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APPLIED ISSUES

Effects of hydrogeomorphic region, catchment storage and mature forest on baseflow and snowmelt stream water quality in second-order Lake Superior Basin tributaries

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SUMMARY

1. In this study we predict stream sensitivity to non-point source pollution based on the non-linear responses of hydrological regimes and associated loadings of non-point source pollutants to catchment properties. We assessed two hydrologically based thresholds of impairment, one for catchment storage (5–10%) and one for mature forest (<50% versus >60% of catchment in mature forest cover) across two different hydrogeomorphic regions within the Northern Lakes and Forest (NLF) ecoregion: the North Shore [predominantly within the North Shore Highlands Ecological Unit] and the South Shore (predominantly within the Lake Superior Clay Plain Ecological Unit). Water quality samples were collected and analysed during peak snowmelt and baseflow conditions from 24 second-order streams grouped as follows: three in each region × catchment storage × mature forest class.

2. Water quality was affected by a combination of regional influences, catchment storage and mature forest. Regional differences were significant for suspended solids, phosphorus, nitrogen: phosphorus ratios, dissolved organic carbon (DOC) and alkalinity. Catchment storage was significantly correlated with dissolved silica during the early to mid-growing season, and with DOC, specific conductance and alkalinity during all seasons. Total nitrogen and dissolved nitrogen were consistently less in low mature forest than in high mature forest catchments. Catchment storage interacted with the influence of mature forest for only two metrics: colour and the soluble inorganic nitrogen : phosphorus ratio.

3. Significant interaction terms (region by mature forest or region by storage) suggest differences in regional sensitivity for conductance, alkalinity, total organic carbon, and colour, as well as possible shifts in thresholds of impact across region or mature forest class.

4. Use of the NLF Ecoregion alone as a basis for setting regional water quality criteria would lead to the misinterpretation of reference condition and assessment of condition. There were pronounced differences in background water quality between the North and South Shore streams, particularly for parameters related to differences in soil parent material and glacial history. A stratified random sampling design for baseflow and

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snowmelt stream water quality based on both hydrogeomorphic region and catchment attributes improves assessments of both reference condition and differences in regional sensitivity.

Keywords: catchment, classification, Lake Superior, tributaries, water quality

Introduction

Existing catchment and landscape classification schemes can be characterised as either geographically dependent (e.g. Omernik & Gallant, 1988; Maxwell *et al*., 1995) or geographically independent (Detenbeck *et al*., 2000). Geographically dependent classification schemes have categories that describe specific places or regions; often a category in such a classification scheme contains only one geographical place. These strata tend to cover broad geographical regions at a predetermined scale or nested scales. Geographically independent schemes have categories that can describe similar features occurring at many locations and are not limited to a specific scale, place or region. Both geographically dependent and independent schemes can be either non-hierarchical or hierarchical in nature, lending themselves to management issues that must be addressed at different scales.

Classification systems have been used primarily for inventory purposes, for stratifying landscapes prior to characterisation of reference condition or assessment of regional condition, and for facilitating communication with natural resource managers and the public (Omernik & Gallant, 1988; Heiskary & Wilson, 1990; Herlihy *et al*., 2000; Pan *et al*., 2000; Waite *et al*., 2000). However, it is not known whether these classification systems can explain differences in vulnerability to stressors across aquatic ecosystems.

Catchment properties and surface-water hydrogeological types can be used to classify lakes or streams according to relative risk of impact. These approaches commonly use multivariate statistical analysis to explain differences in sensitivity after monitoring has already been conducted (Momen & Zehr, 1998). Classification schemes can also be developed *a priori* (Huang & Ferng, 1990).

Here we propose an approach to predict stream sensitivity to non-point source pollution based on the non-linear responses of hydrological regimes and associated loadings of non-point source pollutants to catchment properties (Richards, 1990; Jennings, Thomas & Riggs, 1993). Selected hydrological thresholds are related (1) to natural variation or altered levels of catchment storage, defined as the fraction of catchment area covered by lakes and wetlands and (2) to land-use activities affecting runoff and, thus, the hydrological regime. Here we define a hydrological threshold as a breakpoint or inflection point in a non-linear relationship between a catchment property and hydrological response variable such as peak flows. The United States Geological Survey has defined a series of empirical non-linear equations relating catchment properties such as catchment area, channel slope, catchment storage and land-use (percentage of forested, urbanisation or impervious surface area) to peak flows of given recurrence intervals (Q2, Q_5,…, Q_{100}; Jennings *et al*., 1993). When peak flows per unit catchment area are plotted as a function of catchment storage, a non-linear response is shown, with peak flows increasing exponentially as catchment storage decreases below a given threshold. For north-western Wisconsin and north-eastern Minnesota, the critical thresholds appear to be between 5 and 10% catchment storage (Krug, Conger & Gebert, 1992; Jacques & Lorenz, 1988). A second threshold, for peak snowmelt related to forest fragmentation from logging or other land-clearing activity, has been predicted to occur after 50–60% of a catchment logged within the last 15 years (Verry, 1976).

Our development of landscape classification schemes links geographically and structurally based schemes (e.g. ecoregions and Ecological Units) with functional (flow-regime) classification schemes that can be related to ecological susceptibility. In our initial demonstration project, we assess two hydrologically based thresholds of impairment, one for catchment storage (≤5% versus ≥10%) and one for mature forest coverage (≤50% versus ≥60% of catchment in mature forest cover) across two different hydrogeomorphic regions within the Northern Lakes and Forest (NLF) Ecoregion, i.e. the North Shore Highlands (NSH) Ecological Unit and the Lake Superior Clay Plain (LSCP) Ecological Unit (Maxwell *et al*., 1995). In 1997–98, we selected 24 second-order stream catchments (Strahler, 1964) to establish a three-way factorial design. Within each region, we classified catchment by catchment storage and mature forest classes (above and below threshold ranges). We examined the following endpoints: hydrological regime (e.g. indicators of stream flashiness), thermal regime, baseflow water quality, sediment and nutrient loadings, habitat structure, and algal, macroinvertebrate and fish communities. In this initial analysis, we describe the utility of our classification framework for explaining variation in water quality of second-order streams in the Lake Superior Basin during baseflow and snowmelt conditions.

We hypothesise that catchments with less mature forest will have more unpredictable stream flows, increased water temperatures, greater suspended sediment loads and greater nutrient export. Furthermore, catchment storage will mediate effects of loss of mature forest cover on aquatic community structure and function, sedimentation rates, discharge rates and nutrient retention. Our design also allows us to examine potential interactions between geographical regions at the scale of ecological units and catchment storage or mature forest cover effects to determine if thresholds differ among regions.

Methods

Study region

Our target population included second-order catchments overlapping with the North Shore [Hydrological cataloging units (HUCs) 4010101 and 4010102] and the South Shore (HUC 4010301) of the western arm of Lake Superior. North Shore catchments were located predominantly within the NSH while South Shore catchments were located predominantly within the LSCP Ecological Units, as defined by Keys *et al.* (1995). These catchments also overlapped with the Mille Lacs Uplands and Bayfield Sand Plains Ecological Units on the South Shore; thus we refer to the two hydrogeomorphic regions of interest as North and South Shore regions. All of these Ecological Units are contained within the single NLF Ecoregion (Omernik & Gallant, 1988; Fig. 1).

The NSH is characterised by low mountains, with an altitude range of 366–610 m above mean sea level. Underlying bedrock is a complex of Precambrian volcanic rock and the Duluth Complex (gabbroic anorthosite, troctolite, gabbro, anorthosite and felsic rocks). Unconsolidated glacial sediments in overlying ground and end moraines consist of red to brown sandy and stony till, with occasional outwash deposits of sand and gravel and red silty to clayey lake deposits. Most of the rivers in this area are relatively short (mean = 36 km length), have relatively small catchments (60–1580 km^2) and steep gradients (range: 4.0–17.1 m km^{-1}, average = 10.8 m km^{-1}) from headwaters to mouth, with steepest gradients in the lowest reaches 4.8–8.0 km directly upstream from Lake Superior. Wetlands, including forested, emergent and bog wetlands, are more common in the headwaters than in the steep, rocky lower reaches of the rivers. Thin soils and relatively impermeable bedrock provide relatively little groundwater storage, but surface water storage can be expected to moderate both extreme high and low flows (Olcott *et al.*, 1978; Keys *et al.*, 1995).

The LSCP is dominated by a relatively flat lake plain formed on thick deposits of red clay, with thin lenses of silt and sand. South of an escarpment along the boundary of the lake plain lie glacial sediments, primarily end moraine (till, stratified sand and gravel) with smaller areas of ground moraine and pitted outwash (stratified sand and gravel). The Bayfield Ridge comprising the inland portion of the Bayfield Peninsula, consists of thick end moraines and pitted outwash, forming knob-and-kettle topography, with sediments dominated by red sandy to clayey till and stratified deposits of sand and gravel in areas of end moraine, and stratified sand and gravel within outwash zones. Bedrock within the study area is Precambrian in origin, consisting mainly of sandstone, shale and conglomerate in the central and north-west portions, with some lava flows (mainly basalt and andesite) exposed by uplifting in the south-west portion of the basin (Young & Skinner, 1974).

Soil permeability varies significantly across the South Shore. Areas of highest permeability (>6.4 cm hr^{-1}) are found on outwash and end moraine on the Bayfield Ridge, while areas of moderate permeability (2–6.4 cm hr^{-1}) dominate in the southern deposits of end moraine. Soils of low permeability (<2 cm hr^{-1}), consisting of mainly silty clay loams and loams, have developed over the lake clay deposits. The LSCP contains a dense stream drainage network of predominantly first- to second-order streams, but almost no lakes (Keys *et al.*, 1995). South Shore streams have lower gradients than the rivers along North Shore of Minnesota.

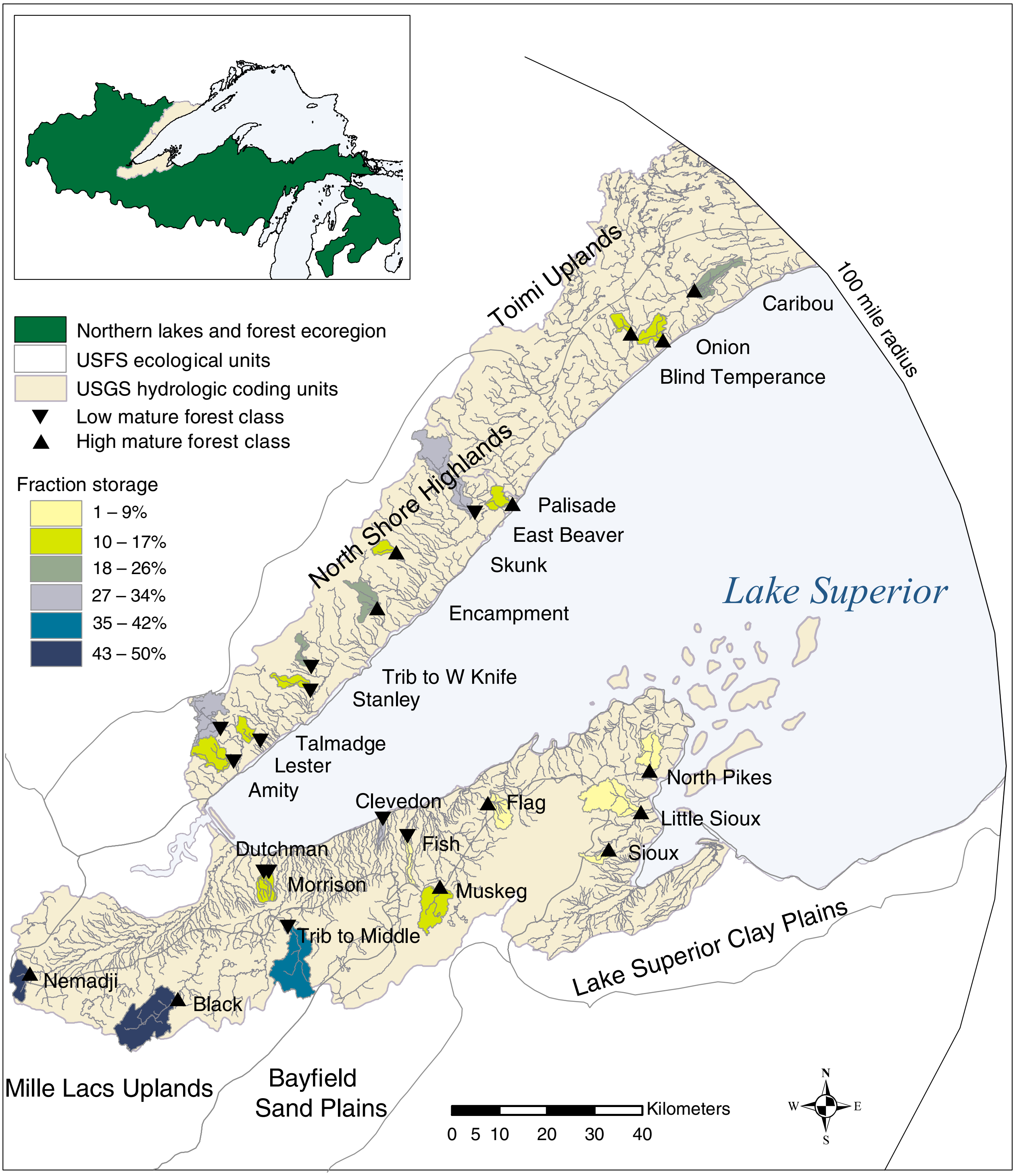

Fig. 1 Location and catchment characteristics associated with 24 second-order study streams surrounding the western arm of Lake Superior.

Average annual precipitation for the North Shore (1941–70) is 71.1 cm (range: 66–76 cm), with approximately 35% lost as stream runoff and 65% lost as evapotranspiration. Average annual precipitation for the South Shore overall is 78.7 cm (range: 71–78.7 cm), increasing inland and to the east within the study region. Runoff averages 32.5 cm, or 45% of average annual precipitation, but is lower on the Bayfield Ridge. Low flow runoff patterns are consistent with surficial geology, with very low flows (<0.29 cfs mil^{-2}) for most of the lake plain and moderate to high (0.3 to >0.99 cfs mil^{-2}) in areas of thick outwash and end moraine.

Second-order catchment site selection

We delineated catchments of all second-order streams within the three HUCs on the North and South Shores: 4010101, 4010102, and 4010301. Stream order was defined using US Environmental Protection Agency (EPA) Reach III files (1 : 100 000) as a base coverage and topographical maps at a scale of 1 : 24 000 to define drainage boundaries. Within each hydrogeomorphic unit (North Shore versus South Shore), we selected catchments randomly within high versus low catchment storage classes (less than and greater than 10% storage area as lakes + wetlands) and within either high or low mature forest based on the percentage of mature forest (≤50% versus ≥60%) and intensity of recent logging activity over the last 15 years. We assessed the percentage of mature forest and recent logging activity based on ARC/INFO coverages derived from classified Thematic Mapper and Multi-Spectral Scanner imagery from the late 1980s (Wolter *et al.*, 1995). We calculated catchment storage based on wetland and lake coverages in the National Wetlands Inventory for Minnesota and the Wisconsin Wetland Inventory (WI DNR, 1990–2000; US FWS, 1992–98). We supplemented estimates of recent logging activity with logging file data spatially referenced by township/range/section for the Superior National Forest (Terry Gokee, personal communication) and an ARC/INFO rural land-use coverage generated from 1992 aerial photography by the state of Wisconsin (WI DNR, 1998). From within the population of all accessible second-order catchments, we randomly selected three from each of eight classes to yield a balanced factorial design with two levels of each of three factors: hydrogeomorphic region, catchment storage and mature forest (Fig. 1). We selected representative study reaches within each catchment based on existing access points by road or trails and re-delineated basins to the base of study reaches and re-characterised catchments. In some cases, catchment categories shifted from original designations, particularly as improved land-cover data became available (e.g. Nemadji River Basin). Data were eventually analysed using ANCOVA with catchment storage as a covariate, rather than simple ANOVA.

Sampling methods

We sampled second-order streams monthly during mid- to late-summer 1997 (July to August) and during peak snowmelt (March) until mid-summer (June) in 1998, using Environmental Monitoring and Assessment Program protocols (Lazorchak, Klemm & Peck, 1998). We measured in-stream temperature, pH, dissolved oxygen, conductance and turbidity with Hydrolab© DataSonde3 multiprobe instruments (Hydrolab-Hach Co., Loveland, CO, USA) both during sample collection and diurnally in midsummer at 1-h intervals over 24–48 periods.

Analytical methods

Samples were kept at 4 °C during the day, split and filtered within 12 h and preserved by freezing (nutrients), addition of HNO_3 (cations) or H_3PO_4 (organic carbon), or by refrigeration at 4 °C (suspended solids, physical parameters). Turbidity was measured in the laboratory within 48 h with a Hach 2100AN turbidimeter, Hach Co., Loveland, CO, USA.

Total and volatile suspended solids were filtered onto Whatman GF/C (Whatman Int., Kent, UK) filters following EPA Methods 160.2, 160.4 (US EPA, 1983) and Standard Methods (APHA, 1992). Gran alkalinity was measured using a Mettler DL70 ES automatic titrator system (Mettler-Toledo Int., Columbus, OH, USA). Apparent colour was measured using a Perkin Elmer Lambda 2S UV/Vis Spectrometer (Perkin Elmer Corp., Norwalk, CT, U.S.A.; Buffle *et al.*, 1982) and platinum cobalt solution standards.

Dissolved and total phosphorous and nitrogen samples were digested prior to analysis (Ebina, Tsutsui & Shirai, 1983). Phosphate levels in digested and undigested samples were measured following Standard Methods (APHA, 1992) using a Perkin Elmer UV/Vis Spectrometer. Nitrate + nitrite and digestates from dissolved nitrogen (DN) and total nitrogen (TN) analysis were analysed on an automated ion analyser (Lachat Instruments, 1988; QuikChem Method 10-107-04-1-O), ammonium

(QuikChem Method 10-107-06-1-F) and silica (QuikChem Method 10-114-27-1-A). Dissolved and total organic carbon (TOC) were analysed on a Dohrmann DC190 carbon analyser (Tekmar-Dohrmann, Cincinnati, OH, U.S.A.; EPA Method 415.1).

Data analysis/statistical methods

We analysed water quality parameters using repeated measures analysis of variance with PROC GLM in SAS© (SAS, 1990), and tested model assumptions using Bartlett's test (homogeneity of variance), Wilk–Shapiro test (normality of residuals) and Mauchly's Criterion (test for sphericity). Variables were $\log_{10}$-transformed where necessary to meet model assumptions. Experiment-wise type I errors were controlled by Bonferroni's correction to α-values (0.05) for individual tests. We first analysed data for each water quality parameter representing a 'total constituent' (e.g. total suspended solids, total phosphorus) using a P-value of α/n_1, where n_1 = total number of initial repeated measures ANOVAS. For significant treatment effects, we then analysed data for the n_2 sub-constituents or correlated parameters [e.g. total dissolved phosphorus (DP) and soluble reactive phosphorus (SRP)] using a P-value of α/n_2.

Results

Catchment characteristics

The catchments selected in the stratified random design have a more restricted range of some properties than exists in the study area, but median values for sample catchments are representative (Table 1). Purposeful selection of catchments from both high and low storage categories creates a set of sample catchments with higher median fraction storage in South Shore catchments and lower median fraction storage in North Shore catchments than in the full population of second-order catchments in each region. Median fraction mature forest is lower in the sample catchments than in the full population.

North and South Shore study catchments are similar in catchment area (median = 2000–2400 ha), but channel gradient tends to be greater in North Shore systems and soils in North Shore catchments are predominantly well-drained as compared with an even distribution across drainage classes in South Shore catchments (Table 1). Although the median and range of agricultural land in all South Shore catchments are higher than in North Shore catchments, these regional differences are smaller for sample catchments.

Precipitation and flow regime differences across years

The maximum snowpack during the winter of 1996–97 was above average, exceeding 100 cm in depth, as compared with a below-average maximum snowpack (50 cm) during the winter of 1997–98. Site set-up and sampling was initiated in early to mid-July in 1997, just after a major summer storm event of 7 cm recorded at the Duluth Airport, but subsequent major rainfall events over the growing seasons of 1997 and 1998 were relatively infrequent. The cumulative

Table 1 Median and range of important regional and study site catchment properties for second order streams as defined by Strahler (1964)

	Regional catchments				Study site catchments			
	North Shore second-order (n = 110)		South Shore second-order (n = 242)		North Shore second-order (n = 12)		South Shore second-order (n = 12)	
	Range	Median	Range	Median	Range	Median	Range	Median
Area (ha)	220–9600	1800	160–30 000	1200	1000–7300	2000	670–9700	2400
Channel gradient (m km^{-1})	2.0–105	9.60	0.3–70	7.10	3.7–26	11.0	0.9–30	6.9
Poorly drained soils (%)	7–60	30	10–74	33	15–41	32	25–73	29
Well-drained soils (%)	26–84	61	0–79	27	26–72	60	2–51	40
Mature forest (%)	38–92	67	12–97	55	26–81	48	36–88	43
Storage (%)	1–50	21	0–73	7	10–34	15	1–50	13
Developed land (%)	0–26	1	0–13	1	0–5	1	0–5	1
Agricultural land (%)	0–29	0	0–97	11	0–10	2	1–27	6

annual rainfall recorded for 1997 was only 53 cm at the Duluth Airport, well below the long-range North and South Shore averages of 71 and 79 cm, respectively, while the cumulative annual rainfall recorded for 1998 of 80 cm was just above average.

Dissolved oxygen and temperature regimes

Baseflow or snowmelt temperature records from single hydrolab measurements are complete only for July–August 1997, snowmelt 1998 and June 1998. Over these time periods, time × region interaction effects were detected. No significant regional or treatment differences in baseflow dissolved oxygen levels were detected ($P > 0.007$; Table 2).

Major ion chemistry

Overall, there was a significant effect of storage on specific conductance, as well as a significant region × mature forest interaction (Table 2). Similarly, there was a region × mature forest effect on alkalinity, as well as significant effects of storage and region which vary over time. Alkalinity tended to increase with catchment storage (Fig. 2). Time × region effects and storage effects on pH are generally consistent with effects on alkalinity.

Particulates, carbon and apparent water colour

Total suspended solids vary significantly over time (Fig. 3). Total suspended solids are greater in South Shore systems, with values peaking during snowmelt and differences most accentuated during spring to early summer. Turbidity is affected by a region × mature forest interaction, with highest seasonal values occurring in low mature forest systems on the South Shore and slightly elevated values in high mature forest systems on the North Shore (Table 2). In contrast, time and region effects are significant but independent for organic suspended solids. Organic suspended solids are highest during snowmelt and mid- to late-summer periods and overall, tend to be greater in South Shore systems.

Table 2 Summary of results of repeated measures ANCOVA (Regional Class × Mature Forest Class × Catchment Storage Covariate) on snowmelt and baseflow water quality parameters in second-order streams in the western arm of Lake Superior. Letters indicate significant main effect (H, S, F), two- or three-way interaction of main effects (H × S, H × F, S × F), or interaction of main effects with time (*T*). To apply Bonferroni's correction, $\alpha = 0.05/n$ where n is the number of multiple tests of summary parameter for each variable group (TSS, TP, TN, Si, TOC, conductivity) or of multiple tests within each category of parameters

			Catchment attributes			Region × catchment attribute interactions		
Parameter	Time (*T*)	Region HGM (H)	Storage (S)	Mature forest (F)	F × S	H × F	H × S	H × S × F
Total suspended solids	*T**	H*						
Volatile suspended solids	*T****	H*						
Turbidity	*T**	H***				H × F**		H × S × F**
Total phosphorus	*T****	H*						
Particulate phosphorus	*T****							
Dissolved phosphorus	*T***	H***						
Soluble reactive phosphorus		H***						
Total nitrogen	*T***			F***				
Dissolved nitrogen			S*	F*				
Total N : P	*T***	H***	S**	F*				
Inorganic N : P					*T* × F × S*			
Silica	*T****		*T* × S***					
Total organic carbon							*T* × F × S*	
Dissolved organic carbon		H*	S*					
Colour	*T****				F × S**		H × S*	
Specific conductivity			S***			H × F**		
Gran alkalinity		*T* × H**	*T* × S**			H × F**		
Temperature	*T****	*T* × H**						

$*P < 0.05$, $**P < 0.01$, $***P < 0.001$; HGM, Hydrogeomorphic Region.

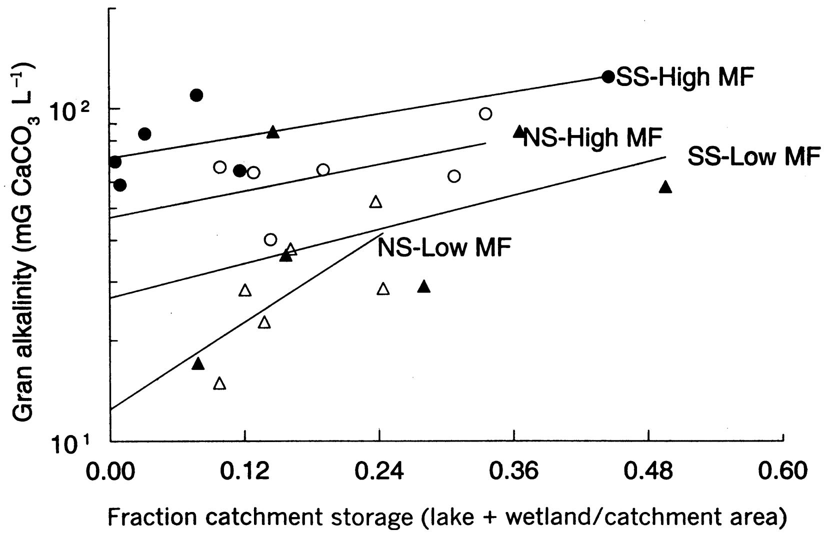

Fig. 2 Results of repeated measures ANCOVA showing one of seven time periods. Region × mature forest interaction ($n = 23$, $P_{\text{April}} = 0.005$) and catchment storage effect ($n = 23$, $P_{\text{April}} = 0.0003$) for Gran alkalinity in 24 second-order North and South Shore streams, April 1998. (Δ) North Shore low mature forest, (▲) South Shore low mature forest, (○) North Shore high mature forest, (●) South Shore high mature forest.

The TOC is significantly affected by time × region × storage interactions; however, snowmelt samples show no significant region and storage effects. Dissolved organic carbon (DOC) is significantly affected (independently) by region and catchment storage. Overall, least square means for DOC are higher for South Shore streams than North Shore streams and DOC increases with fraction storage for all systems.

Apparent colour is significantly affected by time period and by mature forest × storage and region × storage interactions. During all sample periods except for snowmelt, colour tends to increase with catchment storage. However, colour increases as a function of catchment storage more rapidly for South Shore than North Shore streams and for catchments with a high degree of mature forest for both regions (Fig. 4a,b).

Nutrients

In general, regional effects on total phosphorus are consistent with effects on total suspended solids, with greater suspended solids and phosphorus values in South Shore streams. Regional effects on total DP and SRP are significant.

Unlike phosphorus (P), neither TN nor organic or inorganic nitrogen constituents vary significantly amongst regions. However, TN and DN are consistently lower in low mature forest catchments; mature forest effects on nitrate + nitrite are not detectable (Fig. 5).

Total N : P ratios are greater in North Shore streams as a result of regional differences in total P concentrations and are greater in low mature forest catchments, which is consistent with effects on TN

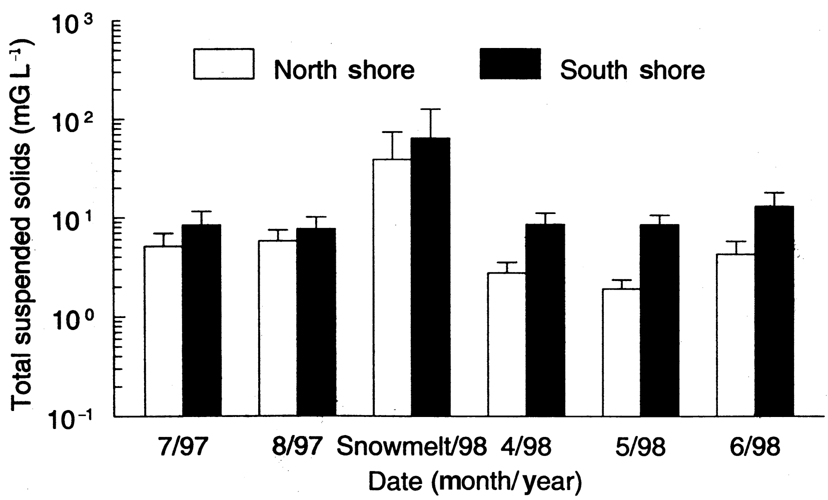

Fig. 3 Results for repeated measures ANCOVA. Region effects on total suspended solids (mg L^{-1}) in North versus South Shore streams ($n = 24$, $P = 0.008$). Total suspended solid is higher overall in South Shore streams, particularly during higher flows.

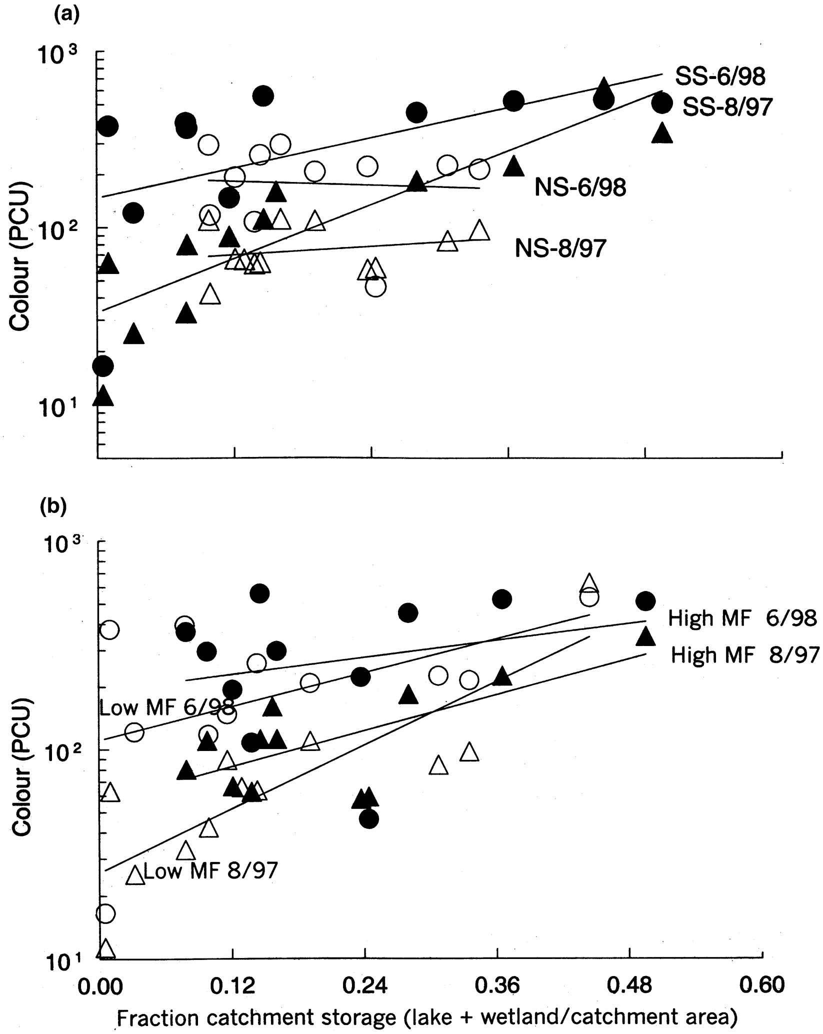

Fig. 4 Results of repeated measures ANCOVA showing two of seven time periods. Effects on apparent colour (PCU) in 24 second-order streams related to: (a) region × catchment storage interactions [$P = 0.02$, June 1998: (○) North Shore, (●) South Shore; August 1997: (Δ) North Shore, (▲) South Shore] and (b) mature forest × catchment storage [$P = 0.003$, June 1998: (○) Low mature forest, (●) High mature forest; August 1997: (Δ) Low mature forest, (▲) High mature forest]. Colour is more sensitive to fraction catchment storage in South Shore catchments and in low mature forest catchments. Graphs show partial residuals after second effect is removed.

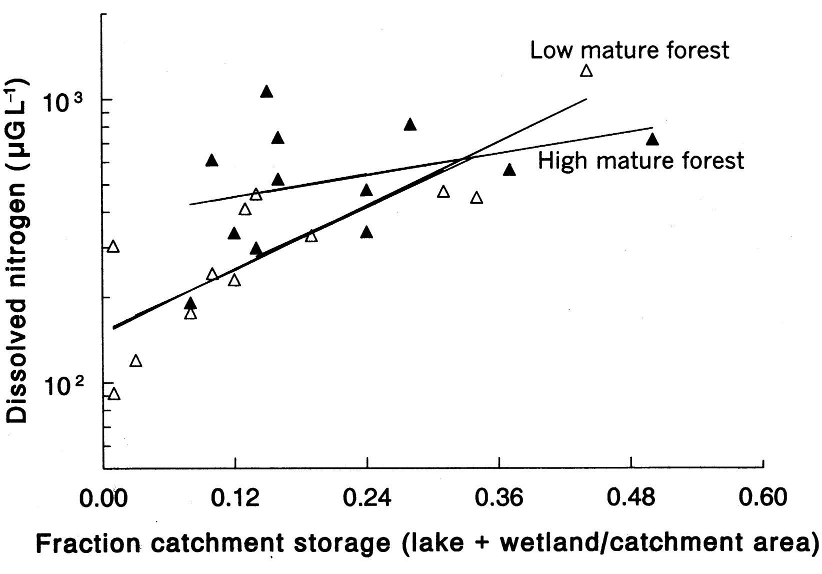

Fig. 5 Results for repeated measures ANCOVA. Effect of level of mature forest ($P = 0.017$) and catchment storage ($P = 0.013$) on dissolved nitrogen (N) (μN per litre) in 24 second-order streams. Dissolved N is higher in high mature forest catchments independent of catchment storage, but increases with fraction storage for both mature forest classes. [(Δ) Low mature forest, (▲) High mature forest].

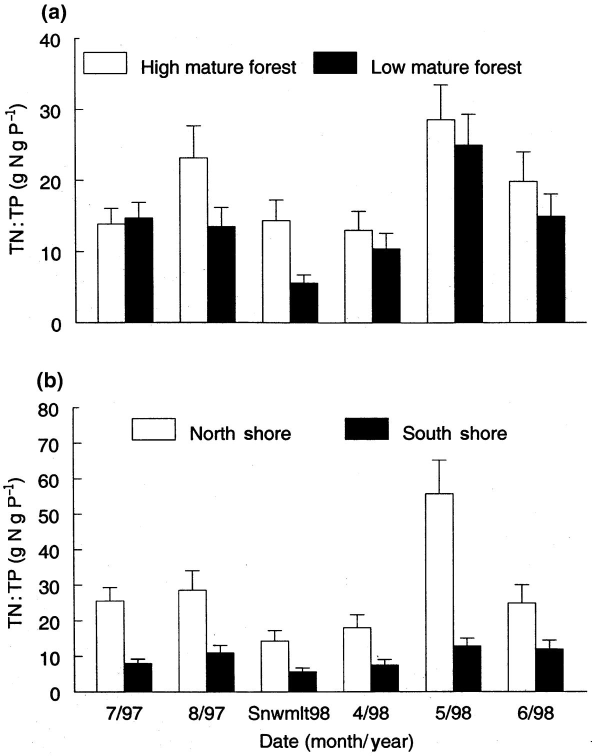

Fig. 6 Results for repeated measures ANCOVA. Effects of time ($P = 0.001$) and (a) mature forest ($P = 0.03$) and (b) hydrogeomorphic region ($P = 0.0001$) on total N : P ratios (gN : gP) in 24 second-order streams. Plots show least square means.

(Fig. 6a,b). In contrast, the ratio of dissolved inorganic nitrogen (DIN): soluble reactive P shows a significant time × mature forest × storage interaction. During summer months (August 1997, May–June 1998), the ratio of DIN : SRP declines as a function of catchment storage for high mature forest catchments (Fig. 7a), but not for low mature forest catchments (Table 2). Unlike other major nutrients, dissolved silica demonstrates a significant time × storage interaction; dissolved silica decreases with fraction catchment storage during spring and summer months (April–June, Fig. 7b).

Discussion

Regional effects

Regional differences in (background) phosphorus concentrations between the North and South Shore streams are consistent with higher mean export coefficients reported for forested catchments underlain by sedimentary bedrock (10.7 mg P m^{-2} year^{-1}) as compared with igneous bedrock (4.8 mg P m^{-2} year^{-1}) (Dillon & Kirchner, 1975). Current or past agricultural land-use probably do not contribute to regional differences between North and South Shore streams. Although median values for percentage of agricultural land are slightly higher for South Shore than North Shore streams (6.3% versus 1.5%), they are still very low as compared with published studies of effects of pasture inputs in similar landscapes (Dillon & Kirchner, 1975). Residual soil phosphorus values should have decreased to near background levels over the past 70–80 years since the peak of agricultural activity on the South Shore (Burton & Hook, 1979; Gough & Marrs, 1990; Fitzpatrick, Knox & Whitman, 1999).

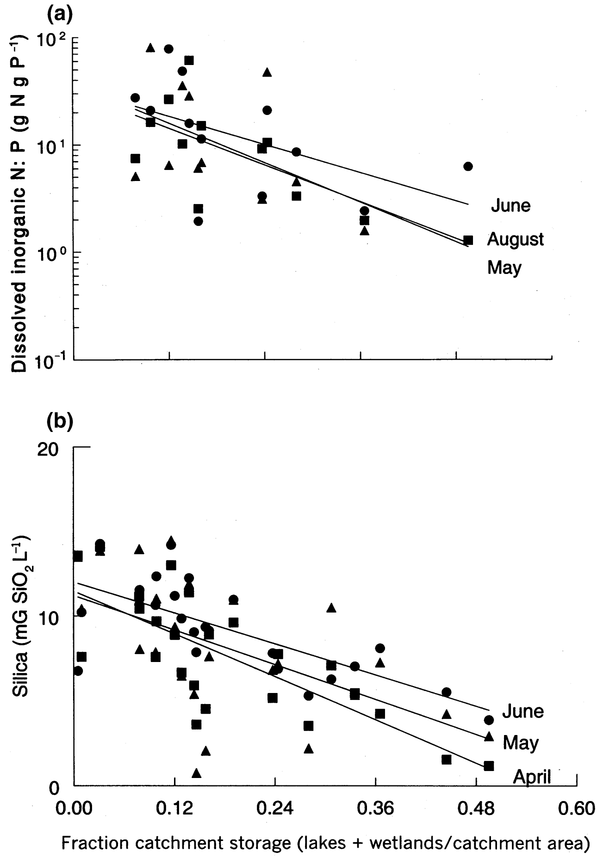

Fig. 7 Results for repeated measures ANCOVA, showing three of seven time periods. Seasonal effect of fraction catchment storage in reducing nutrients in 24 second-order streams. (a) Dissolved inorganic N : P ratio (g N : g PO_4-P per litre) in high mature forest catchments during the middle portion of the growing season [(▲) May, (●) June, (■) August; mature forest × storage effect: $P = 0.04$) and (b) dissolved silica (mg SiO_2 per litre) [(■) April, (▲) May, (●) June; $P < 0.005$].

Regional differences in total P, but not total N, are sufficiently large to cause significant differences in the total N : P ratio, with greater values in North Shore streams. The greater N : P ratio increases the probability of phosphorus limitation in North Shore streams as compared to South Shore streams, or conversely, increases the probability of N limitation in South Shore streams. Periphyton bioassays in North Shore streams have shown a variety of nutrient limitation patterns, varying both across streams and over time; no limitation, colimitation, N-limitation and P-limitation have all been observed (Wold & Hershey, 1999).

Total suspended solids are greatest overall in South Shore streams and the magnitude of the difference between regions is accentuated during periods of high flow. The greater supply of fine sediments stored within South Shore stream channels is consistent with the greater suspended solids in South Shore streams even within high mature forest/high storage catchments [Average fraction fine sediment (<2 mm) in North Shore streams = 0.16, South Shore streams = 0.51]. The majority of South Shore stream catchments are located on the LSCP, which has a high proportion of clay and silt-size particles. In addition, higher baseflows are maintained in South Shore streams throughout the summer in mature forest systems on the Bayfield Peninsula because of high groundwater inputs (Young & Skinner, 1974) and in high storage systems because of contributions from surface storage.

Most of the sediment supply to North Fish Creek is from eroding bluffs rather than upland erosion (Rose & Graczyk, 1996). South Shore streams located on the LSCP have not fully recovered from the historic impact of massive clear cutting and associated fires which removed the surficial organic soils in the late nineteenth century, followed by intensive agriculture and frequent heavy rains in the first half of the twentieth century. Two-year flood peaks and sediment delivery from North Fish Creek are estimated to be double that of presettlement forest cover conditions (Fitzpatrick *et al*., 1999).

Higher organic particulate matter, TOC and DOC values in South Shore, as compared with North Shore streams, could be related either to the predominance of deciduous vegetation (and more rapid litter decay rates) or the rarity of lakes on the clay plain (Melillo, Aber & Muratre, 1982). The Autochthonous organic carbon associated with algal products and macrophyte exudates in lakes decays readily, and the light-absorbing fraction of DOC in particular decreases over time through photolysis (Molot & Dillon, 1997; Gorham *et al*., 1998).

Mature forest effects

Our study does not show an increase in inorganic N or total N as mature forest decreases. In contrast, comparisons of total inorganic N and total N in streams across the US show decreasing levels for catchments with forest cover over 90%; although it is not clear whether this trend is statistically significant (Omernik, 1979).

More rapid growth during early to mid-successional stages tends to reduce N export from forested ecosystems, as a greater fraction of mineralised N is incorporated into biomass (Vitousek & Reiners, 1975). Both the presence of early to mid-successional stages and a conversion of coniferous forests to deciduous species (e.g. second-growth aspen) can be expected to reduce N exports initially, although eventually the loss of inorganic nitrogen is expected to accelerate (Aber *et al*., 1991). In both North and South Shore streams of our study region, inorganic N is still being immobilised and converted to more recalcitrant dissolved organic matter, as evidenced by the predominance of dissolved organic N during the growing season.

Export of DIN is greatest during snowmelt, both as the result of the concentrated flush of nitrates from the snowpack itself and the build-up of mineralised N in a mobile soil N pool under the snowpack (Hendershot *et al*., 1992; Brooks *et al*., 1999). In low mature forest catchments, snowmelt peaks are higher and occur over a shorter time period (Verry, 1976), which should concentrate the flush of nitrate from the snowpack and the soil pool in early spring. Our data show a strong pulse of nitrate loadings during snowmelt in all systems (88–3579 μg NO3-N per litre), but no significant overall effect of mature forest on nitrate + nitrite concentrations. Median and ranges for snowmelt nitrate + nitrite are higher for low mature forest catchments, but extremely high variability limits our power to detect significant differences. It is possible that more time-intensive sampling during snowmelt would allow for better detection of peak concentrations and more accurately reflect differences between high and low mature forest catchments.

Catchment storage effects

In many regions, percentage of wetlands in catchments and DOC or colour in streams and lakes are correlated, as was found in this study (Johnston, Detenbeck & Niemi, 1990; Detenbeck, Johnston & Niemi, 1993; Gorham *et al.*, 1998). In contrast, lakes in North Shore catchments can attenuate DOC and associated colour by increasing retention time and photodegradation (Molot & Dillon, 1997; Gorham *et al.*, 1998), consistent with the lesser responsiveness of water colour to catchment storage on the North Shore.

Mature forest × storage interactions

Mature forest × catchment storage interactions for inorganic N : P ratios suggests that the function of wetlands in the landscape depends on the relative magnitude of inputs, and may differ in disturbed versus pristine landscapes. Although the influence of wetlands on nitrogen and phosphorus in streams and lakes has been examined separately, there are no accounts of the influence of wetlands on N : P ratios and relative nutrient limitation in downstream receiving waters (Johnston *et al.*, 1990; Detenbeck *et al.*, 1993). During summer months (August 1997, May–June 1998), the ratio of DIN : SRP declines as a function of catchment storage for high mature forest catchments, but not for low mature forest catchments. This could be caused by a more efficient removal of DIN than of SRP in wetlands. In urbanised catchments, the phosphorus removal function of stormwater wetlands has been described as a second-order reaction (Walker, 1987), while denitrification is modelled as an apparent first order reaction (Canale, Gelda & Effler, 1996). This would suggest that phosphorus removal rates should increase initially more rapidly as hydraulic retention time increases as compared with nitrogen removal efficiency, thus leading to a shift in N : P removal ratios towards greater P retention as hydraulic retention time decreases. However, most phosphorus in urban streams is adsorbed to and transported with fine mineral particulate matter. Adsorption capacity for inorganic phosphorus to wetland and stream sediments tends to increase with the mineral content of sediments, reflected in extractable aluminium and iron and will be less efficient for wetlands with highly organic soils (Richardson, 1985). With increased loading rates related to higher catchment : wetland ratios, saturation of wetland soils is more likely to occur, whereas denitrification is not limited by sorption capacity.

Regional differences in sensitivity: region × catchment factor interactions

Colour increases as a function of catchment storage more rapidly for South Shore than North Shore streams. North Shore catchments have a greater contribution of lakes to catchment storage than South Shore catchments. Autochthonous production of carbon in lakes is more readily degradable and imparts less colour than humics. In addition, colour will be attenuated by storage in lakes, particularly as residence time increases (Engstrom, 1987). South Shore catchments also have a greater contribution of wet meadows and scrub-shrub wetlands to catchment storage as compared with more open water marshes, ponds and lakes in which DOC is exposed to greater photolysis. The relationship between percentage of wetlands and lake colour is dependent on the percentage of wet meadows in catchments, but not on the percentage of coverage of cattail marshes (Detenbeck *et al.*, 1993)

Seasonal differences in sensitivity

The time × region interaction with respect to total suspended solids is related to seasonal differences in discharge, with greater transport of particulates during periods of high flow. However, differences in total suspended solids and marginally significant differences in turbidity are still demonstrated during baseflow conditions during the growing season.

Dissolved silica decreases with fraction catchment storage only during spring and summer months (April–June). This is consistent with the importance of biological uptake by diatoms in lakes and wetlands during the early portion of the growing season (Wetzel, 1975). If decreases in dissolved silica were a result of reduced contact with mineral soils and bedrock in systems with high catchment storage, we would expect the apparent effect of storage to be greatest in July and August during maximum temperatures when weathering rates are higher.

The effect of storage on the total N : P ratio is evident only during the growing season. This is probably because denitrification increases during periods of low flow and with increased temperature, whereas P sorption is exothermic (Johnston *et al*., 1990; Prairie & Kalff, 1988).

Additive versus interactive effects of geography versus catchment properties

A combination of regional influences, catchment storage and mature forest affect baseflow and snowmelt water quality in second-order streams of the western Lake Superior basin. Suspended solids, phosphorus, N : P ratios, DOC and alkalinity differ significantly amongst regions. Catchment storage is significantly correlated with dissolved silica during the early to mid-growing season, DOC, specific conductivity and alkalinity. Catchment storage effects interact with the influence of mature forest for only two metrics: the dissolved inorganic N : P ratio and colour. We had hypothesised that mature forest and catchment storage would act in an additive, if not synergistic fashion, but in most cases, chemical constituents are influenced by either storage or by mature forest. We expect a greater frequency of combined influences for effects on event-based water quality and catchment yields.

Significant region × mature forest or region × storage interaction terms for conductivity, alkalinity, TOC, and colour suggest differences in regional sensitivity and possible shifts in thresholds of impact. Apparent interactions between mature forest and region effects are probably confounded by the influence of soil characteristics and site productivity on land-use history and forest management practices on the South Shore. A greater proportion of South Shore catchments with high mature forest overlap with, or are located downgradient from, the Bayfield Sand Plain, and thus receive greater inputs from groundwater relatively low in major ion concentrations. However, region × storage interactions for TOC and colour probably reflect regional differences in the relative contribution of lakes versus wetlands to catchment storage, and the effect of increased residence time in lakes on organic carbon photolysis and colour depletion.

Implications for development of regional criteria

The use of the NLF Ecoregion alone as a basis for setting regional water quality criteria would have led to misinterpretation of reference condition and assessment of condition. There are pronounced regional differences in background water quality between the North and South Shore streams, which are both within a single ecoregion. Regional differences are most apparent for water quality constituents related to differences in soil parent material and glacial history, i.e. for suspended solids, alkalinity, phosphorus, N : P ratios and associated parameters. Detenbeck *et al*. (2000) also reported regional differences in bank erosion and percentage of fines in sediments, as well as differences in sensitivity, as evidenced by region × mature forest interactions. Preliminary analysis of biological community response suggests that these differences will be most significant for periphyton and macroinvertebrate communities (Detenbeck *et al*., 2000).

Implications for regional catchment-based development of target loadings

Use of a stratified random sampling scheme for baseflow and snowmelt stream water quality, based on both hydrogeomorphic region and catchment properties, can improve assessments of reference condition, differences in regional sensitivity, and potential causes of impairment. However, in interpreting results of monitoring based on random stratified designs, we must still take into account potential confounding associations between soil type and land-use history.

The approach to catchment classification described above should be valid for other parts of the country with humid climates, where precipitation exceeds evapotranspiration. In these regions, empirical equations derived to describe effects of catchment properties on peak flows tend to include catchment storage or some form of wetland (Jennings *et al*., 1993). In regions where logging is not the predominant human activity driving landscape change, thresholds tied to other land-uses, such as percentage of impervious surface area for developing landscapes, may be more appropriate (Detenbeck *et al*., 2000). The exact transition zone or threshold at which hydrological regimes start to change rapidly along with associated water quality parameters will need to be regionalised based on differences in soils, topography and climate.

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