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Searching for similarity in topographic controls on carbon, nitrogen and phosphorus export from forested headwater catchments

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Abstract:

Topography influences hydrological processes that in turn affect biogeochemical export to surface water on forested landscapes. The differences in long-term average annual dissolved organic carbon (DOC), organic and inorganic nitrogen [NO_3^--N, dissolved organic nitrogen (DON)], and phosphorus (total dissolved phosphorus, TDP) export from catchments in the Algoma Highlands of Ontario, Canada, with similar climate, geology, forest and soil were established. Topographic indicators were designed to represent topographically regulated hydrological processes that influence nutrient export, including (1) hydrological storage potential (i.e. effects of topographic flats/depressions on water storage) and (2) hydrological flushing potential (i.e. effects of topographic slopes on potential for variable source area to expand and tap into previously untapped areas). Variations in NO_3^--N export among catchments could be explained by indicators representing both hydrological flushing potential (91%, $p < 0.001$) and hydrological storage potential (65%, $p < 0.001$), suggesting the importance of hydrological flushing in regulating NO_3^--N export as well as surface saturated areas in intercepting NO_3^--N-loaded runoff. In contrast, hydrological storage potential explained the majority of variations among catchments in DON (69%, $p < 0.001$), DOC (94%, $p < 0.001$) and TDP (82%, $p < 0.001$) export. The lower explanatory power of DON (about 15% less) compared with that of DOC and TDP suggests another mechanism influencing N export, such as controls related to alternative fates of nitrogen (e.g. as gas). This study shows that simple topographic indicators can be used to track nutrient sources, sinks and their transport and export to surface water from catchments on forest landscapes.

KEY WORDS forest; catchment; topography; nutrient; surface water quality; similarity

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INTRODUCTION

General rules of nutrient export derived from careful study of gauged headwater catchments are important for many reasons. Process-oriented rules that are transferrable will assist in making informed predictions of nutrient export from ungauged catchments. These rules will also assist in calculating cumulative effects of terrestrial–aquatic linkages in larger catchments. With a clear articulation of these rules coupled with simple methods for calculating them, the nutrient export signal in streams may be used by both scientists and managers as a key indicator of the prevailing ecological condition of the ecosystem.

On landscapes, climate, topography, geology, forest type and age, and soils each influence hydrological and biogeochemical processes (Devito *et al*., 2005), including catchment nutrient pools and export. For example, vegetation has been found to be an important determinant of dissolved organic carbon (DOC) and dissolved organic nitrogen (DON). Currie *et al*. (1996) found that fluxes of DOC and DON were higher beneath the organic-rich layer of the A-horizon in coniferous stands compared with hardwood, with forest floor of hardwood stands exhibiting a much stronger sink for NO_3^--N. Furthermore, broadleaf cover dominated by N-fixing alder was related to high NO_3^--N and DON concentrations, leading Compton *et al*. (2003) to conclude that this single plant species was a major control on N export from coastal watersheds in the northwest USA. Soils have also been found to be an important determinant of nutrient export. For example, Aitkenhead-Peterson *et al*. (2005) found that mean catchment soil C : N ratio was a good predictor of DOC and DON export from forested catchments. They postulated that the soil C : N was an indicator that integrated climate (temperature and precipitation), edaphic

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(soil texture and nutrients) and biological (vegetation and microflora) controls (Aitkenhead-Peterson *et al.*, 2005). Lovett *et al.* (2002) found that forest type influences soil C : N, with red oak associated with higher soil C : N and red maple with lower C : N in the Catskills Mountains of the USA.

On landscapes where climate, geology, forest and soils are similar, topography may be a key control on nutrient accumulation, transformation and transport through its fundamental influence on energy and water mass balances (Sommer and Schlichting, 1997; Creed *et al.*, 2002). Topographic characteristics, which are measured or mathematically quantified configurations of the landform shape and structure, influence the flow of water on the landscape (Wagener *et al.*, 2007). In turn, hydrologic flow paths influence the transport and transformation of nutrients. Several studies have shown strong associations between topographic properties and nutrient export behaviour of carbon (Creed *et al.*, 2003, 2008), nitrogen (Creed and Beall, 2009) and phosphorus (Devito *et al.*, 2000). However, the nature of topographic controls on nutrient dynamics is complex, suggesting that the dominant hydrologic process influencing export may be different for each nutrient.

Topography is important for understanding the flux of dissolved carbon, nitrogen and phosphorus to receiving water. For example, following a rain event on landscapes where topography is controlled by bedrock, the groundwater table rises towards the surface and intersects with surface soils that have accumulated nutrients in the intervening dry period. These nutrients are then mobilized and flushed to receiving water, resulting in the export of carbon (Hornberger *et al.*, 1994), nitrogen (Creed *et al.*, 1996) or phosphorus (Evans *et al.*, 2000). In these cases, topography influences the hydrological flushing through transport of nutrients to surface water as a function of the size and spatial organization of the variable source area (VSA). The VSA provides a conduit for nutrient export, initially through slower, shallow, subsurface flow paths and then more rapidly as nutrients reach zones of saturation directly connected to streams. However, there are instances in which topography creates flat areas and/or depressions that intercept VSA runoff. The result of this interception may either reduce the amount of nutrient export from catchments (e.g. NO_3^--N, Creed and Beall, 2009) or increase the supply of nutrients for export (e.g. carbon, phosphorus, Creed *et al.*, 2008, and organic nitrogen, Creed and Beall, 2009).

Linking hydrologic processes to nutrient cycling requires an understanding of biogeochemical transformations along hillslope flow pathways. Of primary importance is the impact of hillslope water residence time on reduction–oxidation (redox) conditions. Changes in the redox state of dissolved nutrients can result in losses of nutrients to the atmosphere (e.g. DOC to CO_2 or NO_3^- to N_2O) or as storage (e.g. DOC to soil organic carbon or DOC to sorbed DOC). Webster *et al.* (2008a, b) found that topographic controls on soil moisture and the quantity and quality of carbon substrates were important determinants of CO_2 efflux from soils. Transiently wet areas adjacent to wetlands, streams and lakes were a major source of soil CO_2 because of synchronicity in optimal temperature and moisture conditions during the growing season and a large pool of high-quality substrate within freshly fallen leaves that accumulated in these depositional areas. In contrast, upland areas had insufficient soil moisture, which limits CO_2 production as a result of lack of soluble substrates; however, excess water in the wetland areas also limits CO_2 production as a result of lack of sufficient oxygen that would support aerobic respiration with subsequent decline in DOC as it would be oxidized to CO_2. Similarly, topography regulates N_2O efflux. During winter (Fairweather, 2007) and snow-free (Casson, 2008) periods of the year, the transiently wet areas adjacent to wetlands and the wetlands themselves were found to be the major sources of soil N_2O efflux, and wetlands with redox conditions promoting denitrification processes were a major source of N_2 (a sink for NO_3^--N) and a source for DON (Creed and Beall, 2009). Wetlands containing saturated soils with low redox conditions may also reduce Fe^{3+} to Fe^{2+}, which frees elements associated with oxidized Fe^{3+} including phosphorus (Liptzin and Silver, 2009).

Defining general rules that link hydrologic processes to nutrient export requires tools that precisely and accurately detect topographic characteristics within catchments. Digital terrain analyses generate terrain attributes related to hydrological processes that can assist in relating topographic composition and configuration to hydrological and biogeochemical response characteristics (Wagener *et al.*, 2007). The potential of digital terrain analyses has been revolutionized by lidar, an airborne remote-sensing technology that measures the distance to surfaces by illuminating the surface with laser beams and then analysing the backscattered light. Lidar has been used to produce fine-resolution digital elevation models (DEMs) of surfaces from which subtle topographic features can be detected. From lidar DEMs, terrain analyses can better define catchment boundaries, represent low-order streams, delineate local depressions that form potentially wet areas and identify ephemeral and permanent streams that connect these features to the stream (cf. Creed and Sass, 2011). For example, small hydrological features (first-order streams or small wetlands) that were previously not detected, particularly in areas where vegetation is dense or the ground is otherwise shielded from aerial view (Bishop *et al.*, 2008), can now be mapped. Thus, digital terrain analyses can now be used to

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derive topographic indicators for tracking hydrological and biogeochemical dynamics across topographically simple to complex landscapes. Such knowledge will assist in generalizing process controls so that they can be applied to ungauged catchments (Tetzlaff *et al.*, 2008).

Creed and Beall (2009) provided a conceptual basis of topographic controls on NO_3^--N and DON export in undisturbed headwater catchments on a sugar maple forested landscape. They described how topography influences (1) hydrological flushing potential (i.e. effects of topographic slopes on potential for VSA to expand and tap into previously untapped nutrient source areas in the forest floor and surface mineral layers) and (2) hydrological storage potential (i.e. effects of topographic flats/depressions in catchment that represents wetlands, which may result in either increased runoff when the water table in the wetland is near or at the surface or decreased runoff when the water table in the wetland is well below the surface, preventing water contributing to the wetland from being exported to the stream). They developed novel topographic indicators using digital terrain analyses to capture these topographic influences on dissolved nitrogen export from catchments.

The current study builds on the work of Creed and Beall (2009) by exploring similarity in topographic controls on other nutrient species, DOC and total dissolved phosphorus (TDP), and determining if topographically regulated shifts in hydrological flushing *versus* storage potentials can explain differences in NO_3^--N, DOC, DON and TDP export among catchments. Exploring the similarity in topographic controls among carbon, nitrogen and phosphorus would enable us to use simple topographic indicators to track nutrient sources, sinks and their transport and export to surface water from both gauged and ungauged catchments on forest landscapes. It would also enable us to develop a predictive understanding of the stoichiometry of nutrient export, which is an important driver of productivity and biodiversity of downstream surface water (Meyer *et al.*, 2007).

STUDY AREA

The Turkey Lakes Watershed (TLW) is a 10.5-km^2 experimental watershed in the Algoma Highlands, about 60 km north of Sault Ste. Marie, Ontario (Figure 1). This watershed is located in the northern portion of the Great Lakes-St. Lawrence Forest Region, the second largest forest region in Canada, which extends from south-eastern Manitoba to the Gaspe Peninsula. Climate is continental with mean annual precipitation and temperature of 1200 mm and 5.0 °C, respectively (Creed and Beall, 2009), and is strongly influenced by the proximity of Lake Superior to the west of the watershed and local orographic effects at locations of high relief. There is typically snowpack from late November, early December through to late March and early April. Peak stream discharge occurs during snowmelt and again in October to November during autumn storms.

Bedrock geology is primarily Precambrian silicate greenstone, except north of the Batchawana Lake area

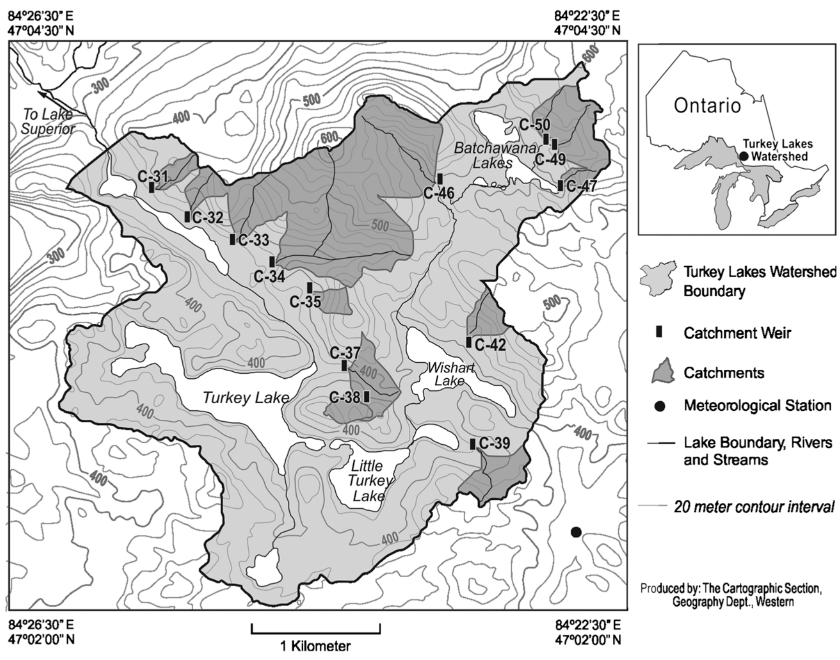

Figure 1. Map of the Turkey Lakes Watershed depicting the 13 experimental catchments (from Creed and Beall, 2009)

and near the main inflow to Little Turkey Lake, where there are small outcrops of more felsic igneous rock (Semkin and Jefferies, 1983). Surficial geology of upland areas is glacial till with a depth of <1 m and frequent bedrock exposure, lowland areas are glacial till of 1–2 m on average and bedrock depressions are characterized with deep till reaching up to 71 m in depth (Elliot, 1985). The glacial till is double layered, comprising sandy loam ablation till overlying a compacted lower silt loam basal till. The upper layer is thin (<1 m) and permeable (10^{-3} cm s^{-1}), whereas the lower layer is thicker with lower permeability (10^{-5} cm s^{-1}) (Johnston and Craig, 1986; Craig and Johnston, 1988). The glacial till has been weathered to present-day loam, sandy loam and silty loam soil textures. The soils on the tills are orthic ferro-humic and humo-ferric podzols with dispersed pockets of ferric humisols found in bedrock-controlled depressions and adjacent to streams and lakes (Wickware and Cowell, 1985). The forest is comprised of mature to overmature sugar maple ($>90\%$). Stand density (904 stems ha^{-1}), dominant height (20.5 m), diameter at breast height (15.3 cm) and mean basal area (25.1 m^2 ha^{-1}) are relatively uniform across vegetation types. The sparse understories of upland stands are dominated ($>95\%$) by saplings and seedlings of sugar maple with a depauperate herb flora and a variety of ferns. The wetland understories are composed of the seedlings and saplings of the overstory trees, various ferns, herbs and a mix of feather and sphagnum mosses (Wickware and Cowell, 1985).

The landscape exhibits substantial topographic variability, with gentle to steep hillslopes (11.5–20.8° in the experimental catchments) of different curvatures and lengths that drain into streams. These hillslopes often drain through topographic flats and/or depressions containing organic-rich mineral or organic soils that are often transiently or permanently saturated. The presence of these topographic flats and depressions influences hydrological flow partitioning and pathways (Lindsay *et al.*, 2004; Lindsay and Creed, 2005) and biogeochemical cycling (Webster *et al.*, 2008a). Topography may influence soil properties, both through static factors (e.g. radiation, temperature, precipitation and atmospheric deposition) and dynamic factors (e.g. factors that influence drainage conditions, transport and deposition of suspended materials and/or leaching and translocation and redeposition of soluble materials). Creed *et al.* (2002) found that static factors had greater influence at regional scales (i.e. slope and aspect explained the highest proportion of heterogeneity in soil nutrient pools), but dynamic factors had greater influence at local scales (e.g. no significant differences in soil environmental conditions among backslopes, where slope and aspect effects would be expected, during the summer months, when these effects would be expected to be most significant; however, there were significant differences in soil environmental conditions moving down the hillslope from uplands to bottomlands) (Webster *et al.*, 2008b).

The TLW has been used as an experimental watershed by the federal government agencies since 1980, initially to study the potential impact of acid rain and climate change in terrestrial and aquatic ecosystems in the Canadian Shield area (Foster, 1985; Jeffries *et al.*, 1988). Since 1980, daily meteorological data (maximum and minimum temperature, precipitation and solar radiation data) around the watershed have continuously been measured at the meteorological station close to the watershed. In addition, since 1981, discharge and various water chemistry parameters have been monitored for 13 gauged headwater catchments within the TLW (Figure 1). A harvesting experiment was carried out in 1997 at three of the headwater catchments (c31, c33 and c34) to investigate the hydrological consequences of different forest management alternatives: a diameter limit harvest, shelterwood harvest and a selection harvest. For this study, preharvest data from 1981 to 1997 are used for c31, c33 and c34, whereas data from 1981 to 2008 are used for the ten, unharvested catchments.

METHODS

Topographic indicators

A 5-m lidar, hydrologically conditioned DEM with a vertical accuracy of 0.15 m in open canopy and 0.30 m in closed canopy was used to derive topographic metrics. Hydrological conditioning of DEMs is the process of removing erroneous sinks and pits in elevation data for the purpose of enforcing drainage through raster cells, allowing us to properly characterize drainage networks. After hydrological conditioning of the DEM, the remaining pits and depressions were filled (Planchon and Darboux, 2002), and the D8 algorithm was used to determine catchment-contributing areas and surface drainage networks (O'Callaghan and Mark, 1984; Jenson and Domingue, 1988). A specific contributing area of 2000 m^2 and a stream length threshold of 25 grid cells (125 m) were selected because they resulted in drainage networks that matched most closely those observed in the catchments.

Topographic indicators representing hydrological storage mechanisms (i.e. topographic flats/depressions that were assumed to be wetlands) were identified following a stochastic probability approach (Lindsay and Creed, 2005; Figure 2). The approach involved deriving a grid map of the probability of depression (*pdep*) using Monte Carlo simulation where (1) the elevation error term was stochastically drawn from a frequency distribution of elevation error terms with a standard deviation equal to the vertical accuracy of the DEM (i.e. 0.30 m), (2) this

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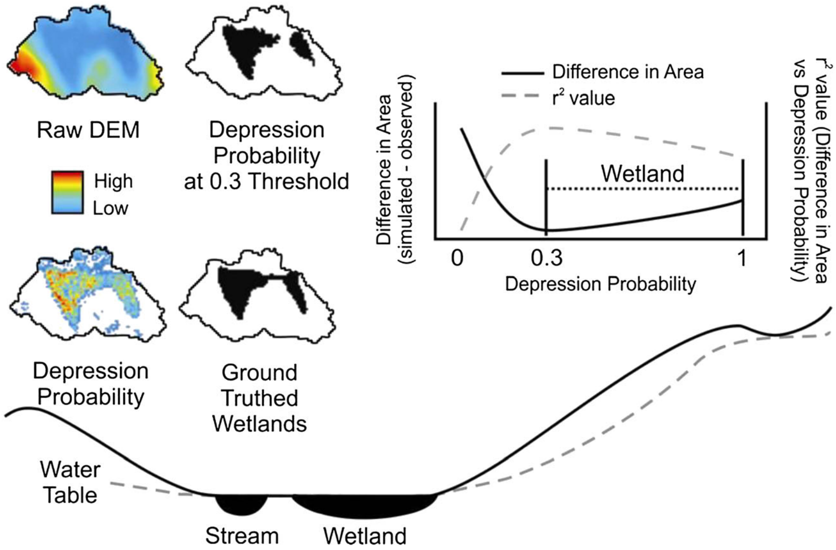

Figure 2. Method used to derive topographic indicators for hydrologic storage potential. Random errors were introduced into the DEM to calculate depressions; this process was repeated iteratively, and the probability of depression was calculated. Wetlands were delineated using a 0.3 threshold determined by the minimum difference in area between simulated and observed (ground-truthed) wetlands

error term was added to the DEM, (3) the flats/depressions in this modified DEM were filled and each grid cell modified by the depression filling process identified and (4) a probability of depression occurrence (*pdep*) was calculated by the number of times each grid cell was contained in a depression, with *pdep*s ranging from 0 (area with no probability of being a depression) to 1 (area with 100% probability of being a depression). The Monte Carlo simulation was repeated using different elevation error terms until a stable solution occurred, defined by when the root mean square difference in *pdep* between two consecutive simulations was <0.001. Grid cells with *pdep* values greater than a defined critical threshold were identified as topographic depression and/or flat areas (e.g. wetlands). The critical threshold in *pdep* (0.30), above which a depression was defined, was determined by calculating the lowest area difference and highest kappa statistics between stochastically derived and field-surveyed wetlands.

Topographic indicators representing hydrological flushing mechanisms were derived using the following methods (Figure 3). The topographic index (TI) is an indicator of topographically driven soil moisture conditions and was calculated as $\ln(a/\tan\beta)$, where a is an upslope contributing area of a given site based on drainage directions calculated using the D-infinity algorithm (Tarboton, 1997) from a specific contributing area and slope gradient maps and β is the local slope angle (Beven and Kirkby, 1979). To facilitate a direct comparison of TI among catchments, the TI grid map of each catchment was normalized (TI_n) by subtracting catchment average TI values from specific TI for each grid cell. VSAs as an indicator of potential hydrological flushing areas were estimated by starting at the stream grid cells, where the TI_n values are the highest, and recursively moving outwards from the stream grids to grid cells of lower TI_n value until a point where the TI_n values start to increase again or the catchment boundary is reached (Figure 3A). The proportion of VSA where hydrological flushing is likely to occur on an annual basis was referred to as the effective VSA (*eff*VSA) and was estimated by grid cells with TI_n values greater than or equal to the 75th percentile of the TI_n frequency distribution within the VSA. Selection of the 75th percentile was reasonable but arbitrary; it was the threshold that produced the best prediction of NO_3^--N export when different thresholds (i.e. from the 50th to 90th percentiles) in the frequency distribution of TI_n were used to define *eff*VSA (Creed and Beall, 2009) (Figure 3B). A situation was possible where the same pixel can function as both hydrological storage and hydrological flushing (i.e. if topographic flats/depressions occurred within the *eff*VSA). For this reason, *eff*VSAs both with and without topographic flats/depressions (i.e. no wetlands, NW*eff*VSA) were derived and considered in the development of models (Figure 3C). The potential rates of *eff*VSA expansion and contraction ($d^2 effVSA/dTI_n{}^2$) were calculated as a second derivative of the best-fit polynomial to the TI_n frequency distribution within the *eff*VSA.

Ratios of the topographic metrics were also considered because the relative presence of one metric with respect to another might increase predictive capacity. For example, the ratio of topographic sinks of a nutrient (e.g. the proportion of topographic flats/depressions that denitrify NO_3^--N) to topographic sources of a nutrient (e.g. the proportion of

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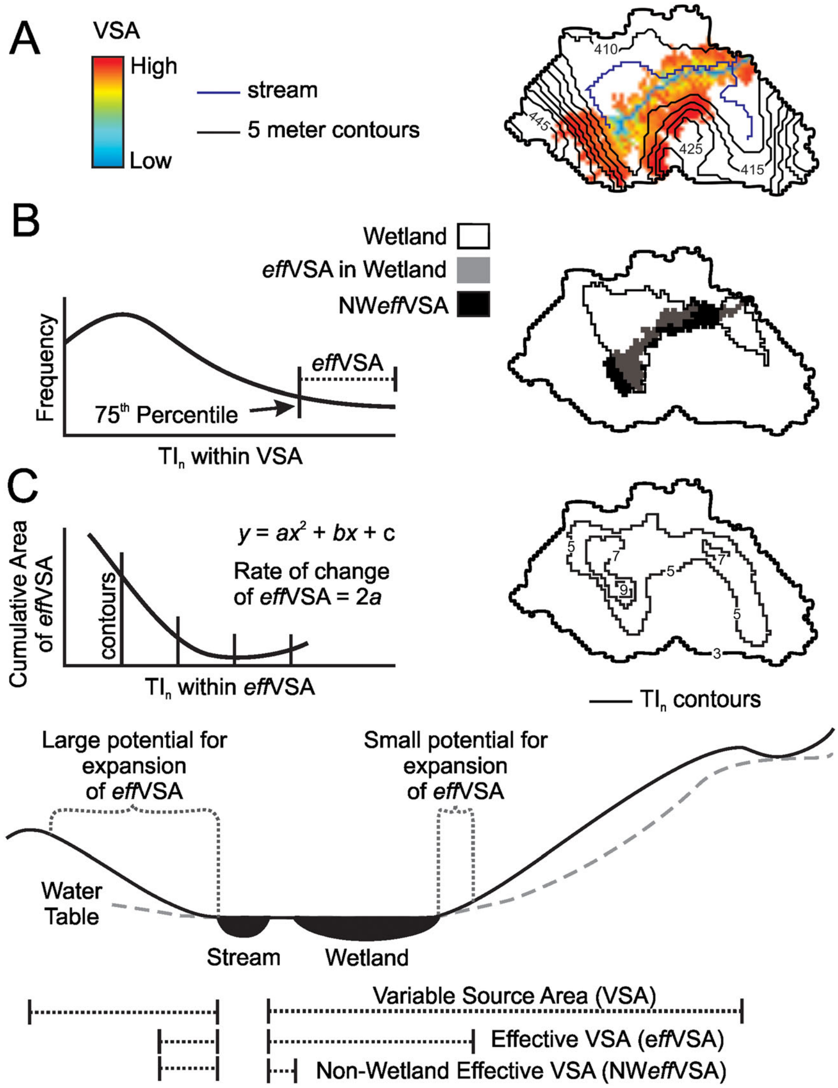

Figure 3. Description of methods used to derive topographic indicators for hydrological flushing potential: (A) the variable source area (VSA) is calculated spatially from the TI_n map by starting at the stream and going recursively to lower TI_n values until there is a breakpoint where values increase; (B) the effective VSA (*eff*VSA) is the upper quartile of the TI_n values within the VSA and describes the portion of the VSA where return flow is likely to occur on an annual basis; the area of *eff*VSA without wetland (NW*eff*VSA) is calculated spatially as the area of the *eff*VSA outside wetlands; and (C) the rate of change of *eff*VSA is calculated as the second derivative of the polynomial best fit of the curve

VSA, *eff*VSA or NW*eff*VSA that are sources of NO_3^--N) was derived to see if they improved the predictive capacity of topographic metrics for NO_3^--N export.

All digital terrain analyses were performed using the Terrain Analysis System software (Lindsay, 2005).

Nutrient pools

Soil carbon and nitrogen pools were determined from samples collected in 2005 at each point on a 25 m × 25 m grid that covered catchments representing extremes in area of topographic features – c35, which had one of the smallest areas of wetlands (1.06%) and highest NW*eff*VSAs (13.12%), and c38, which had one of the largest areas of wetlands (20.54%) and smallest NW*eff*VSAs (1.55%) (Table I). For forest floor, six samples were collected by cutting 15 cm × 15 cm blocks of the entire layer, dried at 25 °C and analysed for carbon and nitrogen (Carlo-Erba NA2000 analyser, Milan, Italy) concentrations. A second set of forest floor samples was collected at the same time and was dried at 60 °C, weighed and measured to provide estimates of bulk density. For upland soils, six samples of the organic-rich A-horizon (i.e. Ah) were collected at each of the upland topographic features with an open-sided sampler (40 cm × 4.4 cm inner diameter; for carbon and nitrogen analysis) or a split-core sampler (32 cm × 4.8 cm inner diameter; for bulk density determination; stones >2 mm were removed and weighed to correct bulk density for coarse fragment content). For wetland soils, six peat

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Table I. Topographic metrics and ratios or topographic metrics among headwater catchments in the Turkey Lakes Watershed

Catchment	Area (ha)	Wetlands (%)	VSA (%)	*eff*VSA (%)	NW*eff*VSA (%)	$W : VSA$	$W : NWeffVSA$	$d^2effVSA/dTI_n^2$
c31	4.94	2.88	61.66	13.10	11.33	0.05	0.22	2.00E−06
c32	6.50	1.00	54.54	14.32	14.05	0.02	0.07	4.00E−06
c33	23.38	0.50	45.13	16.04	15.75	0.01	0.03	2.00E−05
c34	68.59	1.12	36.04	9.70	9.22	0.03	0.12	4.00E−05
c35	4.02	1.06	36.38	13.18	13.12	0.03	0.08	4.00E−06
c37	15.36	15.01	33.63	6.82	1.73	0.45	2.20	1.20E−06
c38	6.46	20.54	31.57	6.34	1.55	0.65	3.24	6.00E−07
c39	17.25	5.97	47.13	12.96	11.05	0.13	0.46	4.00E−06
c42	18.52	8.48	51.84	13.71	10.06	0.16	0.62	4.00E−06
c46	43.19	1.35	30.57	9.73	9.08	0.04	0.14	8.00E−06
c47	3.43	0.36	23.62	7.58	7.58	0.02	0.05	2.00E−06
c49	14.81	3.97	47.27	9.65	8.62	0.08	0.41	2.00E−06
c50	9.47	10.03	38.09	7.84	3.72	0.26	1.28	1.00E−06

VSA, variable source area; *eff*VSA, effective VSA; NW*eff*VSA, area of *eff*VSA without wetland; $d^2effVSA/dTI_n^2$, rate of *eff*VSA expansion and contraction.

samples from the top 10 cm were collected with a Jeglum sampler (7.6 cm × 7.6 cm × 50 cm; Jeglum *et al*., 1992). Soil samples were dried at 25 °C and analysed for carbon and nitrogen concentrations using the same techniques described before or dried at 60 °C (for organic soil) or 105 °C (for mineral soil) and measured for bulk density. Soil nutrient pools were calculated by multiplying nutrient concentrations ($g\,g^{-1}$) by bulk density ($g\,m^{-1}$) and then by depth (m).

Nutrient export

The concentration of nutrients discharged into the streams was determined from samples collected at midday biweekly during the winter, daily during spring snowmelt and weekly or biweekly during the summer and autumn. Samples were collected at the same sampling point, the centre of the stream, for each stream. From each sample, particulate matter was removed by filtration through Fisher Q8 (coarse, fast flow) paper filters. Samples were analysed within 48 h of collection for NH_4^+-N, NO_3^--N and total dissolved nitrogen (TDN) using sodium nitroprusside, cadmium reduction and cadmium reduction, respectively, after autoclave digestion methods on Technicon autoanalysers. DON was calculated from TDN minus dissolved inorganic nitrogen (NH_4^+-N + NO_3^--N). DOC was determined by removing dissolved inorganic carbon (DIC) by purging with N_2 after acidification, converting DOC to DIC by persulfate oxidation catalysed by ultraviolet and then converting the resulting DIC to CO_2 by acidification, which was measured by colorimetry. TDP was analysed on a Technicon autoanalyser IIC after autoclave digestion using the molybdophosphoric acid colour reaction.

Daily concentrations of nutrients were estimated by interpolating measured values directly before and after the unknown value. Daily fluxes of nutrients were then estimated by the product of the total daily discharge from continuously logged stream stage at V-notch weirs on the catchments and the interpolated daily concentrations of nutrients. Annual nutrient fluxes of nutrients were calculated as the sum of daily flux for the water year (June 1 to May 31) from 1981 to 2008 (except for the three harvested catchments, c31, c33 and c34, where the period was from 1981 to 1996 water years).

Topographic indicators versus nutrient export

The nature, strength and significance of the relationships between the catchment's topographic indicators and its nutrient export characteristics were evaluated using correlations and linear regressions. Differences among soil carbon and nitrogen pools and C : N ratios were assessed using one-way analyses of variance. Where statistically significant differences were found, Holm–Sidak pairwise comparisons were performed. An α of 0.05 was used, and all statistical analyses were performed using Sigma Plot (version 11, Systat Software Inc., 2008).

RESULTS

Topographic indicators

Topographic indicators of hydrological storage potential (i.e. topographic flats/depressions) varied substantially (Table I). Catchments c37, c38 and c50 had substantially more wetlands (>10% topographic flats/depressions), whereas c33, c35 and c47 had very few wetlands (<2% topographic flats/depressions). The distribution of wetlands within the catchments varied, with some containing large contiguous wetlands (e.g. c38) and others smaller discontiguous wetlands that cascaded one to the next *via* the surface drainage network (e.g. c50).

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Topographic indicators of hydrological flushing also varied substantially (Table I). VSA was smallest in c47 (23.62%) and largest in c31 (61.66%). The patterns in *eff*VSA did not follow VSA, reflecting differences in concavity *versus* convexity of the lower hillslopes draining into the stream. The *eff*VSA was smallest in c38 (6.34%) and c37 (6.82%), where water moves down steep hillslopes, draining into much more gentle hillslopes before exiting the catchment, and largest in c33 (16.04%), where steep to moderate slopes drain directly to the stream. Topographic flats/depressions that would detain the movement of water from the hillslopes to the stream were prevalent in some of the *eff*VSAs. When these topographic flats/depressions were removed from *eff*VSA, the proportion of areas contributing to VSA runoff decreased among all catchments (except c47 where it stayed the same), but the rank order of the NW*eff*VSA in catchments generally remained the same, with c37 (1.73%) and c38 (1.55%) having lowest NW*eff*VSA and c33 having highest NW*eff*VSA (15.75%). These topographic indicators of VSA were correlated with one another (Table II), because they were refinements of the same process. For this reason, they were not combined in the models constructed to predict nutrient export. Topographic properties of hillslopes that would affect the rate of potential expansion of *eff*VSA ($d^2effVSA/dTI_n{}^2$) varied by orders of magnitude, from high rates of potential expansion in c33 (2×10^{-5}) and c34 (4×10^{-5}) [tapping into relatively high $NO_3{}^-$-N-generating areas that exist on less concave (less flat) hillslopes] to low rates in c38 (6×10^{-7}) [tapping into relatively low $NO_3{}^-$-N-generating areas that exist on more concave (more flat] hillslopes) (Figure 2).

A broad range existed in the topographic indicators of hydrological flushing *versus* storage potential among the catchments. Catchments c37, c38 and c50 had the largest proportion of wetlands, but the smallest *eff*VSA and NW*eff*VSA and the least expandable *eff*VSA ($d^2effVSA/dTI_n{}^2$). For example, c38 had the largest wetland (20.54%) but among the smallest VSAs (31.6%), the smallest *eff*VSAs (6.3%) and the smallest NW*eff*VSAs (1.55%). In contrast, c35, which is geographically closest to c38, had among the smallest wetlands (1.0%) and an average VSA (36.4%) but had among the largest *eff*VSAs (13.2%) and NW*eff*VSAs (13.1%) and a more expandable *eff*VSA ($d^2effVSA/dTI_n{}^2$). Catchments c35 and c38 are representative of the range of topographic indicators of hydrologic flow, and therefore, comparisons of these two sites are highlighted in subsequent analyses.

When the ratio of the proportion of topographic flats/depressions (where rising water table leads to inundation) to proportion of VSAs (where rising water table leads to expansion into unsaturated soils) (W : *effVSA*) was calculated, the magnitude of difference among the catchments increased. For example, the W : *effVSA* for c35 was 0.08 (emphasizing the role of *eff*VSA relative to W), whereas the W : *effVSA* for c38 was 3.24 (emphasizing role of W relative to *eff*VSA).

Nutrient pools

Soil nutrient pools varied among the wetland, NW*eff*VSA and the remaining portion of the VSA (i.e. *VSA* minus *effVSA*; Figure 4). Soil C and N pools covaried; they were high in the wetland for both forest floor and organic-rich A-horizon. For the forest floor (Figure 4A), the soil nutrient pools dropped sharply in the NW*eff*VSA and remained low in the remaining portion of the VSA. In contrast, for the organic-rich A-horizon (Figure 4B), soil nutrient pools remained high in the NW*eff*VSA, then dropped sharply in the remaining portion of the VSA to levels approaching those observed in the forest floor. The ratio of soil C : N was significantly higher in the forest floor (average of 19.3) than in the organic-rich A horizon (average of 15.4), and neither changed with topographic indicators.

Nutrient export

The concentrations and fluxes of nutrient export from the catchments varied substantially. Catchments with high

Table II. Pearson correlation between average topographic metrics, including ratios between metrics, for 13 catchments in the Turkey Lakes Watershed

Metric	VSA (%)	*eff*VSA (%)	NW*eff*VSA (%)	W : *VSA*	W : *effVSA*	W : *NWeffVSA*	$d^2effVSA/dTI_n^2$
Wetlands (%)	NS	−0.575	−0.813	0.986	0.978	0.932	NS
VSA (%)		0.707	NS	NS	NS	NS	NS
*eff*VSA (%)			0.929	−0.628	−0.644	−0.629	NS
NW*eff*VSA (%)				−0.828	−0.834	−0.787	NS
W : *VSA*					0.998	0.977	NS
W : *effVSA*						0.983	NS
W : *NWeffVSA*							NS

VSA, variable source area; *eff*VSA, effective VSA; NW*eff*VSA, area of *eff*VSA without wetland; $d^2effVSA/dTI_n^2$, rate of *eff*VSA expansion and contraction; NS, not significant (all other relationships $p < 0.05$).

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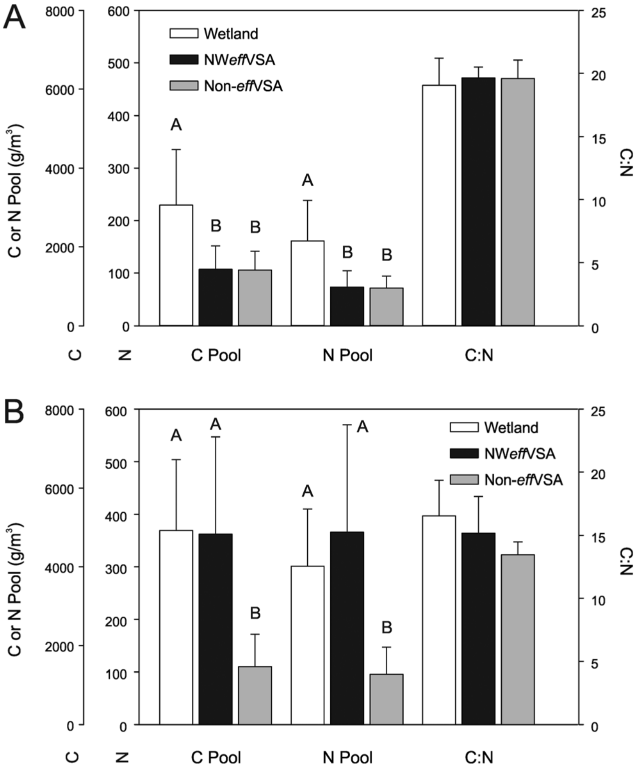

Figure 4. Average soil carbon and nitrogen pools and C : N ratios (with standard deviations) for samples taken from areas of wetland ($n = 9$), effective variable source area (*eff*VSA) without wetland (NW*eff*VSA) ($n = 4$) and variable source area minus *eff*VSA and wetland (non-*eff*VSA) (n = 7) in the (A) forest floor and (B) organic-rich A-horizon

wetland (%) had low NO_3^--N concentrations but high DOC, DON and TDP concentrations (Table III). The same pattern was observed in fluxes (Table III).

Despite an increase in DON, catchments with a large proportion of wetlands had lower total mobile nitrogen export (i.e. NO_3^--N plus DON; Figure 5). As DOC increased, TDP also increased whereas TDN decreased (Figure 6). Catchments representing lows in inorganic nutrient export tended to be the highest in organic nutrient export, and vice versa. For example, catchment NO_3^--N export ranged from a low of 1.02 kg ha^{-1} a^{-1} (c38) to a high of 5.15 kg ha^{-1} a^{-1} (c35). In contrast, catchment organic nutrient export ranged from a low of 13.19 kg ha^{-1} a^{-1} for DOC, 1.02 kg ha^{-1} a^{-1} for DON and 0.0169 kg ha^{-1} a^{-1} for TDP in c35 to a high of 47.22 kg ha^{-1} a^{-1} for DOC, 2.00 kg ha^{-1} a^{-1} for DON and 0.0558 kg ha^{-1} a^{-1} for TDP for c38 (Table III).

Catchment differences in nutrient export were also examined by calculating the residuals between each catchment and the average across all catchments for each nutrient (Figure 7). For example, c35 had 49% higher NO_3^--N export than the average export among catchments, whereas c38 was 70% lower in NO_3^--N export than the average. The higher-elevation catchments (e.g. c42, c46, c47 and c49)

Table III. Annual nutrient concentrations and flux export (with coefficient of variation) of nitrate (NO_3^--N), dissolved organic carbon (DOC), dissolved organic nitrogen (DON) and total dissolved phosphorus (TDP) from the Turkey Lakes Watershed for water years (June through May) from 1981 to 2008, except for catchments c31, c33 and c34 where data from 1981 to 1996 were used because of disturbance

Catchment	Water (mm a^{-1})	NO_3^- (mg N l^{-1})	NO_3^- (kg N ha^{-1} a^{-1})	DOC (mg C l^{-1})	DOC (kg C ha^{-1} a^{-1})	DON (mg N l^{-1})	DON (kg N ha^{-1} a^{-1})	TDP (mg P l^{-1})	TDP (kg P ha^{-1} a^{-1})
c31	569 (21)	0.75 (171)	3.98 (26)	2.19 (41)	13.51 (24)	0.19 (82)	1.06 (29)	0.0035 (0.89)	0.0174 (37)
c32	495 (30)	0.95 (52)	4.56 (35)	2.06 (35)	10.00 (25)	0.14 (85)	0.77 (55)	0.0029 (0.84)	0.0138 (49)
c33	531 (19)	1.03 (68)	5.19 (20)	2.43 (28)	13.13 (15)	0.20 (92)	1.03 (28)	0.0029 (0.73)	0.0143 (48)
c34	663 (14)	0.88 (55)	5.43 (19)	1.94 (39)	14.16 (14)	0.18 (70)	1.26 (49)	0.0032 (1.06)	0.0186 (38)
c35	632 (26)	0.83 (49)	5.15 (29)	2.06 (43)	13.19 (29)	0.15 (91)	1.02 (41)	0.0030 (0.91)	0.0169 (54)
c37	633 (21)	0.35 (65)	1.88 (33)	4.95 (43)	34.11 (23)	0.24 (58)	1.60 (26)	0.0053 (0.58)	0.0340 (25)
c38	612 (26)	0.20 (96)	1.02 (43)	8.39 (46)	47.22 (24)	0.36 (51)	2.00 (29)	0.0100 (0.46)	0.0558 (30)
c39	518 (24)	0.76 (52)	3.93 (30)	2.52 (44)	15.92 (24)	0.14 (74)	0.87 (35)	0.0031 (0.83)	0.0165 (31)
c42	457 (22)	0.68 (58)	2.84 (41)	3.89 (42)	20.61 (22)	0.19 (61)	0.96 (33)	0.0038 (0.82)	0.0165 (26)
c46	654 (29)	0.51 (73)	3.18 (36)	2.39 (33)	14.22 (41)	0.16 (69)	1.09 (49)	0.0045 (5.93)	0.0199 (40)
c47	555 (26)	0.54 (67)	2.72 (38)	2.15 (27)	12.72 (32)	0.14 (72)	0.83 (37)	0.0036 (7.17)	0.0135 (40)
c49	710 (29)	0.46 (71)	2.93 (39)	2.48 (36)	18.90 (42)	0.15 (62)	1.16 (34)	0.0035 (0.75)	0.0228 (31)
c50	776 (22)	0.28 (88)	2.02 (40)	4.24 (30)	32.48 (19)	0.21 (56)	1.67 (31)	0.0047 (0.60)	0.0344 (30)

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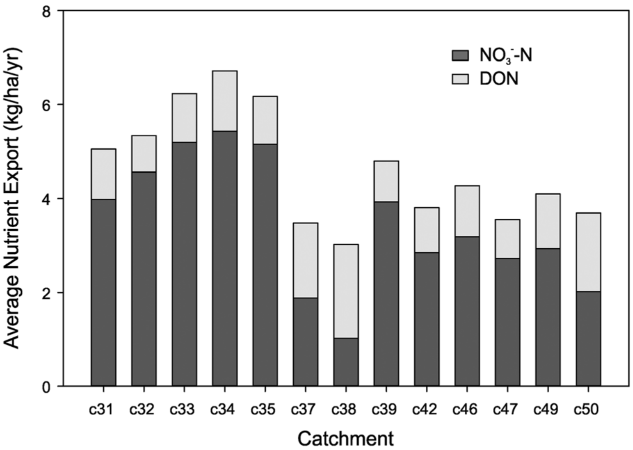

Figure 5. Average total mobile nitrogen [nitrate-N (NO_3^--N) and dissolved organic nitrogen (DON)] from 13 catchments in the Turkey Lakes Watershed

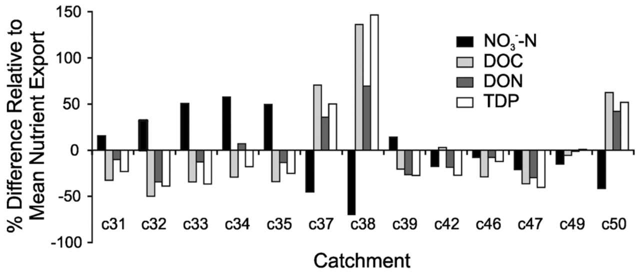

Figure 7. Spatial variation in annual nitrate-N (NO_3^--N), dissolved organic carbon (DOC), dissolved organic nitrogen (DON) and total dissolved phosphorus (TDP) in the Turkey Lakes Watershed

that had little to no topographic flats/depressions were the exception, showing little difference from average export or slightly lower export than the average export across all catchments (Figure 7). NO_3^--N export behaviour was distinct from DOC, DON and TDP export behaviours. For example, c35, which had higher NO_3^--N export, had lower export of organic nutrients. Spatially, c35 exported 14% less DON, 34% less DOC and 26% less TDP than the average export across all catchments, whereas c38 exported 69% more DON, 136% more DOC and 146% more TDP than the average export across all catchments (Figure 8).

Topographic indicators versus nutrient export

There were generally no significant correlations between topographic indicators and water export (Table IV); the one exception was *eff*VSA *versus* water export, where an increase in *eff*VSA led to a decrease in water export ($r^2 = 0.379$, $p < 0.05$), but an increase in NW*eff*VSA had no significant effect on water export. There were significant

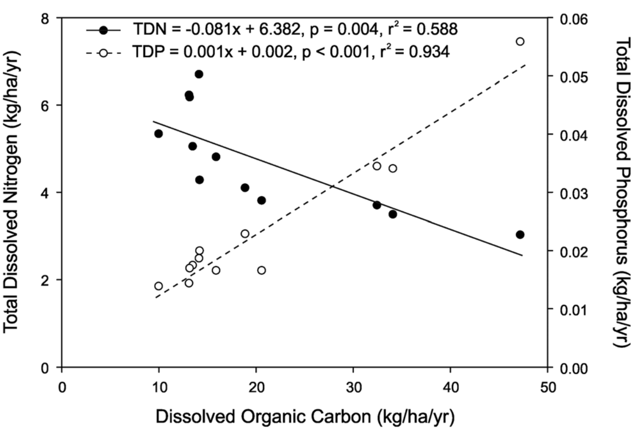

Figure 6. Annual total dissolved nitrogen (TDN) and total dissolved phosphorus (TDP) *versus* dissolved organic carbon (DOC) from 13 catchments in the Turkey Lakes Watershed

correlations between topographic indicators and nutrient export (Table V).

For NO_3^--N export, the best linear model was the simple indicator of NW*eff*VSA ($r^2 = 0.759$, $p < 0.001$), whereas the best multiple linear model was the combination of simple indicators of NW*eff*VSA and $d^2effVSA/dTI_n^2$ ($r^2 = 0.907$, $p < 0.001$). The $d^2effVSA/dTI_n^2$ indicator varied substantially, and its inclusion in the model resulted in an additional 15% explanation of variation in NO_3^--N export. Compound indicators, including $W:VSA$ or $W:effVSA$, did not improve the explanation of variance in NO_3-N export over the linear or multiple linear models (Table V).

Similarly, for DOC, DON and TDP export, the best linear model using simple indicators was topographic flats/depressions within the catchment ($r^2 = 0.935$ for DOC, 0.694 for DON and 0.821 for TDP). Multiple linear models did not improve performance, whereas compound indicators did increase the explanation of variance. For DOC, DON and TDP export, the best linear model using compound indicators was $W:effVSA$ ($r^2 = 0.957$ for DOC, 0.783 for DON and 0.912 for TDP), which resulted in improvements of up to 10% in the explanation of variation in organic nutrient export (Table V). Among the organic nutrient export, model results for DON explained less variation (about 13–17% less) than did those for DOC and TDP (Table VI).

DISCUSSION

Catchment-based water quality monitoring programmes are few and far between and are increasingly at risk of being closed because of budget constraints. Although often perceived as 'expensive and wasteful' (Lovett *et al*., 2007), these long-term monitoring programmes are in fact unique and valuable scientific assets, providing insights into spatio-temporal hydrological and biogeochemical dynamics that cannot be gained using other research approaches, such as experimentation or modelling. Importantly, the value and impact of these scientific assets can be increased by developing a 'similarity metric'

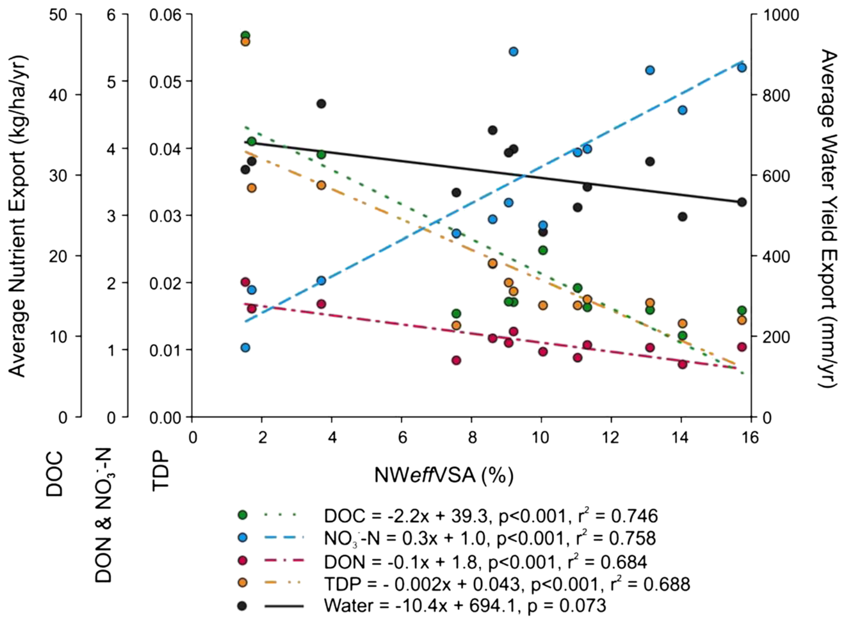

Figure 8. Average water yield and nutrient export *versus* no-wetland effective variable source area (NW*eff*VSA) in 13 catchments of the Turkey Lakes Watershed. DOC, dissolved organic carbon; DON, dissolved organic nitrogen; TDP, total dissolved phosphorus

Table IV. Relationships between topographic metrics and annualized water export from headwater catchments in the Turkey Lakes Watershed

	Water	
Topographic metrics	Direction	r^2
Wetlands (%)	NS	NS
VSA (%)	NS	NS
*eff*VSA (%)	—	0.379
*NWeff*VSA (%)	NS	NS
$d^2 effVSA/dTI_n^2$	NS	NS
$W: VSA$	NS	NS
$W: effVSA$	NS	NS
*NWeff*VSA and $d^2 effVSA/dTI_n^2$	NS	NS

Direction, direction of relationship; r^2, coefficient of determination; NS, not significant (all other relationships $p < 0.05$).

approach, in that heterogeneities in environmental factors (e.g. topography, geology and climate) are related to catchment functional responses (Tetzlaff *et al.*, 2008). By developing an indicator-based approach, we not only capitalize on the unique long-term records these studies provide but also provide a means to extract general principles that can be used in unmonitored basins, thereby increasing efficiencies by removing the need to expand or create new monitoring programmes.

Prediction in ungauged catchments

Using catchment classification and similarity for predictions in ungauged catchments based on the characterization of appropriate metrics of both temporally variable (e.g. timing of extreme precipitation events, Castellarin *et al.*, 2001) and spatially heterogeneous (e.g. soil and topography, Larsen *et al.*, 1994) catchment properties on runoff responses has a long tradition in hydrology. The strength of this approach has improved with advances in DEM resolution and new digital terrain analysis methods (e.g. Lindsay and Creed, 2005; Creed and Beall, 2009), allowing for precise characterization of the topography used in these metrics. Although considerable effort has been made to apply metrics for defining similarities in hydrologic response (Larsen *et al.*, 1994; Castellarin *et al.*, 2001), little work has been performed on developing metrics relevant for predicting nutrient export dynamics, despite various studies relating nutrient export to environmental controls of spatial and temporal nature (Heathwaite and Johnes, 1996; Fraterrigo and Downing, 2008; Andrews *et al.*, 2011).

We examined the effect that topography has on nutrient export from headwater catchments to find key metrics that can be applied to prediction in ungauged basins. We found considerable variation in nutrient export at the TLW, despite uniformity in climate, geology, forest type and forest age (Creed *et al.*, 2002). Topographic characteristics were largely responsible for explaining variation in nutrient export among catchments, with topography controlling hydrological processes that influence the production, availability and delivery of nutrients to the downstream surface water. In particular, metrics related to hydrological storage potential (i.e. topographic flats/depressions) and hydrological flushing potential

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Table V. Relationships between topographic metrics and annualized nutrient export from headwater catchments in the Turkey Lakes Watershed

	NO_3^--N		DOC		DON		TDP	
Topographic metrics	Dir.	r^2	Dir.	r^2	Dir.	r^2	Dir.	r^2
Wetlands (%)	–	0.646	+	0.935	+	0.694	+	0.821
VSA (%)	NS	NS	NS	NS	NS	NS	NS	NS
*eff*VSA (%)	+	0.561	–	0.456	–	0.489	–	0.484
*NWeff*VSA (%)	+	0.759	–	0.747	–	0.682	–	0.687
$d^2effVSA/dTI_n^2$	+	0.394	NS	NS	NS	NS	NS	NS
$W:VSA$	–	0.619	+	0.951	+	0.752	+	0.887
$W:effVSA$	–	0.618	+	0.957	+	0.783	+	0.912
*NWeff*VSA and $d^2effVSA/dTI_n^2$	+	0.907	NS	NS	NS	NS	NS	NS

Dir., direction of relationship; r^2, coefficient of determination; NS, not significant (all other relationships $p < 0.05$).

Table VI. The best regression models for predicting average annual nutrient export from headwater catchments in the Turkey Lakes Watershed

Response variable	r^2	Equation
NO_3^--N ($kg\,N\,ha^{-1}\,a^{-1}$)	0.907	$NO_3^-\text{-N} = 0.978 + (0.235 \times NWeffVSA) + (50\,557.598 \times d^2effVSA/dTI_n^2)$
DOC ($kg\,C\,ha^{-1}\,a^{-1}$)	0.957	$DOC = 12.499 + (10.956 \times W:effVSA)$
DON ($kg\,N\,ha^{-1}\,a^{-1}$)	0.783	$DON = 0.954 + (0.326 \times W:effVSA)$
TDP ($kg\,P\,ha^{-1}\,a^{-1}$)	0.911	$TDP = 0.0146 + (0.0117 \times W:effVSA)$

All models were significant at $p < 0.001$

(i.e. NW*eff*VSA and $d^2effVSA/dTI_n^2$) explained the majority of variations in nutrient export.

Wetlands as interceptors and transformers of nutrients

Wetlands that form in topographic flats/depressions have been identified as a sink for NO_3^--N and a source of DOC, DON and TDP. Previous studies have shown that wetlands can act as sources (Lee *et al*., 1975; Sloey *et al*., 1978; Creed *et al*., 2003, 2008), sinks (Peterjohn and Correll, 1984; Kadlec, 1986; Seitzinger *et al*., 2006; Creed and Beall, 2009) and/or transformers of nutrients (Burgin *et al*., 2011). Their importance in nutrient export is disproportionate to their area on the landscape. Wetlands can be distributed throughout the catchment or occur as a single entity – in humid forested landscapes; even if they are distributed, they are often connected via a surface drainage network, such that they are connected during hydrological events and efficiently transport nutrients to the catchment outlet. In either case, although wetlands generally cover only a small proportion of the catchment, they are usually positioned such that much of the discharge water from hillslopes, and the associated nutrients, pass through them on their way to the receiving water bodies (Devito *et al*., 1989; Creed *et al*., 2003).

Wetlands were a sink of NO_3^--N, suggesting that NO_3^--N from upland drainage water that is intercepted in the wetland is transformed. The NO_3^--N could be transformed via denitrification to N_2O and/or N_2 and exported to the atmosphere (Creed, unpublished data). Alternatively, NO_3^--N from upland drainage water that is intercepted in the wetland can be retained via abiotic immobilization (Davidson *et al*., 2003) and/or biotic immobilization (Gundersen and Bashkin, 1994; Sirivedhin and Gray, 2006), although we did not quantify the importance of these nitrogen retention mechanisms.

Higher C and N pools in wetland surface soils compared with other topographic positions and similar C : N ratios at all the positions suggest that, because of their low redox potential, wetlands acted as a transformation zone for NO_3^--N by reducing NO_3^- to gaseous products or immobilizing N in DON. This resulted in the catchment with a substantial wetland (c38) exporting less NO_3^-N, more DON and less TDN. The combination of these processes results in the ratio of C : N remaining constant in the soil pools. The controls on C and N distribution among the different topographic positions ensure constancy in the ratio of C to N, which strongly points towards a biological process because only biological processes utilize elements/nutrients in specific stoichiometric ratios, thereby maintaining a constant ratio in the remaining soil pools. Therefore, whatever process or processes that are causing the reduction of both C and N in upland areas compared with those in the wetland

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areas maintain a constant ratio of the two elements. On the other hand, the intermediates produced during denitrification may be soil bound, hence the temporary constancy in soil C : N before the nutrients are converted to gaseous forms that escape into the atmosphere from the wetland position. This would maintain a constant ratio in soil pools while lowering dissolved N export from catchments with substantial wetlands compared with upland wetlands. Another possible pathway could be that hydrologic connectivity transports C and N in the same proportions as they appear in the upland areas, leading to accumulation in the wetland soils and high levels of both C and N in wetland soils (as they await further transformations before exiting the catchment in dissolved form) but similar soil C : N ratios at all topographic positions.

In contrast, wetlands were a source of DOC, DON and TDP, with the magnitude of nutrient export proportional to wetland area. There are several mechanisms to explain this observation. The physical and chemical environment within wetlands affects the solubility, lability and mobility of nutrients. Of particular importance are the organic deposits as a major source of soluble organic by-products (Qualls and Richardson, 2003). For example, saturation may suppress mineralization of DON to inorganic nitrogen (NH_3^+-N) (Yang and Fan, 2003), leading to organic forms accumulating in wetlands. The wet conditions also have a large impact on the redox state of nutrients (Sorrell and Armstrong, 1994; Reddy and DeLaune, 2008). Low redox potentials may also facilitate abiotic conversion of NO_3^--N to organic forms of nitrogen through the ferrous wheel hypothesis, which involves reduction of Fe(III) hydroxide by organic matter in the forest floor to release Fe(II) (Davidson *et al*., 2003) accompanied by liberation of phosphorus, which may be exported in dissolved form as TDP (Liptzin and Silver, 2009) and results in more export from catchments with a wetland. Low redox potentials may also facilitate biotic conversion of NO_3^--N to gaseous forms of N_2O and N_2. The potential for alternative fates of nitrogen from uplands passing through wetlands en route to the stream may explain the relatively weak relationship between wetland proportion and DON compared with that of DOC and TDP.

Variable source areas as conduits of nutrients. Uplands and their VSAs (Hewlett and Hibbert, 1967) have been important in predicting nutrient export in many studies (e.g. Govindaraju, 1996; Walter *et al*., 2000; Creed and Beall, 2009; Marjerison *et al*., 2011). In this study, despite noticeable variations in VSA proportion among the studied catchments, the VSA proportion did not explain the variation of nutrient export among catchments. However, we did find that different derivatives of VSA were important indicators in predicting nutrient export.

For example, the proportion of *eff*VSA, which represents the proportion of frequently flushed areas within the VSA, was more effective in predicting NO_3^--N export. The direct relationship observed between *eff*VSA and NO_3^--N export suggested an increased rate of hydrological flushing of NO_3^--N from catchments with larger *eff*VSAs. Aerobic conditions in *eff*VSA surfaces, when not saturated, favour nitrification (oxidation of NH_3^+-N to NO_3^--N), making *eff*VSA a net source of NO_3^--N. Nitrate accumulates in these areas until sufficient precipitation events cause the water table to rise and flush the accumulated NO_3^--N for export to streams (Creed *et al*., 1996; Creed and Band, 1998a). If not absorbed by plants, NO_3^--N, which naturally possesses less affinity for adsorption to mineral soils (Foster *et al*., 1982; Andrews *et al*., 2007), can be easily mobilized from *eff*VSA to receiving water bodies.

The proportion of *eff*VSA without topographic flats/depressions (NW*eff*VSA) was even more effective in predicting NO_3^--N export. *Eff*VSA may contain wetlands, and NW*eff*VSA removed the potential effects of wetlands within *eff*VSA. NW*eff*VSA explained more variation than either of these indicators did on their own. Coupling NW*eff*VSA with the potential lateral expansion of *eff*VSA ($d^2 effVSA/dTI_n^2$) further improved predictions of NO_3^--N export. The size of the hydrologically connected portion of VSA (*eff*VSA) varies with season and storm characteristics. Expansion of *eff*VSA in response to climatic forcing can result in larger flushable areas and longer flushing time, causing greater NO_3^--N export (Creed and Band, 1998b). The role of expanding saturated VSA in terms of increasing flushable nutrient concentrations has also been reported for NO_3^--N by Sickman (2001) and Oeurng *et al*. (2010) and for DOC by Boyer *et al*. (1995).

It is important to recognize that the VSA and its derivatives are not related to water export (i.e. expansion of rising water table into upland areas does not correspond to an increase in water at the stream). Rather, as VSA increases, the amount of water in contact with NO_3^--N-rich soil layers increases and flushes NO_3^--N to the stream. Consequently, as VSA increases, water export shows no significant trend whereas NO_3^--N export increases and is the only nutrient to increase with increasing VSA (Figure 8).

The different derivatives of VSA were also significantly related, but negatively correlated, to organic nutrient and TDP export, suggesting different controls on their export. Generally, catchments with a large *eff*VSA proportion contained few or no wetlands, whereas those with a small *eff*VSA proportion contained substantial wetlands. The inverse relationship between *eff*VSA and DOC, DON and TDP relative to NO_3^--N may be linked to physical processes. For example, the increased adsorption of

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dissolved organic matter by mineral soils in upland-dominated catchments may decrease export of organic forms of nutrients from these catchments (McDowell and Likens, 1988; Fellman *et al.*, 2009). As the *eff*VSA proportion increases, the potential of dissolved organic matter in upland-dominated catchments to reach stream networks would decrease because the transport pathways are through mineral-rich soils that strongly adsorb dissolved organic matter (Wallis, 1979; Qualls *et al.*, 2000). Mineral soil adsorption has been well recognized as a primary process responsible for reducing dissolved organic matter export (McDowell and Likens, 1988; Moore *et al.*, 1992; Kalbitz *et al.*, 2000; Moore and Turunen, 2004), whereas organic soils with little DOC adsorption capacity and the potential to generate soluble carbon compounds are known to be large exporters of DOM (Aitkenhead and McDowell 2000; Aitkenhead-Peterson *et al.*, 2007). For example, because of efficient adsorption by mineral soils, percolation of DOC through subsurface soil can cause a typical decline of DOC concentration by 50–90% (McDowell and Wood, 1984; Neff and Asner, 2001). The inverse relationship between *eff*VSA and DOC, DON and TDP relative to NO_3^--N may also be linked to biological processes. Aerobic conditions in *eff*VSA soils of uplands would facilitate microbial organic matter mineralization, providing an additional source of NO_3^--N for export while depleting dissolved organic matter reserves faster than what is generated by decomposing detritus (Aiken *et al.*, 2011).

However, the wetland proportion was a more important metric than VSA derivatives for predicting DOC, DON and TDP export. We developed new metrics reflecting the relative proportion of wetland area with respect to VSA ($W:VSA$) and *eff*VSA ($W:effVSA$). In general, $W:VSA$ and $W:effVSA$ metrics were more effective in predicting export of organic forms of nutrients (DOC, DON and TDP) than wetland proportions (percentage of wetland). Whereas the improvement in DOC prediction was marginal (~2%), it was larger for DON and TDP with $W:VSA$ and $W:effVSA$, improving predictions by ~6% and 9%, respectively. Catchments with larger wetland area with respect to their VSA and *effVSA* tended to export more organic nutrients, likely because the sources of DOC, DON and TDP had a greater influence than the sinks. Possible exceptions are catchments with large wetlands that are remote from the catchment outlet (e.g. c42). In these catchments, processing nutrients within the streams that connect the wetland to the outlet likely resulted in modified nutrient concentrations and fluxes.

Predicting annual export of nutrients is useful in tracking interannual trends, but many ecosystem responses (e.g. algal blooms) occur over shorter periods. These time-sensitive responses are driven by rapid hydrologic events such as those that occur during snowmelt or storm runoff. Although considering how topographic indicators influence event-driven nutrient export was outside the scope of this paper, it should be considered as an important next step in refining our understanding of how the physical landscape interacts with biogeochemical processes.

CONCLUSIONS

We need tools to scale our process-based understanding from experimental catchments to the landscape where policy and management decisions are made. Topography is an important determinant of nutrient export through its regulation of hydrological processes that in turn influence formation of nutrient hot spots (sources for export) *versus* cold spots (sinks for export), transformation of the nutrients to dissolved and/or gaseous forms and transport to the stream. Specifically, topography exerts an influence on hydrological storage potential (i.e. topographic flats/depressions where wetlands form, allowing the accumulation of nutrient-rich organic deposits) and hydrological flushing potential (i.e. topographic controls on the effVSA and its potential for expansion where rising water table allows the prolonged flushing of nutrient-rich near-surface/surface soils as rising water table reaches new soils). Topographic characteristics of individual catchments create different potentials for hydrological storage *versus* flushing, which contributes to the substantial variation in nutrient export among catchments, and the relative proportion of one with respect to the other should be considered to improve prediction of nutrient export. Recent developments have revolutionized topographic models of catchments, which means that tools can be developed to incorporate topographic indicators representing hydrological and biogeochemical controls on nutrient export behaviour of catchments to characterize responses in ungauged catchments.

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