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Research article

Landscape characteristics driving spatial variation in total phosphorus and sediment loading from sub-watersheds of the Nottawasaga River, Ontario

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ABSTRACT

Eutrophication from agricultural runoff is a global problem, often resulting in formation of anoxic zones in receiving water bodies. The Nottawasaga River Watershed (NRW) is dominated by agricultural land-use, and drains into Nottawasaga Bay, Georgian Bay (Lake Huron). A fundamental feature of the NRW is the Minesing Wetlands, a Ramsar site and the largest inland wetland in southern Ontario. We used total phosphorus (TP) concentration-discharge relationships to estimate annual loading from six sub-watersheds and compared these against published models, which did not offer a way to account for the unique properties of the Minesing Wetlands. We developed predictive loading models specifically for the NRW to account for these characteristics, which accurately predict daily summer base-flow TP ($r^2 = 0.76$, $p = < 0.0001$) and total suspended solids (TSS; $r^2 = 0.65$, $p = < 0.0001$) loads for 11 subwatersheds using geomorphic and land-cover variables. Drainage area and % pasture land were the most significant predictive variables driving spatial variability in TP and TSS loading rates among subwatersheds. The positive relationship between TP and % wetland ($r^2 = 0.22$, $p = 0.0063$) also suggested that the Minesing Wetlands are a source of nutrients to the Nottawasaga River. Watershed geomorphology (e.g. slope) was a good predictor of land cover, and produced accurate loading estimates. This study is the first to offer a new approach to predict TP and TSS loading rates during the growing season using readily available geospatial data.

1. Introduction

Eutrophication is strongly influenced by agricultural runoff, and has become a major environmental problem globally (Matson et al., 1997; Smith, 2003). The positive relationship between nutrient loading and agricultural land-use is well documented (Carpenter et al., 1998); the primary nutrients, phosphorus (P) and nitrogen (N), originate from both pasture land (including livestock) and crop land, with pollutants entering watercourses through runoff contaminated with fertilizers and livestock manure (Reckhow et al., 1980; Beaulac and Reckhow, 1982; Johnes, 1996; Chambers and Dale, 1997; Taylor et al., 2016; Pan et al., 2017; Sharara et al., 2017). Both practices also increase sediment loading through livestock grazing and tilling, which loosens soil particles and leads to soil erosion from pasture and crop land respectively (Fullen, 1985; Dunne et al., 2011). Nutrients, such as phosphate, are easily adsorbed onto soil particles and become particulate phosphorus, which enters tributaries with sediments through runoff (McDowell and Sharpley, 2003).

The Nottawasaga River Watershed (NRW), located in south central Ontario, is a relatively small (2900 km^2) watershed, but a major source of nutrients and sediment to Nottawasaga Bay, Georgian Bay (Chow-Fraser, 2006; Brown et al., 2011) because of its predominant agricultural land-use (Greenland International Consulting Ltd., 2006). The annual TP load of the NRW (TP = 47,092 kg/year; TSS = 37,009,600 kg/year) was modelled by Greenland International Consulting Ltd. (2006) to be similar to that of its' neighboring watershed, the Lake Simcoe Basin (TP = 37,000 kg/year; TSS = 42,388,000 kg/year). Previous research by Rutledge et al. (2015) identified that majority of phosphorus in the main branch of the Nottawasaga River is sediment bound (ranging from 62 to 100% particulate phosphorus during summer base flow). The runoff not only affects the ecology of the near-shore ecosystem of Nottawasaga Bay, it also threatens the socio-economic vitality of the region since the outflow of the Nottawasaga River is adjacent Wasaga beach, which attracts millions of visitors and seasonal residents each year. Another unique feature of the NRW is the Minesing Wetlands, a Ramsar site and Provincially Significant Wetland, and the largest contiguous inland wetland in southern Ontario (6000 ha; Ramsar Sites Information Service, 1996). Although wetlands are known to filter out nutrients and sediment from upstream sources, Chow-Fraser (2006) found elevated levels of

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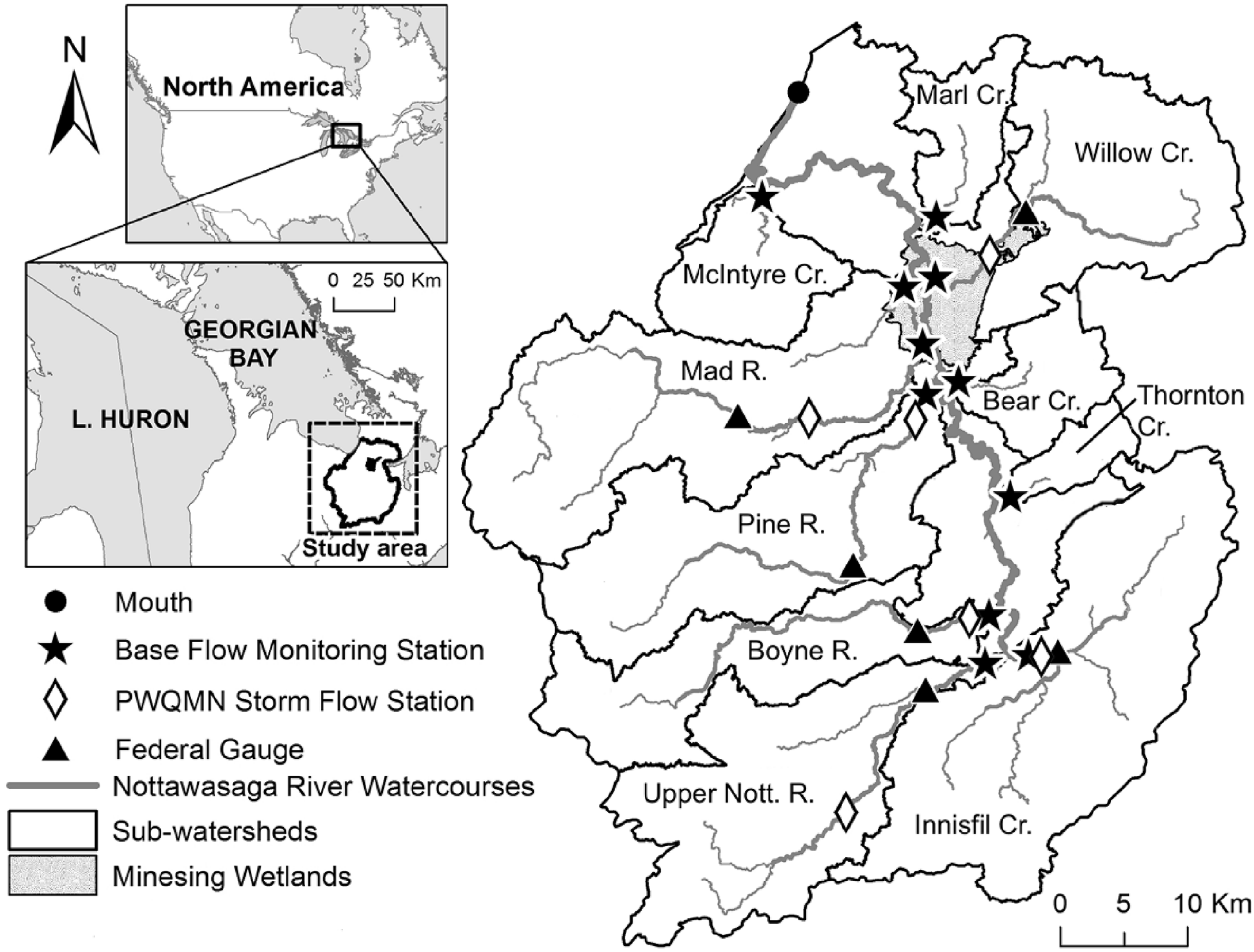

Fig. 1. The Nottawasaga River watershed study area. Sub-watersheds included in the study are labeled with the site code.

phosphorus, turbidity, and chlorophyll-α in the Nottawasaga River after it ran through the Minesing Wetlands, and hypothesized that the wetlands no longer provide nutrient and sediment filtration as an ecosystem function. Up until this point, no study has examined water quality of the Nottawasaga River and its tributaries as it flows through the Minesing Wetlands.

A simple and inexpensive approach to determine the total nutrient or sediment load for a watershed is to apply published export coefficients to areal extent of specific land-use (human-altered; agriculture, urban) or land cover (natural; forest, wetland) classes (Johnes, 1996; Mattikalli and Richards, 1996; Winter and Duthie, 2000). For these calculations, many export coefficients have been published pertaining to a variety of agricultural practices, but most of these have been developed with data from U.S. watersheds, and only a few exist for Canadian watersheds. The few exceptions include Chambers and Dale (1997), which examined nutrient loading using export coefficients from non-point sources in northern Canada (Alberta and Northwest Territories), and Dillon and Kirchner (1975), which measured phosphorus export in predominantly forested watersheds in southern Ontario.

The relationship between surface water quality and land cover for predicting loading is well documented in the literature (Reckhow et al., 1980; Beaulac and Reckhow, 1982; Johnes, 1996; Chambers and Dale, 1997; Carpenter et al., 1998; Tong and Chen, 2002); however, using geometric variables to predict loading, such as slope, soil and drainage area are less prominent. Kang et al. (2001) found that land slope played a key role in runoff and sediment loading. Additionally, several studies document that degree of slope can determine land use suitability, suggesting that gentle slopes be reserved for crop land to reduce nutrient runoff and soil erosion, and using steeper slopes for other purposes such as pasture land or wood land (Chen et al., 2001, 2003). Sicat et al. (2005) also found that slope, soil texture and soil depth predicted the suitability of land for agriculture land uses. In addition, it has been shown that catchment size influences runoff (Pilgrim et al., 1982), and that a linear relationship exists between nutrient export and watershed drainage area (T-Prairie and Kalff, 1986). This emphasizes the importance of considering subwatershed area when modelling the effects of geomorphology on nutrient and sediment loading.

There are few studies that explore the impacts of geomorphology on total phosphorus (TP) and total suspended solids (TSS) loading. Perhaps a more serious problem is that many loading models have been developed with base flow data, without any consideration of storm flow, which could greatly elevate nutrient and sediment concentrations in the river (Inamdar et al., 2006; Oda et al., 2011). Furthermore, no studies have considered the potential influences of a large inland freshwater wetland complex in a mixed agricultural watershed in Ontario to date. The extent to which these information gaps may impede accurate assessment of the impact of pollutant loading to Nottawasaga Bay is unknown, and should be investigated given the ecological and socio-economical importance of this region. Specifically, a new loading model for the NRW should be developed that investigates the influence of the Minesing Wetlands on TP and TSS loading to the Nottawasaga River.

The objectives of this study are three-fold. First, we will determine if three existing loading models can be applied directly to the NRW. Secondly, we will use TP concentration-discharge relationships for six NRW sub-watersheds to calculate annual TP loads and compare our results to those from published models. Thirdly, we will develop predictive landscape models using daily summer base flows for TP and TSS that are specific to the NRW via readily available geospatial data. Specifically, we test the hypothesis that watershed geomorphology (drainage area and soil type) drives spatial variation in TP and TSS loading rates and that larger sub-watersheds with high proportions of agricultural land-use (crop and pasture land) will contribute to higher TP and TSS loading. This is the first comprehensive study of a mixed agricultural watershed in south central Ontario in which we model nutrient and sediment loading based solely on geomorphic and land-cover features at a regional scale. Results from this study will reveal landscape characteristics that are most influential to nutrient and sediment loading within south central Ontario and permit environmental management agencies to implement appropriate conservation strategies at the scale of subwatersheds.

2. Methods

2.1. Study area

We monitored 11 sub-watersheds of the NRW, all of which drain fourth or fifth order streams and eventually discharge into the main branch of the Nottawasaga River (Fig. 1). These sub-watersheds include the Upper Nottawasaga River, Innisfil Creek, Boyne River, Thornton Creek, Pine River, Bear Creek, Mad River Breach, Mad River, Willow Creek, Marl Creek, and McIntyre Creek. During high spring flows in 2000, the Mad River broke its natural levee and carved out a new channel that discharges into the Nottawasaga River at the southern end of the Minesing Wetlands. We identified the Mad River Breach as an important tributary to monitor because scouring of the new channel increased bank erosion and comprised 70% of the Mad River's natural base flow by 2012, leading to a higher discharge rate (Rootham and Featherstone, 2014).

2.2. Sampling procedures

In order to develop concentration-discharge curves for estimation of annual TP loads, a team from the Nottawasaga Valley Conservation Authority (NVCA) collected grab samples from Provincial Water Quality Monitoring Network (PWQMN) stations (Fig. 1) from April to November 2015. Since only six of the tributaries within our study area have federal gauge stations (Fig. 1), we were only able to estimate annual TP loads for these six subwatersheds (Upper Nottawasaga River, Innisfil Creek, Boyne River, Pine River, Mad River, Willow Creek). PWQMN and gauge stations do not always coincide; their locations range from 1 to 11 km apart from each other. A total of 12 samples, which included nine storm flow and three base flow samples were collected for each tributary, and were subsequently analyzed for TP concentration. Storm flow samples were collected 24 h following an event (to account for a lag period) at PWQMN stations. It is important to note that PWQMN stations were not situated in the same locations as our base flow monitoring stations; in particular, PWQMN stations for the Mad River and Willow Creek were located before the tributaries drain through the Minesing Wetlands. This emphasizes the need for a new loading model specific for the NRW that accounts for influences of the Minesing Wetlands.

To determine daily summer base flow loading rates for landscape modelling, we established base flow monitoring stations for the 11 sub-watersheds in the study area. Stations were located as close as possible to the tributary junction with the Nottawasaga River in order to obtain representative loading rates from the entire subwatershed. In a preliminary study conducted in 2014, Rutledge et al. (2015) determined that base flow TP concentrations in the Nottawasaga River were highest during July; therefore, we sampled main tributaries of the 11 sub-watersheds for TP and TSS once during this month to capture maximal summer base flow loading rates. We measured discharge during base flow conditions at the time of sample collection. Following the Ontario Stream Assessment Protocol (OSAP; Stanfield, 2010), we used the velocity-area method and a SonTek FlowTracker Acoustic Doppler Velocimeter (ADV™) to measure tributary discharge.

We used a Van Dorn sampler to collect discrete samples at each station in freshly acid-washed Corning™ snap-seal containers or Nalgene™ bottles for measurements of TP and TSS (Lind, 1974; Crosbie and Chow-Fraser, 1999). Once collected, all water samples were stored on icepacks in a cooler and placed in a freezer (within 6 h) for storage until they could be transferred back to McMaster University for processing. All grab samples were taken from mid-depth against the current to ensure the samples were thoroughly mixed (Barton, 1977; Shelton, 1997; Poor and McDonnell, 2007).

Willow Creek flows through a substantial portion of the Minesing Wetlands before it discharges into the Nottawasaga River. As no previous studies have accounted for potential influences of the Minesing on the water quality of this tributary, we carried out additional studies to compare dissolved oxygen (DO) concentrations at three locations along Willow Creek as it flows through the wetland complex with those at stations located above the wetland at the PWQMN station, and in the Nottawasaga River downstream of its junction with Willow Creek. The NVCA obtained daytime measurements of DO at Willow Creek stations using a YSI EXO sonde with an optical DO sensor on three occasions in July 2015 and two occasions in August 2015. We also installed an ISCO 6712 automatic sampler and a YSI EXO1 sonde in Willow Creek to continuously monitor TP and DO from June to August 2015 inclusive. The ISCO sampler was programed to collect 250 mL of water every 6 h, which filled a 1 L sample bottle over a 24-h period. Daily composites were collected weekly, with the exception of one biweekly sample collection (Kotlash and Chessman (1998); Seilheimer et al., 2007; Domagalski et al., 2008; deCatanzaro and Chow-Fraser, 2011), and were replaced with freshly acid-washed 1 L bottles.

Sub-samples from daily composites were transferred into acid washed Corning™ snap-seal containers, which were kept frozen until they could be processed. Sub-samples were representative of mean daily TP concentrations. We programed the YSI EXO1 to record DO in situ every 2 h, taking simultaneous measurements when the ISCO collected water samples. Prior to analyses, we calculated mean daily DO concentrations.

2.3. Sample processing

All nutrient and sediment samples were processed in triplicate. TP concentrations were determined with the molybdenum blue method (Murphy and Riley, 1962) following potassium persulfate digestion in an autoclave for 50 min (120 °C, 15 psi). Absorbance values were read with a Genesys 10 UV Spectrophotometer and final TP concentrations were calculated with a standard curve. Known aliquots of river water was filtered through GC filters (0.45 μm pore size) and subsequently used to calculate concentrations of TSS. All filters were dried and pre-weighed before samples were filtered. Filters were then folded in half and kept in small plastic petri plates and placed in a freezer. When we were ready to process the TSS samples, filters were retrieved from the freezer and placed on a crucible of known weight to be dried in the oven for 1 h at 100 °C; subsequently, they were placed in a desiccator for an additional hour, and then weighed to the nearest 0.1 mg.

2.4. Published loading models

We applied three published loading models to the NRW to compare how estimated annual TP loads differed between them (Table 1). Firstly, the use of export coefficients in models to estimate loading has been widely practiced in North America and Europe (Dillon and Kirchner, 1975; Reckhow et al., 1980; Beaulac and Reckhow, 1982; Johnes et al., 1996). The basic equation that describes the export coefficient model is as follows:

Table 1
Comparison of total phosphorus (TP; kg/year) and total suspended solids (TSS; tonnes/year) annual loads predicted using three existing models for 11 sub-watersheds.

Tributary	Annual Load						
	Export Coefficient		Landscape (Jones et al., 2001)		CANWET		Actual Data
	TP	TSS	TP	TSS	TP	TSS	TP
Upper Nott. R.	5510	13,481	44,425	25,028	5200	8045	773
Innisfil Cr.	11,107	29,706	102,231	101,935	7105	4895	6537
Boyne R.	4795	11,536	31,656	24,534	4893	5229	1955
Thornton Cr.	988	2625	4696	4350	–	–	–
Pine R.	5773	13,197	40,471	32,398	4050	3543	2296
Bear Cr.	1800	34,64	13,836	5548	863	702	–
Mad R. Breach	5861	15,170	47,741	13,691	–	–	–
[a] Mad R.	7488	19,670	66,031	17,911	4681	5063	4174
[a] Willow Cr.	4849	9914	59,327	15,332	3802	2445	5044
Marl Cr.	1664	4423	12,786	7725	1929	1784	–
McIntyre Cr.	3007	8210	13,792	13,809	8205	2021	–

[a] Indicates that estimated loads do not account for potential influences of the Minesing Wetlands.

$$L_x = \sum_{i=1}^{m} c_i A_i \quad (1)$$

where L is the loading rate of constituent x (TP or TSS) from land (kg/year), m is the number of land-cover classes, ci is the export coefficient for land cover class i (kg/ha/year), and Ai is the area of land-cover class i (ha) (Soranno et al., 1996). We applied export coefficients from published studies (Supplementary Material, Table S1) to this equation to calculate TP and TSS loading rates for each sub-watershed in our study.

Secondly, Jones et al. (2001) published a landscape model in the Chesapeake Bay Basin that predicted TP and TSS loading rates. Two equations developed by their model are as follows:

$$\log(\mathrm{TP}) = 0.840 + 0.025\,\mathrm{purb} - 0.026\,\mathrm{ripf} \quad (2)$$

$$\log(\mathrm{TSS}) = 8.472 + 0.079\,\mathrm{purb} - 0.116\,\mathrm{pwetl} - 0.038\,\mathrm{ripf} \quad (3)$$

where TP and TSS represent the annual loading rate (kg/ha/year), purb and pwetl are the percent of urban and wetland land cover in the sub-watershed respectively, and ripf is the percent of riparian forest adjacent to the stream edge (within a 30 m × 30 m buffer).

Thirdly, Greenland International Consulting Ltd. (2006) produced TP and TSS loading models for the NRW using the Canadian Nutrient and Water Evaluation Tool (CANWET) interface within a geographic information system (GIS). CANWET models did not include water quality measurements from tributaries of the Nottawasaga River that flow through the Minesing, nor did the models consider water-chemistry data following storm events. Additionally, the Willow Creek sub-watershed, which drains a substantial portion of the Minesing Wetlands, was mislabeled as Matheson Creek (a low order stream that flows into Willow Creek). To account for this misrepresentation, we added the loads predicted for both Willow Creek and Matheson Creek together. Provincial Water Quality Monitoring Network (PWQMN) stations were not located at the base of sub-watersheds, and gauge stations were not situated where water samples were collected. The PWQMN does not monitor Thornton Creek or the Mad River Breach (included in our study); therefore, the CANWET model did not produce loads for these tributaries.

2.5. Loading calculations

Annual TP loads were calculated using concentration-discharge curves produced for the six tributaries with established federal gauge stations (Fig. 2). We regressed TP concentration from the 12 samples collected by NVCA (nine storm flow, three base flow) against discharge obtained from the federal gauge station at the time of sampling for each tributary. We obtained daily discharge data for 2015 from federal gauge stations, and used the equation of the concentration-discharge curve to calculate daily TP concentrations for each tributary. In order to calculate annual loads from the six subwatersheds, we used the following equation:

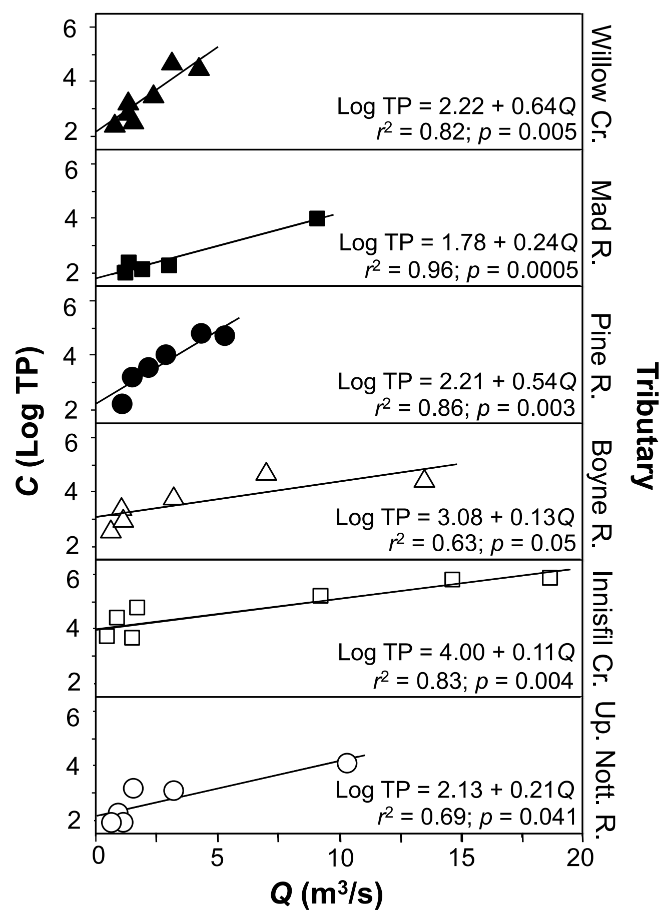

Fig. 2. Tributary specific concentration (c) – discharge (Q) curves used to estimate annual total phosphorus (TP) loads for each sub-watershed.

$$L_x = C_x Q \quad (4)$$

where L is the loading rate of constituent x (TP or TSS; kg/day), C is the concentration of the constituent x in water (TP; kg/L), and Q is the rate of discharge of water (m^3/s). We calculated daily loads using Eq. (4), and summed them for each day of the year to obtain the annual load (kg/year). We compared our annual loads to those predicted with published export coefficients (Dillon and Kirchner, 1975; Reckhow et al., 1980; Van Vliet and Hall, 1991; Chambers and Dale, 1997; Winter and Duthie, 2000) and existing loading models (Jones et al., 2001; Greenland International Consulting Ltd., 2006) (Table 1).

2.6. Landscape analysis

All landscape analyses were performed in a Geographic Information System (GIS; ArcMap 10.3; ESRI Inc., Redlands, California, USA). We delineated subwatersheds and watercourses using a Digital Elevation Model (DEM) with a 10 m cell resolution (Ontario Ministry of Natural Resources and Forestry, 2013). Landscape variables included both geomorphic and land-cover variables (Supplementary Material, Table S2). Geomorphic variables included drainage area (dArea; area of the sub-watershed), mean slope gradient (mSg; the average slope within the sub-watershed), as well as the percent of sandy (sSand) and organic (sOrg) soils within the sub-watershed. Drainage area and slope values were obtained with a DEM (Ontario Ministry of Natural Resources, 2013; 10 m cell resolution). Percent soil type was calculated from the Soil Landscapes of Canada layer (Agriculture and Agri-Food Canada, 2011). We followed a standardized global reference system to reclassify the NRW into seven main types of land cover (refers to both human-altered land-uses and natural areas in this paper): crop (AGC), pasture (AGP), urban (URB; built-up pervious and impervious surfaces, golf courses, recreational areas), forest (FOR), wetland (WET), barren (BAR; beaches, transitional areas, extraction), and water (note that this category included < 1% of the total watershed area and was subsequently removed from further analyses). We subsequently determined the total area and percent cover of each land-cover class within each sub-watershed. We used a land cover layer that was manually digitized from Muskoka and Simcoe County orthophotos (Ontario Ministry of Natural Resources and Forestry, 2008), which were classified at a 1:2000 scale by the NVCA.

2.7. Data analysis

We used R 3.2.1 (R Core Team, 2015) to perform a breakpoint analysis on the segmented linear regression between TP and DO in Willow Creek. We also used JMP 12 software (SAS Institute Inc., Toronto, ON, Canada), to perform multivariate correlation analyses, Principal Components Analysis (PCA), and Ordinary Least Squares (OLS) regressions, which have proven to be an effective method when applied to other scientific fields (Valipour et al., 2013, 2017; Rezaei et al., 2016; Valipour, 2016a, 2016b). Dependent variables were first log (TSS) or box-cox (TP) transformed to achieve normality. We arcsine-transformed all variables expressed as a percent (land-cover variables, percent soil) to normalize variances. Prior to performing OLS regression, we used Pearson's correlation analysis to identify collinearity between independent landscape variables. To reduce redundancy, variables that correlated highly with the primary factors identified in the PCA (e.g. slope, crop land, etc.) were removed from subsequent OLS regression analyses. The OLS regression models were chosen based on lowest AIC values for all possible combinations. Where ΔAIC was less than 2 between models, the model with the fewest predictive variables was chosen to minimize degrees of freedom and to create a simpler model. We ran linear regressions on TP and TSS daily loads against significant predictor variables identified by the OLS regression analyses to investigate the relationship further.

3. Results

The size of sub-watersheds in this study spanned two orders of magnitude from 42 to 498 km^2 (Supplementary Material, Table S2); consequently, stream discharge and daily summer base-flow loadings to the Nottawasaga River also varied widely (Supplementary Material, Table S3). Concentrations of TP varied from 6.1 to 44.2 μg/L (n = 11) while concentrations of TSS ranged from 2.8 to 40.1 mg/L (n = 11). Tributaries with the highest TP and TSS concentrations were associated with high proportions of agricultural land use, such as Innisfil Creek (TP = 40.4 μg/L; TSS = 27.9 mg/L; AGC = 48%; AGP = 16%) and Marl Creek (TP = 41.0 μg/L; TSS = 31.2 mg/L; AGC = 35%; AGP = 16%). Since tributaries with higher discharge rates had a greater volume of water entering the Nottawasaga River, they contributed a higher loading of TP and TSS to the river on a daily basis.

Because the NRW covers a large geographic area, both geomorphology and land-cover characteristics varied widely for the 11 sub-watersheds (Supplementary Material, Table S2). Despite this variability, agriculture consistently accounted for the greatest amount of land cover in all sub-watersheds, with proportion of crop land being higher than that of pasture land in most cases. It is also important to point out that the Minesing Wetlands accounted for a large portion of wetland land-cover class in the Mad River Breach, Mad River and Willow Creek sub-watersheds (16, 17 and 21% respectively).

3.1. Application of existing annual loading models

We used three different approaches to compare annual loading rates of TP and TSS from 11 subwatersheds of the Nottawasaga River (Table 1). We used (1) published export coefficients (Eq. (1); Supplementary Material, Tables 1 and 2 the landscape model of Jones et al. (2001) (Eqs. (2) and (3)), and (3) the CANWET model (Greenland International Consulting Ltd., 2006) to predict annual loading rates for 11 subwatersheds. We also measured concentration and discharge to create concentration-discharge curves to calculate annual TP loads for six subwatersheds with PWQMN and federal gauge stations. The CANWET model, which was developed specifically for the NRW, produced TP loads that were most similar to those we calculated with field data. However, it still produced higher loading values for five of the six subwatersheds that were higher by 507 (Mad River) to 4427 kg/year (Upper Nottawasaga River). The CANWET model produced a lower annual load supplied by Willow Creek by 1242 kg/year. Similarly, the nutrient export model produced higher annual TP loads for all sub-watersheds with the exception of Willow Creek, which produced a lower load by 195 kg/year. The landscape model of Jones et al. (2001) consistently predicted higher TP loads in all sub-watersheds by an order of magnitude compared to all other approaches. Due to sample volume constraints, we did not have measured annual TSS loads of our own to compare with those estimated by the three approaches. Estimated TSS loading rates varied widely among the three published approaches, although the landscape model still tended to produce the highest values. This comparison indicated that all published models would produce higher TP loading rates for our tributaries.

3.2. Impact of the Minesing Wetlands

To determine the potential impact of the Minesing Wetlands on water quality of Willow Creek, we compared the daytime DO measurements in July and August 2015 of three stations in Willow Creek as it flows through the Minesing Wetlands, with those measured in Willow Creek above (PWQMN station) and below (Nottawasaga River below confluence with Willow Creek) the wetland complex (Fig. 3). DO concentration remained above 10 mg/L before Willow Creek entered the Minesing, and gradually decreased through the three Minesing stations (Minesing 1, Minesing 2, Willow Creek confluence), until it increased again when it mixed with the more oxygenated water of the Nottawasaga River (Nottawasaga River confluence). Mean DO concentration above the Minesing (PWQMN station) was significantly higher (10.3 ± 0.2 mg/L) than that measured within the Minesing at the Willow Creek confluence before it drained into the Nottawasaga River

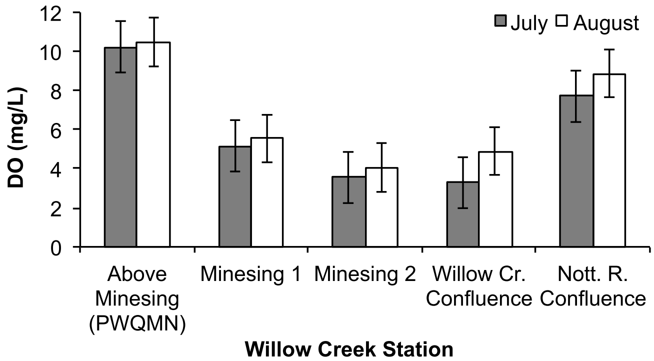

Fig. 3. Mean dissolved oxygen (DO) concentrations measured in Willow Creek above (PWQMN), through (Minesing 1, Minesing 2, Willow Cr. Confluence) and below (Nott. R. Confluence) the Minesing Wetlands.

(3.9 ± 0.9 mg/L) (t(4.4) = 6.9, $p = 0.0016$). Therefore, DO was 6.4 ± 0.9 mg/L lower in Willow Creek as it coursed through the Minesing than before it drained through the wetland complex (t-test, $p = 0.0016$). Through continuous monitoring with the ISCO sampler, we also found that TP concentrations at our Willow Creek base flow monitoring station ranged from 12.1 to 180.8 μg/L. These extremely high TP concentrations in Willow Creek were 5–30 times higher than those measured at our other 10 base flow monitoring stations (Supplementary Material, Table S3). When we performed the segmented regression analysis of daily TP against daily DO concentrations, we found a breakpoint at a DO concentration of 0.101 ± 0.087 mg/L; below this, there was a significant negative correlation between TP and DO, and above this there was no linear relationship (Fig. 4).

3.3. Watershed specific model development

To develop our own daily base flow loading models for the NRW, we first performed a PCA to identify linear combinations of landscape variables that would explain the greatest amount of variation across all sub-watersheds (Supplementary Material, Table S4). The first three Principal Components (PC; eigenvalues > 1) together explained 82% of the total variation in the dataset. PC1 alone accounted for 44% of the variation, and was strongly and positively correlated with mean slope gradient (0.81) and negatively correlated with crop land (−0.95). The negative correlation with crop land explains why there was a positive correlation between PC1 and undeveloped land classes such as forests (0.76), wetlands (0.64) and barren land (0.64). PC2 explained 23% of the remaining variation, and ordinated watersheds according to proportion of urban land (0.84) and sandy soils (0.62). PC3, which accounted for 15% of the remaining variance, was most highly correlated with the proportion of barren land (0.73). Based on these correlations, it appears that land-cover classes depended on watershed geomorphology. When we grouped mean slope gradients in the NRW into three classes, gentle (0–5°), moderate (5–16.5°) and steep (> 16.5°), crop land occupied the highest proportion of gently sloped areas (35%), while pasture land occurred on a greater proportion of moderate (18%) and steeply (3%) sloped areas compared to crops (11% and 0% on moderate and steep slopes, respectively). Majority of the steeply sloped areas in the NRW were covered by forest (84%; Fig. 5).

The PCA confirmed the importance of land-cover and geomorphic variables in explaining variation in the dataset. When we regressed daily TP and TSS loading rates for each sub-watershed against corresponding PC1 scores, we found highly significant positive relationships that explained 46% and 37% of the variation, respectively (Table 2). Willow Creek, Mad River Breach, and Mad River had high PC1 scores, presumably because of the relatively large proportion of their sub-watersheds that drain wetlands (16–21%; Supplementary Material,

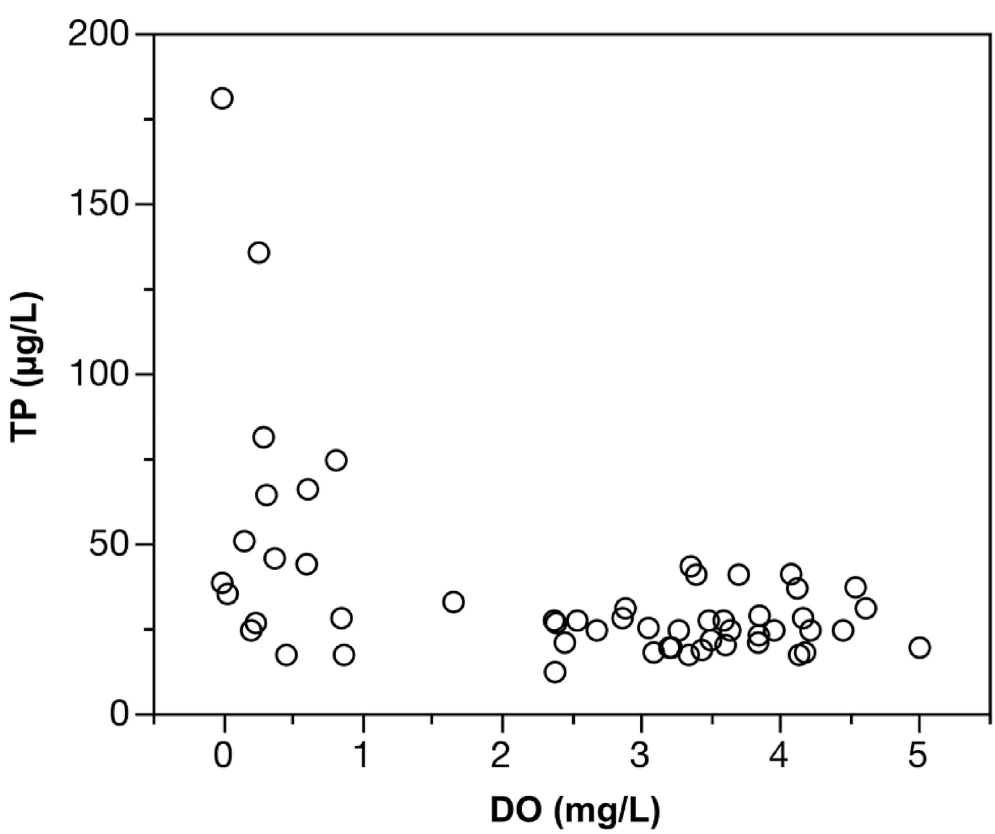

Fig. 4. Mean daily total phosphorus concentration (TP; μg/L) versus dissolved oxygen (DO; mg/L) measured from June to August 2015 inclusive in Willow Creek.

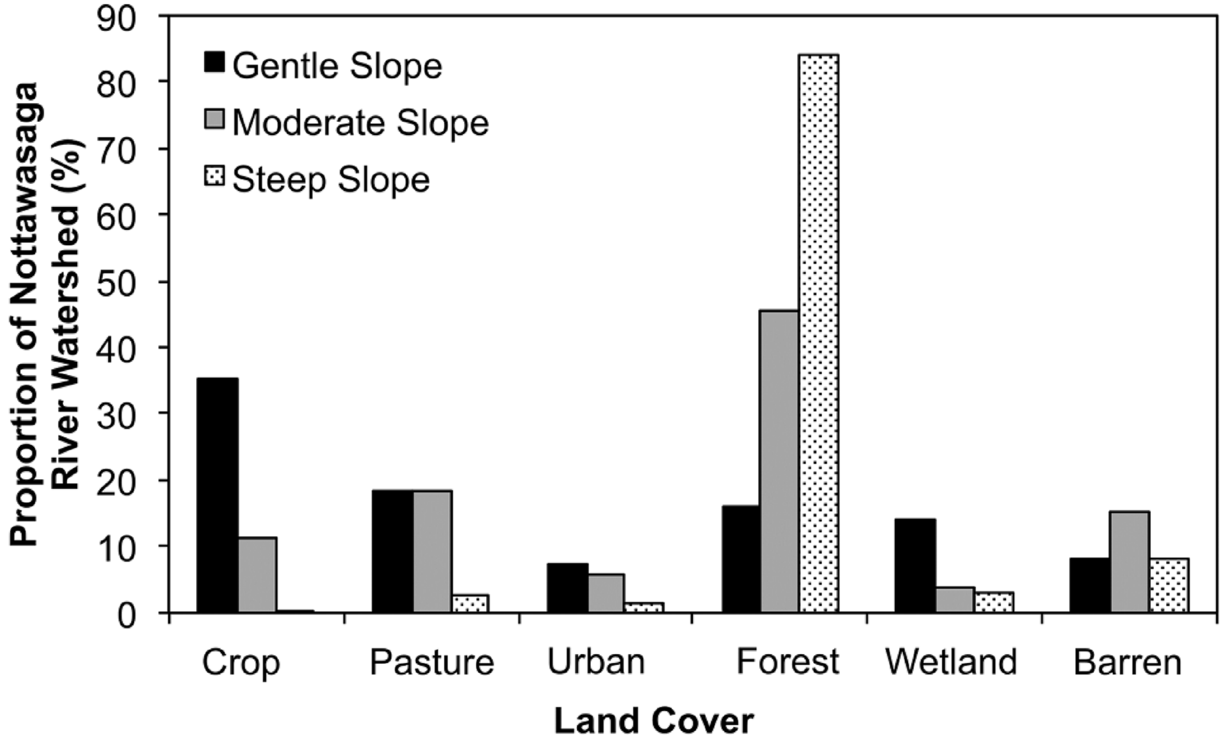

Fig. 5. Proportion of land-cover classes (see Table 4) that exist on gentle (0–5°), moderate (5–16.5°), and steep (> 16.5°) slope classes within the Nottawasaga River watershed.

Table S2), and were associated with the highest daily TP loads (5.55–10.18 kg/day; Supplementary Material, Table S3). By contrast, Bear Creek, with 19% wetland cover in its subwatershed, was associated with a much smaller TP load (0.53 kg/day). It is important to note that Willow Creek, Mad River, and the Mad River breach all drain the Minesing Wetlands complex, whereas Bear Creek does not.

We performed OLS regression models on all possible combinations of independent landscape variables. Three separate models were run with different combinations of predictive landscape variables (Table 3). One model included geomorphic variables only (slope, drainage area, % sandy soils, and % organic soils); a second model included land-cover variables (% crop land, % pasture land, % urban land, % forested land, % wetland, and % barren land); a third model included all landscape variables (i.e. both geomorphic and land-cover variables). These three models were developed for TP and TSS loading rates for a total of six predictive equations (Table 4).

OLS regression analysis identified significant predictive relationships for both TP and TSS for all three models (Table 3). The landscape model explained the greatest amount of variation in TP for the 11 subwatersheds ($r^2 = 0.76$; $AIC_c = 117.5$), and included drainage area ($p < 0.0001$), % wetland ($p = 0.0076$), and % pasture land ($p = 0.0111$) as the most important significant predictive variables. The geomorphic model explained a little less of the overall variation ($r^2 = 0.71$; $AIC_c = 123.7$), with drainage area ($p < 0.0001$), % organic soils ($p = 0.002$), and % sandy soils ($p = 0.0452$) emerging as significant predictive variables. By contrast, the land-cover model explained the least amount of variation ($r^2 = 0.56$; $AIC_c = 134.5$), and included % pasture land ($p < 0.0001$) and % wetland ($p = 0.0308$) as the most significant land-cover variables. In this direct comparison, the combination of geomorphic and land-cover variables together made the best predictive model for TP.

Overall, predictive models for TSS had lower r^2 values compared to predictive models for TP. The geomorphic model explained the greatest amount of variation ($r^2 = 0.67$; $AIC_c = 82.6$), which included drainage area ($p < 0.0001$), % sandy soils ($p = 0.0109$), and % organic soils ($p = 0.0208$) as the most important significant predictive variables. The landscape model only explained slightly less of the variation ($r^2 = 0.65$; $AIC_c = 81.5$), which included drainage area ($p = 0.0002$) and %

Table 2
Summary of linear regression models showing the relationship between a) total phosphorus (TP) and b) total suspended solids (TSS) daily loads and predictor variables.

Dependent variable	Predictor variable	Linear regression equation	r^2	p
a) TP Load (kg/day)	Principal Component 1	Box-cox TP = 1.58 + (0.80 × PC1)	0.46	< 0.0001
	Drainage area (km^2)	Box-cox TP = −1.71 + (0.01 × dArea)	0.59	< 0.0001
	ArcSin % pasture	Box-cox TP = −4.17 + (31.2 × AGP)	0.49	< 0.0001
	ArcSin % wetland	Box-cox TP = −1.31 + (23.7 × WET)	0.22	0.0063
b) TSS Load (kg/day)	Principal component 1	Log TSS = 6.88 + (0.36 × PC1)	0.37	0.0002
	Drainage area (km^2)	Log TSS = 5.26 + (0.0062 × dArea)	0.57	< 0.0001
	ArcSin % pasture	Log TSS = 4.11 + (15.0 × AGP)	0.45	< 0.0001
	ArcSin % wetland	Log TSS = 5.88 + (8.22 × WET)	0.10	0.0688

Table 3
Summary of predictive Ordinary Least Squares regression models based on A) geomorphic B) land-cover and C) landscape variables.

Parameter (kg/day)	Model type	AIC_c	Signif. F	r^2	β_0	Predictor variables	Estimate ± SE	*p*-Value
TP	A)	123.7	< 0.0001	0.71	0.056	dArea	09.44exp-5 ± 1.88exp-5	< 0.0001
						sOrg	25.28 ± 7.46	0.0020
						sSand	−3.40 ± 1.63	0.0452
	B)	134.5	< 0.0001	0.56	−5.25	AGP	27.46 ± 5.62	< 0.0001
						WET	14.56 ± 6.43	0.0308
	C)	117.5	< 0.0001	0.76	−4.96	dArea	08.88exp-5 ± 1.82exp-5	< 0.0001
						WET	13.90 ± 4.84	0.0076
						AGP	13.77 ± 5.08	0.0111
TSS	A)	82.6	< 0.0001	0.67	6.81	dArea	04.87exp-5 ± 1.01exp-5	< 0.0001
						sSand	−2.37 ± 0.87	0.0109
						sOrg	09.78 ± 4.00	0.0208
	B)	91.1	< 0.0001	0.54	3.35	AGP	14.03 ± 2.82	< 0.0001
						FOR	04.55 ± 1.91	0.0239
	C)	81.5	< 0.0001	0.65	4.24	dArea	04.55exp-5 ± 1.08exp-5	0.0002
						AGP	7.92 ± 2.94	0.0115

pasture land ($p = 0.0115$) as the most significant predictors. The land-cover model for TSS explained the least amount of variation ($r^2 = 0.54$; $AIC_c = 91.1$). Land-cover variables that were most important for predicting TSS loads were % pasture land ($p < 0.0001$), and % forested land ($p = 0.0239$). These results indicate that geomorphic and landscape models were better predictors of TSS loading in the NRW than was the model using only land-cover variables.

We regressed measured TP and TSS daily loads against significant predictor landscape variables (Table 2). Drainage area of sub-watersheds was significantly associated with the loading rates of TP ($r^2 = 0.59$; $p < 0.0001$) and TSS ($r^2 = 0.57$; $p < 0.0001$). A strong positive relationship also existed between % pasture land and the loading rates of TP ($r^2 = 0.49$; $p < 0.0001$) and TSS ($r^2 = 0.45$; $p < 0.0001$). % Wetland significantly predicted TP loading ($r^2 = 0.22$; $p = 0.0063$); however, the relationship was not as strong as that of the other two landscape variables. These results indicate that drainage area and pasture land are the main landscape variables driving spatial variability in TP and TSS loading rates among sub-watersheds.

4. Discussion

4.1. Published loading models

In this study, we applied three published approaches (export coefficient, landscape model by Jones et al. (2001), CANWET) to estimate TP and TSS loadings for 11 sub-watersheds of the NRW. Compared to our measured data, all three approaches produced higher annual TP loads, and there was no consistency in how they ranked subwatersheds with respect to loadings. Beaulac and Reckhow (1982) noted that the magnitude of nutrient export from large, mixed agricultural watersheds is difficult to determine because nutrients and sediment from agriculture runoff may be filtered out by vegetation in forest or wetland land cover types. Additionally, agricultural export coefficients encompass numerous practises. This makes it difficult to apply one coefficient across broad spatial scales, and makes comparisons with other watersheds difficult (Beaulac and Reckhow, 1982). The NRW is unique in that it is a mixed agricultural watershed with unique geology and encompasses the Minesing Wetlands. Though the CANWET model was built specifically for the NRW, it used PWQMN station data that did not consider storm flows, or capture influences of the Minesing Wetlands.

These discrepancies point out the inappropriateness of using existing models to produce reliable annual loading estimates for the NRW, and underscore the need for us to create a model specifically for our subwatersheds. In developing our models, we wanted to account for all possible contributions of nutrients from the Minesing Wetlands to the Mad River and Willow Creek subwatersheds. This necessitated sampling the tributaries after they flowed through the Minesing Wetlands, rather than at the PWQMN stations, which are located upstream of the Minesing.

4.2. Watershed specific models

Of the three daily loading models we developed, the landscape model, which incorporated both geomorphic and land-cover variables, was the best predictor for both TP and TSS loading. Drainage area, and proportion of pasture land were the most significant predictors of daily base flow TP and TSS loading rates. Subwatershed area was important because it is directly related to the volume of water that discharges into tributaries, with larger watersheds contributing higher volumes and thus higher loads. This is particularly important following storm events, where loading is amplified (Brezonik and Stadelmann, 2002). We also found that proportion of pasture land in subwatersheds was a significant predictor of nutrient and sediment loading. This is not surprising, since manure contains a very high amount of organic P (Beaulac and Reckhow, 1982), and cattle grazing loosens soil and increases erosion (Dunne et al., 2011). Grazing also compacts soil, which decreases vegetation cover and root structure, thus increasing loading (Menzel et al., 1978; Reckhow et al., 1980).

Watershed geomorphology has a major impact on runoff characteristics and nutrient dynamics (Kalin et al., 2003; Salvia-Castellvi et al., 2005). The effect of slope on runoff has been well documented in the literature (Chen et al., 2001; Fu et al., 2004; Long et al., 2006);

Table 4
Summary of Ordinary Least Squares predictive equations for estimating daily total phosphorus (TP; kg/day) and total suspended solids (TSS; kg/day) loading rates using A) geomorphic B) land-cover and C) landscape models.

	Model	Eq.	Predictive Equation
TP	A)	5	box-cox(TP) = 0.056 + (9.44exp-5 × dArea) + (25.28 × sOrg) – (3.40 × sSand)
	B)	6	box-cox(TP) = −5.25 + (27.46 × AGP) + (14.56 × WET)
	C)	7	box-cox(TP) = −4.96 + (8.88exp-5 × dArea) + (13.9 × WET) + (13.77 × AGP)
TSS	A)	8	Log(TSS) = 6.81 + (4.87exp-5 × dArea) – (2.37 × sSand) + (9.78 × sOrg)
	B)	9	Log(TSS) = 3.35 + (14.03 × AGP) + (4.55 × FOR)
	C)	10	Log(TSS) = 4.24 + (4.55exp-5 × dArea) + (7.92 × AGP)

however, few studies have addressed how the degree of slope can dictate land cover within a watershed. In the NRW, crop land and forests were almost exclusively found in areas with gentle and steep slopes, respectively. Although Fu et al. (2006), reported similar findings, they did not distinguish between crop and pasture land. Our study indicated that compared to crops, pasture land was more evenly distributed between gentle and moderately sloped areas, and were even found on some steeply sloped areas. Since watershed geomorphology is a good predictor of land cover in addition to being a fundamental feature controlling runoff, it is not surprising that the geomorphic models produced good estimates of TP and TSS loading from sub-watersheds. The model suggests that larger sub-watersheds with greater proportions of organic soils, and lower proportions of sandy soils would yield higher loading rates. This is likely because organic soils have limited nutrient retention capacity, and can increase the rate of runoff (Beaulac and Reckhow, 1982). Conversely, sandy soils are more porous and allow water to percolate downwards, which can decrease erosion and allow nutrients to adsorb to soil particles (Beaulac and Reckhow, 1982).

4.3. Impact of the Minesing Wetlands

We found a positive relationship between TP loading and % wetland cover, which was largely driven by Willow Creek, the Mad River, and the Mad River Breach. This was counterintuitive because wetlands are assumed to function as nature's kidneys, filtering out nutrients and sediment from non-point source runoff, which is particularly important for agricultural watersheds (Weller et al., 1996). This positive relationship implies that the Minesing Wetlands are sources rather than sinks of phosphorus, and are no longer able to filter out nutrients and sediments. Fisher and Reddy (2001) found that impaired wetlands, particularly those dominated by agricultural land-use, and that are subjected to prolonged nutrient loading, may be a source of nutrients under certain conditions. This is because excess loading leads to the accumulation of nutrients in wetland soil over time, particularly in the soluble form. Soluble P can be released to the water column under anoxic conditions (0 mg/L DO; Carpenter et al., 1998). We found TP concentrations in Willow Creek rapidly increased when DO reached 0.101 mg/L. This increase in TP appeared to be unrelated to point source pollution, and did not coincide with storm events. We hypothesize that internal loading during anoxic periods was responsible for the spikes in TP recorded in Willow Creek, and we recommend that this hypothesis be properly addressed in future studies of the Minesing Wetlands.

5. Conclusion

Our study identified watershed drainage area and proportion of pasture land as the main drivers of variation in TP and TSS loading within the NRW. Independent of these two variables, subwatersheds that drained through the Minesing Wetlands were also associated with high TP loads, implicating the wetland complex as a major source of nutrients to the Nottawasaga River. Watershed geomorphology was a good predictor of land-cover classes, since steeper slopes coincided with pasture land and forest, while gentle slopes coincided with crop land. These relationships underlie the reasons why geomorphic models made accurate predictions of daily TP and TSS loadings rates. Therefore, if land-cover data (which can be difficult to acquire) were not readily available, geospatial data (drainage area, slope, soil) could be used to estimate TP and TSS loading across subwatersheds. We recognize that our daily base flow predictive models are limited by the fact that tributaries were only sampled in July; however, for the purpose of capturing daily summer base flow loads, we have provided promising models for base-flow loading rates of phosphorus and sediment during the growing season when agricultural practices are most intense. Future studies should be expanded to evaluate annual loading rates to capture seasonality and temporal trends, and should include storm flows for the most accurate loading estimates. Since our study area extended across several subwatersheds with varying landscape features, our loading models should be applicable to other mixed agricultural watersheds, and we recommend that future studies be carried out to validate the usefulness of our models for watersheds in other regions of North America. Due to differences in watershed geomorphology and land cover between regions, the results of our study may only apply to mixed agricultural watersheds in south central Ontario.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2018.12.114.

References

Barton, B.A., 1977. Short-term effects of highway construction on the limnology of a small stream in southern Ontario. Freshw. Biol. 7 (2), 99–108.
Beaulac, M.N., Reckhow, K.H., 1982. An examination of land use – nutrient export relationships. J. Am. Water Resour. Assoc. 18 (6), 1013–1024.
Brezonik, P.L., Stadelmann, T.H., 2002. Analysis and predictive models of stormwater runoff volumes, loads, and pollutant concentrations from watersheds in the Twin Cities metropolitan area, Minnesota, USA. Water Res. 36 (7), 1743–1757.
Brown, C., Cronk, K., Dobbs, F., 2011. Riparian Habitat Restoration Plan and Water Quality Assessment Report for the Lower and Middle Nottawasaga River Reaches. Technical Report No. 100–10–NVCA. Nottawasaga Valley Conservation Authority.
Carpenter, S.R., Caraco, N.F., Correll, D.L., Howarth, R.W., Sharpley, A.N., Smith, V.H., 1998. Nonpoint pollution of surface waters with phosphorus and nitrogen. Ecol. Appl. 8 (3), 559–568.
Chambers, P.A., Dale, A.R., 1997. Contribution of Industrial, Municipal, Agricultural and Groundwater Sources to Nutrient Export, Athabasca, Wapiti and Smoky Rivers, 1980 to 1993. Canada, Edmonton, Alberta Northern River Basins Study Report No. 110.
Chen, L., Messing, I., Zhang, S., Fu, B., Ledin, S., 2003. Land use evaluation and scenario analysis towards sustainable planning on the Loess Plateau in China—case study in a small catchment. Catena 54 (1), 303–316.
Chen, L., Wang, J., Fu, B., Qiu, Y., 2001. Land-use change in a small catchment of northern Loess Plateau, China. Agric. Ecosyst. Environ. 86 (2), 163–172.
Chow-Fraser, P., 2006. A Study of the Water-Quality Conditions in the Innisfil Creek and Nottawasaga River before and after a Summer Storm Event. Technical Report. McMaster University, Hamilton, Ontario, Canada.
Crosbie, B., Chow-Fraser, P., 1999. Percentage land use in the watershed determines the water and sediment quality of 22 marshes in the Great Lakes basin. Can. J. Fish. Aquat. Sci. 56 (10), 1781–1791.
deCatanzaro, R., Chow-Fraser, P., 2011. Effects of landscape variables and season on reference water chemistry of coastal marshes in eastern Georgian Bay. Can. J. Fish. Aquat. Sci. 68 (6), 1009–1023.
Dillon, P.J., Kirchner, W.B., 1975. The effects of geology and land use on the export of phosphorus from watersheds. Water Res. 9, 135–148.
Domagalski, J.L., Ator, S., Coupe, R., McCarthy, K., Lampe, D., Sandstrom, M., Baker, N., 2008. Comparative study of transport processes of nitrogen, phosphorus, and herbicides to streams in five agricultural basins, USA. J. Environ. Qual. 37 (3), 1158–1169.
Dunne, T., Western, D., Dietrich, W.E., 2011. Effects of cattle trampling on vegetation, infiltration, and erosion in a tropical rangeland. J. Arid Environ. 75 (1), 58–69.
Fisher, M.M., Reddy, K.R., 2001. Phosphorus flux from wetland soils affected by long-term nutrient loading. J. Environ. Qual. 30 (1), 261–271.
Fu, B.J., Liu, S.L., Chen, L.D., Lu, Y.H., Qiu, J., 2004. Soil quality regime in relation to land cover and slope position across a highly modified slope landscape. Ecol. Res. 19 (1), 111–118.
Fu, B.J., Zhang, Q.J., Chen, L.D., Zhao, W.W., Gulinck, H., Liu, G.B., Zhu, Y.G., 2006. Temporal change in land use and its relationship to slope degree and soil type in a small catchment on the Loess Plateau of China. Catena 65 (1), 41–48.

Fullen, M.A., 1985. Compaction, hydrological processes and soil erosion on loamy sands in east Shropshire, England. Soil Tillage Res. 6 (1), 17–29.
Greenland International Consulting Ltd, 2006. Assimilative capacity studies: CANWET™ modeling project for Lake Simcoe and Nottawasaga River basins. Technical Report In: Prepared for Lake Simcoe Region Conservation Authority and Nottawasaga Valley Conservation Authority.
Inamdar, S.P., Leary, N.O., Mitchell, M.J., Riley, J.T., 2006. The impact of storm events on solute exports from a glaciated forested watershed in western New York, USA. Hydrol. Process. 20 (16), 3423–3439.
Johnes, P.J., 1996. Evaluation and management of the impact of land use change on the nitrogen and phosphorus load delivered to surface waters: the export coefficient modelling approach. J. Hydrol. 183 (3), 323–349.
Johnes, P.J., Moss, B., Phillips, G., 1996. The determination of total nitrogen and total phosphorus concentrations in freshwaters from land use, stock headage and population data: testing of a model for use in conservation and water quality management. Freshw. Biol. 36, 451–473.
Jones, K.B., Neale, A.C., Nash, M.S., Van Remortel, R.D., Wickham, J.D., Riitters, K.H., O'neill, R.V., 2001. Predicting nutrient and sediment loadings to streams from landscape metrics: a multiple watershed study from the United States Mid-Atlantic Region. Landsc. Ecol. 16 (4), 301–312.
Kalin, L., Govindaraju, R.S., Hantush, M.M., 2003. Effect of geomorphic resolution on modeling of runoff hydrograph and sedimentograph over small watersheds. J. Hydrol. 276, 89–111.
Kang, S., Zhang, L., Song, X., Zhang, S., Liu, X., Liang, Y., Zheng, S., 2001. Runoff and sediment loss responses to rainfall and land use in two agricultural catchments on the Loess Plateau of China. Hydrol. Process. 15 (6), 977–988.
Kotlash, A.R., Chessman, B.C., 1998. Effects of water sample preservation and storage on nitrogen and phosphorus determinations: implications for the use of automated sampling equipment. Water Res. 32 (12), 3731–3737.
Lind, O., 1974. Common Methods in Limnology. Mosby, St. Louis.
Long, H.L., Heilig, G.K., Wang, J., Li, X.B., Luo, M., Wu, X.Q., Zhang, M., 2006. Land use and soil erosion in the upper reaches of the Yangtze River: some socio-economic considerations on China's Grain-for-Green Programme. Land Degrad. Dev. 17 (6), 589–603.
Matson, P.A., Parton, W.J., Power, A.G., Swift, M.J., 1997. Agricultural intensification and ecosystem properties. Science 277 (5325), 504–509.
Mattikalli, N.M., Richards, K.S., 1996. Estimation of surface water quality changes in response to land use change: application of the export coefficient model using remote sensing and geographical information system. J. Environ. Manag. 48 (3), 263–282.
McDowell, R.W., Sharpley, A.N., 2003. Uptake and release of phosphorus from overland flow in a stream environment. J. Environ. Qual. 32 (3), 937–948.
Menzel, R.G., Rhoades, E.D., Olness, A.E., Smith, S.J., 1978. Variability of annual nutrient and sediment discharges in runoff from Oklahoma cropland and rangeland. J. Environ. Qual. 7 (3), 401–406.
Murphy, J., Riley, J., 1962. A modified single solution method for the determination of phosphate in natural waters. Anal. Chim. Acta 27, 31–36.
Oda, T., Ohte, N., Suzuki, M., 2011. Importance of frequent storm flow data for evaluating changes in stream water chemistry following clear-cutting in Japanese headwater catchments. For. Ecol. Manage. 262 (7), 1305–1317.
Ontario Ministry of Natural Resources and Forestry, 2008. County of Simcoe, Muskoka and Dufferin Orthophotography Project. available through Land Information Ontario.
Ontario Ministry of Natural Resources and Forestry, 2013. Provincial Digital Elevation Model (PDEM). available through Land Information Ontario.
Pan, D., Kong, F., Zhang, N., Ying, R., 2017. Knowledge training and the change of fertilizer use intensity: Evidence from wheat farmers in China. J. Environ. Manage. 197, 130–139.
Pilgrim, D.H., Cordery, I., Baron, B.C., 1982. Effects of catchment size on runoff relationships. J. Hydrol. 58 (3–4), 205–221.
Poor, C.J., McDonnell, J.J., 2007. The effects of land use on stream nitrate dynamics. J. Hydrol. 332 (1), 54–68.
Ramsar Sites Information Service, 1996. Minesing Swamp, Ontario: Information Sheet on Ramsar Wetlands. Ramsar Convention, Glands, Switzerland. https://rsis.ramsar.org/RISapp/files/RISrep/CA865RISformer1996_EN.pdf, Accessed date: 14 July 2016.
R Core Team, 2015. R: a Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria.
Reckhow, K.H., Beaulac, M.N., Simpson, J.T., 1980. Modeling Phosphorus Loading and Lake Response under Uncertainty: a Manual and Compilation of Export Coefficients. United States Environmental Protection Agency, Washington.
Rezaei, M., Valipour, M., Valipour, M., 2016. Modelling evapotranspiration to increase the accuracy of the estimations based on the climatic parameters. Water Conserv. Sci. Eng. 1 (3), 197–207.
Rootham, P.B.S., Featherstone, D., 2014. 60 Years of Forest Change in the Minesing Wetlands (1953-2013): Causal Factors, Ecological Implications and recommendations for Reforestation. (Technical Report, prepared by NVCA).
Rutledge, J.M., Narini, M., Kirkwood, A., Duval, T., Chow-Fraser, P., 2015. Land-use Effects on Nutrient and Algae in the Middle and Lower Nottawasaga River and the Minesing Wetlands. Technical Report. prepared for Environment Canada.
Salvia-Castellvi, M., Iffly, J.F., Vander Borght, P., Hoffman, L., 2005. Dissolved and particulate nutrient export from rural catchments: a case study from Luxembourg. Sci. Total Environ. 344 (1–3), 51–65.
Seilheimer, T.S., Wei, A., Chow-Fraser, P., Eyles, N., 2007. Impact of urbanization on the water quality, fish habitat, and fish community of a Lake Ontario marsh, Frenchman's Bay. Urban Ecosyst. 10 (3), 299–319.
Sharara, M., Sampat, A., Good, L.W., Smith, A.S., Porter, P., Zavala, V.M., Runge, T., 2017. Spatially explicit methodology for coordinated manure management in shared watersheds. J. Environ. Manag. 192, 48–56.
Shelton, L.R., 1997. Field Guide for Collecting Samples for Analysis of Volatile Organic Compounds in Stream Water for the National Water-Quality Assessment Program. U.S. Geological Survey Open-File Report. USGS Sacramento, California.
Sicat, R.S., Carranza, E.J.M., Nidumolu, U.B., 2005. Fuzzy modeling of farmers' knowledge for land suitability classification. Agr. Syst. 83 (1), 49–75.
Smith, V.H., 2003. Eutrophication of freshwater and coastal marine ecosystems: a global problem. Environ. Sci. Pollut. Res. 10 (2), 126–139.
Soranno, P.A., Hubler, S.L., Carpenter, S.R., Lathrop, R.C., 1996. Phosphorus loads to surface waters: a simple model to account for spatial pattern of land use. Ecol. Appl. 6 (3), 865–878.
Stanfield, L. (Ed.), 2010. Ontario Stream Assessment Protocol, Version 8.0. Technical Report. Ontario Ministry of Natural Resources and Forestry, Peterborough.
Taylor, S.D., He, Y., Hiscock, K.M., 2016. Modelling the impacts of agricultural management practices on river water quality in Eastern England. J. Environ. Manag. 180, 147–163.
Tong, S.T., Chen, W., 2002. Modeling the relationship between land use and surface water quality. J. Environ. Manag. 66 (4), 377–393.
T-Prairie, Y., Kalff, J., 1986. Effect of catchment size on phosphorus export. J. Am. Water Resour. As. 22 (3), 465–470.
Valipour, M., 2016a. How much meteorological information is necessary to achieve reliable accuracy for rainfall estimations? Agriculture 6 (4), 53.
Valipour, M., 2016b. Variations of land use and for next decades under different scenarios. IRRIGA 1 (1), 262–288.
Valipour, M., Banihabib, M.E., Behbahani, S.M.R., 2013. Comparison of the ARMA, ARIMA, and the autoregressive artificial neural network models in forecasting the monthly inflow of Dez dam reservoir. J. Hydrol. 476, 433–441.
Valipour, M., Sefidkouhi, M.A.G., Raeini, M., 2017. Selecting the best model to estimate potential evapotranspiration with respect to climate change and magnitudes of extreme events. Agric. Water Manag. 180, 50–60.
Van Vliet, L.J.P., Hall, J.W., 1991. Effects of two crop rotations on seasonal runoff and soil loss in the Peace River region. Can. J. Soil. Sci. 71, 533–544.
Weller, C.M., Watzin, M.C., Wang, D., 1996. Role of wetlands in reducing phosphorus loading to surface water in eight watersheds in the Lake Champlain Basin. Environ. Manag. 20 (5), 731–739.
Winter, J.G., Duthie, H.C., 2000. Export coefficient modeling to assess phosphorus loading in an urban watershed. J. Am. Water Resour. Assoc. 36 (5), 1053–1061.