC:TN	ratio	18.32±3.75	11.24±2.24	15.27±6.95	14.93±5.29
Extractable NO_3^{-}[a]	µg $N\text{-}NO_2^{-}+NO_3^{-}\cdot g^{-1}$ soil	0.05±0.11	5.71±5.25	0.22±0.45	2.12±4.03
Extractable NH_4^{+}[a]	µg $N\text{-}NH_4^{+}\cdot g^{-1}$ soil	8.07±6.83	3.04±0.53	21.41±12.41	10.08±10.49
Soil accretion rate	$cm\cdot year^{-1}$	0.09±0.06	0.2±0.11	0.25±0.14	0.18±0.12
Hydrologic properties[b]					
Mean water level	cm	−4.41±39.61	−47.25±25.85	−21.38±23.97	−24.16±33.15
Maximum water level	cm	41.05±24.87	17.98±10.7	33.59±32.79	31.04±25.43
Minimum water level	cm	−25.81±28.26	−73.83±20.22	−66.65±31.15	−56.13±33.18
Time water level above 30 cm	%	76.82±0.41	33.76±0.33	69.30±0.29	60.54±0.37
Time water level above 10 cm	%	58.60±0.47	16.70±0.24	50.11±0.27	42.32±0.36
Time water level above ground level	%	43.01±0.44	6.17±0.1	33.19±0.31	27.81±0.33
Time water level between 10 and 30 cm	%	18.30±0.26	17.23±0.15	19.36±0.12	18.36±0.17
Mean 24-h water level difference	cm	2.04±0.45	3.29±0.33	3.54±2.31	2.99±1.52
Mean 7-day water level difference	cm	7.63±0.88	13.1±2.43	13.92±9.64	11.7±6.39

[a]Extractable N concentrations were averaged across 5 sites for “Forested” and “Agricultural” landscapes, and across 4 sites for “Urban” landscapes. Thus, 14 of the 20 sites were used in the “All Site” summary

[b]Hydrologic metrics were averaged across 5 sites for “Forested” and “Agricultural” landscapes, and across 4 sites for “Urban” landscapes. Thus, 16 of the 20 sites were used in the “All Site” summary

At smaller scales (LDIs for 100 and 200 m distances) the Low Disturbance group was defined by higher levels of soil TN (≥0.31 %TN) and higher soil C:N ratios, corresponding to the significantly higher mean soil C levels in these sites. TN and TC are lower overall in the High Disturbance sites, which is reflected in the lower C:N values. Lovette et al. (2002) reported that nitrate release from soils in forested watersheds is strongly affected by the C:N ratio of its soils; as C:N ratios increased, nitrate export decreased. These wetland sites may be behaving the same way; the high demand of heterotrophic bacteria for N when C:N ratios are high, leaves less N available (as evidenced by lower levels of extractable ammonium in the Low Disturbance sites) for processes such as nitrification and denitrification. This predisposes the more disturbed sites to perhaps act as biochemical "hot-spots" in the processing of N because of the convergence of the substrates and hydrological flows (see below) that are needed for biochemical reactions (McClain et al. 2003).

1.3.2 Hydrology

In general, the majority of hydrology metrics in this study are highly correlated with one another, as can be expected (Table 1.4). For example, a great number of the metrics are descriptive of general position of the water table (Average Water Level, Minimum Water Level, 25th Percentile, 50th Percentile, 75th Percentile, %Time Upper 30 cm, %Time in Upper 10 cm, %Time Above Ground), and they are highly correlated with each other (all $R^2>0.56$). In general, four metrics are remarkably poorly correlated with these general water table metrics: Maximum Water Level, %Time 10–30 cm, Mean 24-h Difference, and Mean 7-Day Difference. Of these four metrics, only Mean 24-h Difference and Mean 7-Day Difference are highly correlated ($R^2=0.95$). Based on this, we would propose that any general description of hydrologic character would include, at a minimum, a metric for average position of the water table, a metric to describe inundation or maximum water level, and a metric to describe flashiness. Other metrics could be added to indicate specific conditions: for example, %Time Above Ground as a metric of inundated and highly anaerobic conditions, and % Time 10–30 cm as a descriptor of optimal aerobic/anaerobic conditions within a zone of carbon availability.

In general, the CART analyses utilizing hydrology metrics differentiated high from low disturbance sites better than nitrogen and carbon metrics, as evidenced by relatively high R^2 values for LDI values at 100 m and 1000 m (Fig. 1.6). The differentiation between high and low disturbance sites is most pronounced in terms of Minimum Water Level for LDI at 1000 m, where low disturbance sites with an average LDI of 4.1 are characterized by a Minimum Water Level that is within the upper 64 cm relative to ground surface, while high disturbance sites with an average LDI of 2.3 are characterized by a Minimum Water Level that goes below 64 cm from the ground surface. The relationship between Minimum Water Level and LDI at 1000 m was linear, with a significant negative slope (i.e., Fig. 1.7a, Adj $R^2=0.29$, $n=16$, p-value$=0.0193$). Urban and suburban land cover (expressed in this study as higher

Table 1.4 Correlation matrix of hydrologic metrics used in this study

Hydrologic metrics	WL_{max} (cm)	WL_{min} (cm)	25th percentile	50th percentile (median)	75th percentile	$WL_{upper30cm}$ (%)	$WL_{upper10cm}$ (%)	$WL_{aboveground}$ (%)	$WL_{10\text{-}30cm}$ (%)	$WL_{24\text{-}HrDiff}$ (cm)	$WL_{7\text{-}DayDiff}$ (cm)
WL_{avg} (cm)	0.26	**0.81**	**0.91**	**0.97**	**0.92**	**0.90**	**0.90**	**0.87**	0.03	–0.35	–0.45
WL_{max} (cm)		0.18	0.04	0.27	0.40	–0.04	0.24	0.40	**–0.58**	–0.20	–0.20
WL_{min} (cm)			**0.88**	**0.69**	**0.58**	**0.68**	**0.67**	**0.75**	0.03	**–0.53**	**–0.62**
25th percentile				**0.81**	**0.70**	**0.82**	**0.80**	**0.77**	0.07	–0.38	–0.47
50th percentile (median)					**0.96**	**0.91**	**0.89**	**0.83**	0.06	–0.37	–0.47
75th percentile						**0.84**	**0.85**	**0.80**	0.02	–0.26	–0.34
$WL_{upper30cm}$ (%)							**0.89**	**0.74**	0.27	–0.35	–0.43
$WL_{upper10cm}$ (%)								**0.92**	–0.19	–0.33	–0.43
$WL_{aboveground}$ (%)									–0.34	–0.37	–0.47
$WL_{10–30cm}$ (%)										–0.06	–0.03
$WL_{24\text{-}HrDiff}$ (cm)											**0.98**

Numbers in bold indicate R values that are significant at $p \leq 0.05$. Numbers in bold indicate correlation coefficients (R) that are significant at $p \leq 0.05$. Metrics include: WL_{avg} average water level, relative to ground surface (cm), WL_{max} maximum water level, relative to ground surface (cm), WL_{min} minimum water level, relative to ground surface (cm), 25th Percentile = water level, relative to ground surface, at the 25th percentile of all recorded water levels over the sampling period for an individual well, 50th Percentile = similar to preceding, 75th Percentile = similar to preceding, $WL_{upper30cm}$ percent time water level was in the upper 30 cm of the soil profile, $WL_{upper10cm}$ percent time the water level was in the upper 10 cm of the soil profile (%), $WL_{abovegound}$ percent time the water level was above ground (%), $WL_{10–30cm}$ percent time the water level was between 10 and 30 cm (%), $WL_{24HrDiff}$ the mean water level difference over a 24-h period (cm), and $WL_{7DayDiff}$ mean water level difference over a 7-day period (cm)

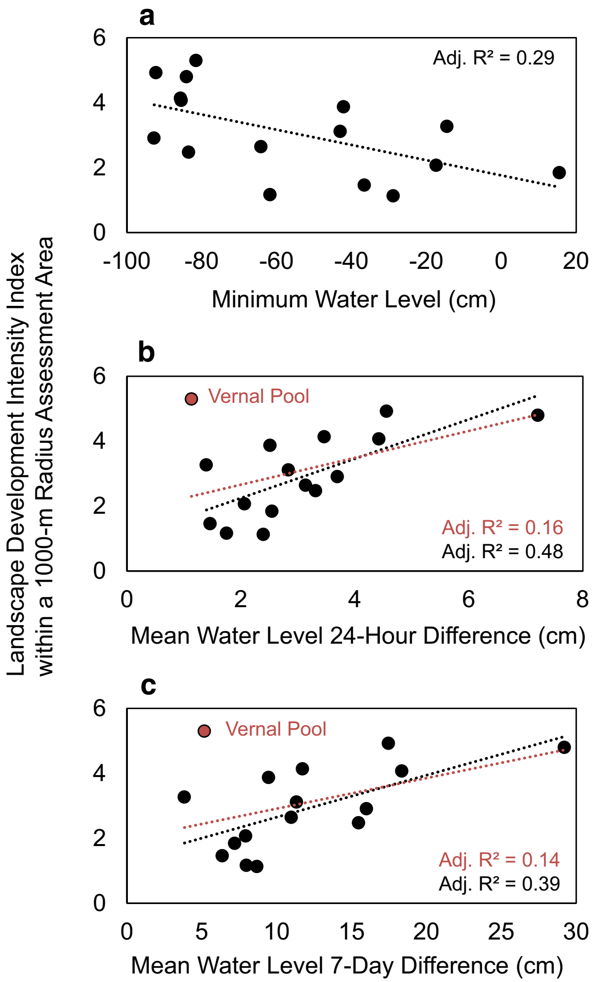

Fig. 1.7 Regression analyses showing the relationship between LDI index scores and (**a**) Minimum Groundwater Level, (**b**) Mean 24-h Difference in Water Level, and (**c**) Mean 7-day Difference in Water Levels. Note that the site Vernal Pool was an outlier in panels (**b**) and (**c**); the regression line including this site is shown in *red*, and excluding it is shown in *black*

LDI values) has been associated with stream incision and lowered water tables (Groffman et al. 2002), potentially inhibiting the interaction of nitrate-rich groundwater with near-surface soils, with an accompanying low probability of denitrification. However, some studies have noted relatively higher levels of denitrification in agricultural settings (Xiong et al. 2015), indicating that perhaps at intermediate LDI values, both nitrate rich groundwater from upgradient agricultural areas is able to interact with these surface soils. The LDI at 200 m split sites based on the percent of time the water level was within the top 30 cm, with high disturbance sites exhibiting lower percentages of time within this rooting zone, and again is reflective of lowered water tables. The LDI at 100 m split high and low disturbance sites fairly well, based on Maximum Water Level, with low disturbance sites having Maximum Water Levels of 26 cm or greater above ground surface. The correlation of Maximum Water Level to LDI at 100 m may be indicative of connectivity to nearby streams or collection of precipitation and groundwater, since both floodplain and depression sites are combined in the analyses. In the case of floodplain settings, greater connectivity to streams has been associated with higher inputs of sediment, sediment-N, and ammonium, and greater soil net ammonification, N mineralization, and N turnover, but not denitrification potential (Wolf et al. 2013). These wetter sites may be too anaerobic (as evidenced by high Soil C values) for appreciable denitrification.

Although metrics describing water level stability did not characterize the initial splits in the CART analyses, on average Mean Water Level 24-h and 7-day differences were lower in forested sites compared to agricultural and urban landscape sites (Table 1.1). Using linear regression we see a positive relationship between both flashiness metrics for LDI at 1000 m (Fig. 1.7b, c). One outlier in this regression, Vernal Pool, had only one working well for metric calculations. Removing this outlier, the positive relationships between mean water level 24-h (p-value = 0.0025) and 7-day differences (p-value = 0.0079) and LDI at 1000 m were statistically significant. The link between relatively high LDIs and relatively large fluctuations in water levels is reflective of a hydrologic pattern that is expected to be controlled at a larger spatial scale, since flashiness should be an expression of a watershed wide characteristic. It is also reflective of the differences in sediment delivery as measured by soil accretion rates. The 'boom and bust' hydrology that characterizes flashy hydrology moves sediment and allochthonous carbon in times of higher flows, depositing it in wetlands as flows subside. However, lack of flashiness and constancy of saturation of the rooting zone may inhibit the adjacency of aerobic and anaerobic zones necessary for denitrification.

1.4 Summary and Conclusions

We determined differences in soil and hydrology characteristics important to water quality services as a function of a gradient of anthropogenic activity, as expressed by the LDI. Our study is unique in that it: (1) investigates anthropogenic activity, as expressed by LDI, as a gradient rather than a categorical variable (e.g., agricultural versus forested), thus allowing determination of potential thresholds of LDI where there are important differences in nitrogen, carbon, and hydrology characteristics; and (2) it seeks to identify the specific process and site-scale variables relevant to water quality improvement that can be inferred by land cover patterns at varying distances from the site. Thus, we can identify useful proxies for the level of water quality improvement services we can expect from a given site.

Thresholds of LDI were determined via the CART analyses that separated sites into two general classes of high and low disturbance wetlands, with associated differences in TN, NH_4^+, Soil Accretion, C:N, Maximum Water Level, Minimum Water Level, and %Time in Upper 30 cm (Fig. 1.6). The LDI thresholds were remarkably consistent, with High Disturbance Sites characterized by average LDIs greater than 3 for all parameters except Maximum Water Level (Average LDI = 2.4), indicating agricultural and urban landcovers. Low Disturbance Sites had average LDIs of

1.7–2.3, indicating forested conditions. Only 6 sites exhibit LDIs at both 100 m and 1000 m that are within this range (Laurel Run, Clarks Trail, McCall Dam, Secret Marsh, Shavers Creek, and Mustang Sally), and are consistent with an overall forested setting (Fig. 1.3). These Low Disturbance Sites exhibit relatively higher TN, lower NH_4^+, lower Soil Accretion, higher C:N, higher Maximum Water Level, shallower Minimum Water Level, and higher %Time in Upper 30 cm than the remaining sites. Given the interaction of the carbon, nitrogen, and hydrology factors, we would expect a water quality process such as denitrification to be relatively lower in forested settings, due to the low available nitrogen (associated with high C:N) and constant and saturated conditions. Conditions for maximum denitrification may be found in agricultural settings, where high nitrate groundwater can interact with surface soils through a wetting and drying pattern.

The use of land cover patterns, as expressed by LDI, provided useful proxies for nitrogen, carbon, and hydrology characteristics related to provision of water quality services. LDIs at 100 m and 200 m were best separated into groups of high and low disturbance sites by factors expected to be proximal or local in nature, such as connectivity to streams or inundation from local runoff (Maximum Water Level, %Time Upper 30 cm) and levels of primary productivity and vegetation (C:N, TN). LDIs at 1000 m predicted factors that could be related to larger scale land cover patterns that are more distal in nature, such as Soil Accretion (reflecting erodible soils and flashy hydrology for transport), NH_4^+ (overall eutrophication), and Minimum Water Level (depression of water tables).

While all wetland types serve valuable roles in their watershed, headwater wetland/stream systems may contribute a disproportionate share to watershed functioning and the larger drainage areas and regional watersheds into which they drain. Headwater streams determine much of the biogeochemical state of downstream river networks (Brinson 1993), in part because, for example, in the U.S. low order streams account for 60–75 % of the total stream and river lengths, making their riparian communities of extreme importance for overall water quality (Leopold et al. 1964). We have demonstrated that anthropogenic activity surrounding these wetland systems leads to differences in the primary carbon, nitrogen, and hydrology drivers of the water quality ecosystem services that they are valued for. In addition, we have demonstrated the utility of the LDI as a proxy for these same drivers. Thus, land cover patterns, as expressed by the LDI, should be taken into account when creating, restoring, or managing these systems on a watershed scale.

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