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Key Points:

- Land cover is more important than topography in determining DOC export but similar in DIC export
- Deforestation decreases total carbon export but greatly increases the DIC/DOC ratio
- Catchment shape and %vegetation strongly relate to DOC and DIC exports but in opposite directions

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The relative influence of topography and land cover on inorganic and organic carbon exports from catchments in southern Quebec, Canada

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Abstract Export of carbon (C) from watersheds represents a key component of local and regional C budgets. We explored the magnitude, variability, and drivers of inorganic, organic, and total C exports from 83 temperate catchments in southern Québec, Canada. The average dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), and total C (TC) exports from these catchments were 4.6, 5.1, and 10.2 g m^{-2} yr^{-1}, respectively. Multiple regression models, using a combination of topographical variables (catchment area, shape, and slope), along with land cover variables (%vegetation, %wetland, %lake, and building density), explained 34%, 62%, and 53% of the variability in the DIC, DOC, and TC exports, respectively. Variance partitioning in the models revealed that topography is slightly more important than land cover in explaining the variance in DIC export (19% versus 15%), whereas land cover is much more important than topography in determining DOC export (44% versus 18%). Interestingly, %vegetation had a negative effect on DIC export but a positive effect on DOC export, suggesting that a change in land cover that reduces vegetation (e.g., deforestation) would lead to modest decreases in TC export but large increases in DIC/DOC export ratio. We conclude that topography and land cover together determine DIC, DOC, and TC exports. While topography is static, land cover can be altered, which will determine the quantity, form, and fate of C exported from these catchments. Finally, annual differences in export values that are related to temperature and precipitation suggest that climate change also have an impact on C export.

1. Introduction

The export of materials from land to fluvial networks and eventually to the ocean has been a major focus of research for decades [*Likens and Bormann*, 1974; *Dillon and Molot*, 2005; *Hossler and Bauer*, 2013]. Not only are these land-derived materials transported and transformed during transport but they also influence the functioning of the receiving aquatic ecosystems [*Cole and Caraco*, 2001; *Aufdenkampe et al.*, 2011]. More recently, lateral inputs of C from watersheds have been recognized as important not just to inland and coastal waters but also to our understanding of the terrestrial C budget [*Cole et al.*, 2007; *Battin et al.*, 2009; *Buffam et al.*, 2011; *Stets and Striegl*, 2012; *Dornblaser and Striegl*, 2015]. Most of the dissolved and particulate organic C exported from watersheds originates from terrestrial primary production [*Kardjilov et al.*, 2006; *Wilkinson et al.*, 2013; *Galy et al.*, 2015]. Similarly, most of the dissolved inorganic carbon (DIC) is ultimately of biological origin because bicarbonate and carbonate ions are derived from the interaction between respiratory soil CO_2 and soil minerals through the process of chemical weathering [*Liu et al.*, 2000; *Zhang et al.*, 2009; *Tank et al.*, 2012; *Wang et al.*, 2012]. Regardless of its origin, C export ultimately represents a loss of terrestrial primary production that needs to be accounted for in regional C budgets. How much C is lost from watersheds, in what form, and when these exports occur are issues of major biogeochemical interest.

The form in which C is exported is of critical importance in determining its fate. It largely dictates the extent to which the C will either be retained in the local aquatic system, released to the atmosphere, stored in sediments, or transported downstream, because different forms are not regulated by the same biological, chemical, and physical processes. For example, a significant portion of the dissolved organic carbon (DOC) entering aquatic systems is transformed by microorganisms, such that it is either incorporated into biomass or respired as an energy source [*Tranvik*, 1992; *Neff and Asner*, 2001]. DOC is also affected by photochemical processes that may mineralize into CO_2 [*Lapierre et al.*, 2013], render it more susceptible to microbial processes, or even flocculate into particulate organic carbon (POC) [*von Wachenfeldt et al.*, 2008, 2009]. In contrast, the ionic fraction of DIC (i.e., CO_3^{2-} and HCO_3^{-}) is likely to behave in a more conservative manner [*Zhai et al.*, 2007; *MacPherson et al.*, 2008], whereas the dissolved CO_2 fraction will be largely lost to the atmosphere, with some being assimilated during photosynthesis [*Striegl et al.*, 2012; *Wallin et al.*, 2013]. Because DOC and DIC are processed differently in aquatic systems, the two C species will impact C budgets in different ways and thus should be examined individually. It follows from this that the export of these two general forms of C (DIC and DOC) will likely not be driven by the same factors.

A review of the literature shows that DOC export is at least partly dependent on aspects of catchment topography, such as slope [*Eckhardt and Moore*, 1990; *D'Arcy and Carignan*, 1997; *Hazlett et al.*, 2008], area [*Mulholland*, 1997; *France et al.*, 2000; *Ågren et al.*, 2007], or elevation [*Johnson et al.*, 2000; *Hazlett and Foster*, 2002]. However, land cover changes, such as deforestation, also have an influence on DOC export [*Meyer and Tate*, 1983; *Carignan et al.*, 2000; *McLaughlin and Phillips*, 2006; *France et al.*, 1996; *Wilson and Xenopoulos*, 2008]. Although wetlands are widely regarded as sources of DOC, wetland loss due to human activities can have varying effects on DOC export, depending on land use and management practices [*Royer and David*, 2005; *Armstrong et al.*, 2010; *Stanley et al.*, 2012]. External forcing, such as hydrology [*Eckhardt and Moore*, 1990; *D'Arcy and Carignan*, 1997] and climate [*Freeman et al.*, 2001; *Raymond and Oh*, 2007; *Räike et al.*, 2012; *Lepisto et al.*, 2014], also strongly modulate DOC export.

Dissolved inorganic carbon export, on the other hand, is influenced by catchment geology, in particular by the presence of carbonate deposits in the catchment [*Liu et al.*, 2000; *Zhang et al.*, 2009; *Tank et al.*, 2012]. Some studies have noted that topographical position and basin elevation have a marked effect on concentration and export of DIC from watersheds [*Soranno et al.*, 1999; *Kling et al.*, 2000; *Finlay et al.*, 2010]. Others have shown that changes in land cover affect DIC export, for example, through logging, farming, pasturing, or urbanization [*Daniel et al.*, 2002; *Raymond and Cole*, 2003; *Baker et al.*, 2008; *Barnes and Raymond*, 2009; *Regnier et al.*, 2013]. Topographical position and land cover likely interact with geology and collectively determine the degree of weathering of the underlying rocks, the principal source of carbonate and bicarbonate ions. This interaction between topography and land cover underscores the need for an integrated approach.

Most studies to date have explored DIC and DOC exports separately [*Hope et al.*, 1994; *Wallin et al.*, 2010], and although there is considerable insight to be gained with this form-specific approach, it nevertheless yields a rather fragmented view of the magnitude and regulation of total C export from watersheds. Since the relative influence of topography and land cover may be different for DIC and DOC exports, changes in land cover may lead to shifts not only in total C export but also in the DIC/DOC export ratio. Here we explore topographic and land cover predictors of DIC, DOC, and total carbon (TC) exports in a set of 83 diverse catchments, located in the temperate landscape of southern Québec. The main objectives of this research were threefold: (1) to identify the relative importance of topography and land cover on DIC, DOC, and TC exports from temperate watersheds; (2) to explore the effect of potential land cover changes on the DIC/DOC export ratio; and (3) to compare DIC and DOC exports across three consecutive years of varying hydrologic regimes.

2. Materials and Methods

2.1. Study Area

Estimating carbon export from a large number of catchments over several years requires a considerable sampling effort and necessarily involves a compromise between capturing the temporal (within streams) and spatial (among streams) components of variability. As our focus centered on identifying the landscape drivers most closely associated with export (in $\mathrm{g\,C\,m^{-2}\,yr^{-1}}$), we opted to maximize landscape variability while ensuring a sufficient temporal coverage to obtain robust estimates of annual export of the various carbon forms. We therefore selected 83 catchments in southern Québec, Canada, about 100 km east of Montreal (45°12′17″N–45°49′22″N, 71°49′34″W–72°39′50″W), ranging in area from 0.13 to 520 $\mathrm{km^2}$ (Table 1). The streams and rivers draining these catchments were sampled in 2004 and 2005, and subsets (32) were also sampled in 2003. The rivers sampled range from first-order streams to fourth-order rivers. Vegetation in the watersheds is characterized by mixed temperate forest; dominated by native sugar maple trees; and mixed with basswood, red oak, eastern white pine, eastern hemlock, and yellow birch. Land use varied greatly among catchments, some being largely forested and others dominated by agriculture or pasturelands (Table 1). Geologically, the study area is located in the transition region between the Humber and Dunnage zones of the Appalachian Uplands striking northeastward, has rolling topography, controlled by a series of well-developed faults and folds, is underlain by carbonate-rich and noncalcareous siliceous sedimentary rocks, imbedded with mudstone and sandstone, and is dotted with outcrops of metamorphic and igneous rocks [*Tremblay and St Julien*, 1990; *Robinson and Fyson*, 1976; *Paradis and Lavoie*, 1996]. The geology is thus quite

Table 1. Stream and Catchment Characteristics of the 83 Study Sites[a]

Variable	Min	Mean (SD)	Max
Stream Characteristics			
Discharge ($m^3\ s^{-1}$)	0.0021	0.48 (1.0)	6.1
DIC concentration ($mg\ L^{-1}$)	1.5	8.0 (4.1)	28
DOC concentration ($mg\ L^{-1}$)	1.9	7.7 (4.0)	19
pH	6.0	7.2 (0.38)	8.1
Alkalinity ($\mu eq\ L^{-1}$)	80	530 (280)	1800
Total nitrogen concentration ($mg\ L^{-1}$)	0.14	0.46 (0.19)	1.1
Total phosphorus concentration ($\mu g\ L^{-1}$)	4.1	26 (19)	110
Catchment Topography			
Catchment area (km^2)	0.13	28 (79)	520
Average elevation (m)	150	310 (57)	430
Average slope (°)	1.2	5.1 (2.8)	12
BSI	1.2	1.6 (0.22)	2.4
Catchment Land Cover			
%vegetation	42	83 (15)	100
%forest	27	77 (18)	100
%pasture	0	21 (19)	73
%wetland	0	1.1 (1.9)	9
%lake	0	3.9 (5.9)	25
Buildings per km^2	0	9.9 (12)	56
Catchment Geology and Soil			
%intrusive	0	11 (27)	100
%sedimentary	0	66 (41)	100
%volcanic	0	23 (37)	100
%rock	0	69 (41)	100
%till	0	23 (38)	100
%mud	0	7.7 (24)	100
%brunisolic	0	22 (23)	91
%gleysolic	0	15 (22)	83
%organic	0	2.4 (4.1)	23
%podzolic	0	42 (30)	100
%regosolic	0	0.95 (2.5)	17

[a] Statistics for discharge and water chemistry were determined by first averaging all measured values from 2004 and 2005 for each of the 83 streams, then calculating the minimum, maximum, mean, and standard deviation of these values ($n = 83$). Statistics for topography, land cover, geology, and soil were obtained from digital elevation models and maps of topography, land cover, rock type, surficial deposits, and soil type, using a geographic information system ($n = 83$).

diverse across the 83 catchments, with the dominant rock type being sedimentary in 56 catchments, volcanic in 18, and intrusive in the remaining 9. The surface deposits in the region consist mostly of glacial till and some glaciolacustrine fine sediment [*Prairie et al.*, 2002], such that the dominant general formation is till in 19 of the catchments studied, mud in 6, although rock is the dominant formation in the majority of the catchments in this study (58). Soils are mainly humo-ferric podzolic and dystric brunisolic, with a loamy to sandy loam texture and moderate to good internal drainage, such that the dominant soil order is podzolic in 49 catchments and brunisolic in 23 catchments. Gleysolic soils dominate in 10 catchments, and only 1 catchment is dominated by younger regosolic soils. Mean annual precipitation in the region is about 1000 mm, of which 500–600 mm runs off [*Natural Resources Canada* (*NRC*), 2009], and mean daily temperature in July is about 18°C, while in January it is about −10°C [*Environment Canada*, 1981–2010].

2.2. Sampling, Analyses, and Calculations

The 83 sites were visited 4–6 times each in 2004 and 2005, at about 5 week intervals during the ice-free period between March and November (totaling around 400 site visits per year), and a subset of 32 sites were visited an additional 6–7 times in 2003, at about 4 week intervals between March and October (totaling around 200 site visits). At each of these sites, water samples were collected and filtered in situ using 0.45 μm syringe filters and transported to the lab in 40 mL glass vials with silicone septa (I-CHEM). DIC and DOC concentrations were determined following acidification and oxidation with phosphoric acid and sodium persulfate, respectively, using a TOC1010 total carbon analyzer, equipped with an infrared CO_2 detector (OI Analytical, 2% precision of two replicates per vial, 3% accuracy at 5 $mg\ L^{-1}$ standard).

The carbon export ($g\,m^{-2}\,yr^{-1}$) at any given site is defined as the product of discharge and C concentration per unit catchment area, and it is therefore essential to determine the first two components accurately. We determined discharge ($m^3\,s^{-1}$) at each site for each sampling date as the product of the measured stream cross-sectional area and water velocity (sampled at 0.6 × stream depth at several stations across the stream width using the two-dimensional FlowTracker acoustic Doppler velocimeter, SonTek). These point measurements are, however, inadequate to capture the seasonal variation in discharge, and because the vast majority of these rivers are not gauged it was necessary to develop alternative approaches to reconstruct the full annual discharge pattern for each river. We developed an empirical calibration that would allow us to estimate the discharge for any given river at any given point in time that is based on the relationship between our point discharge measurements and discharge data from a continuous gauging station located in one of our study watersheds, Trois-Lacs (TR) (hydrologic station 030101: 45°47′30″N, 71°58′5″W operated by the Centre d'expertise hydrique du Québec. The gauging station reports an error of ±5% in the stage-discharge relationship. Our 612 instantaneous discharge measurements divided by the corresponding catchment areas were expressed as runoff ($mm\,d^{-1}$), and regressed against daily runoff at the TR gauging station, along with other site-specific attributes that modulate local discharge. For this region, the best predictive model of daily runoff at any given site included elevation and catchment, in addition to the measured daily runoff at the TR station:

$$\log_{10}\mathrm{S}_{\mathrm{EM}} = -0.629 + 0.892 * \log S_{TR} + 0.00188 * E + 0.150 * \log_{10} A_D \tag{1}$$

where S_{EM} is the estimated runoff at a given site ($mm\,d^{-1}$), S_{TR} is the measured value at the TR gauging station, E is the elevation of the sampling site (m), and A_D is the total catchment area upstream of the sampling site (km^2). These estimates of daily discharge generated by the empirical model correlated well with our instantaneous discharge measurements, explaining 81% of the variability ($R^2 = 0.81$, $p < 0.0001$, $n = 612$). We used this relationship to extrapolate discharge to the entire year, including winter months, for which we had no samples. While the relationships that we built between concentration and discharge were based on measurements taken during the ice-free period, we have no reason to believe that these relationships would not hold for flows under ice cover. At the gauged site, where discharge was monitored year-round, the range of discharges recorded during the sampling season encompassed the range of discharges seen in winter. Furthermore, on the specific dates when discharge was measured at various sites and compared to the gauged discharge at Trois-Lacs on those same dates, the gauged discharges cover nearly the full range of discharges seen throughout the year. This allowed us to derive annual export and to compare our results with the literature, which overwhelmingly reports annual export.

Daily C export was calculated as the product of daily discharge, estimated as described above, and DIC and DOC concentrations measured at each site, divided by catchment area. Applying an average DIC or DOC concentration derived from the 7 to 11 point measurements assumes that discharge and concentration are independent, which is not always the case [*Wallin et al.*, 2010; *Birgand et al.*, 2011]. We tested this assumption by exploring the relationship between measured DIC and DOC concentrations and measured discharge for each of our 83 sites using the data from all years combined. For DIC, significant ($p < 0.05$) negative (dilution) relationships were found for 31 sites ($p < 0.05$), and no sites showed a positive (concentration) relationship. For DOC, a significant dilution effect was found for only two sites ($p < 0.05$), whereas five sites showed a significant concentration effect. For sites with significant correlation between concentration and discharge, we used the corresponding site-specific regression to estimate daily concentration from daily discharge. For sites with no significant relationship between discharge and DOC or DIC concentration, we applied the average concentration with the estimated daily discharge in our calculation of DOC or DIC export. Annual DIC and DOC exports ($g\,m^{-2}\,yr^{-1}$) were then calculated as the sum of daily export values.

Particulate organic carbon (POC) export from a catchment was not measured but rather estimated, assuming a POC to DOC ratio of 0.1, typical for lotic systems in the temperate forest [*Schlesinger and Melack*, 1981; *Hope et al.*, 1994]. Particulate inorganic carbon (PIC) export was not included in TC export because previous studies have shown that it accounted for a very small fraction of inorganic C [*Aucour et al.*, 1999]. Thus, in this study, TC export was defined as the sum of DIC, DOC, and POC exports.

2.3. Catchment Topography and Land Cover

The variables used to characterize the 83 catchments are listed in Table 1. Values for topography and land cover were extracted from 1:50,000 digital topographic maps [*Natural Resources Canada* (*NRC*), 2006] as well as 1:50,000 and 1:250,000 land cover maps [*Natural Resources Canada* (*NRC*), 1999]. Geological data (surficial geology and surficial materials) were obtained from 1:5,000,000 digital maps [*Natural Resources Canada* (*NRC*), 1995] and soil data from an amalgamation of four smaller regional maps ranging in scale from 1:20,000 to 1:126,720 [*Institut de Recherche et de Développement en Agroenvironnement Inc*., 2006]. Statistics were extracted from the maps using ArcMap10 (Environmental Systems Research Institute). Here average slope (°) was derived from the digital elevation model with 10 m × 10 m resolution. Basin shape index (BSI), a measure of watershed roundness, is defined as the ratio of the perimeter of the catchment to that of a circle with the same area [*Miller*, 1953]:

$$\mathrm{BSI} = P/\left(2\sqrt{(\pi * (A_D))}\right) \tag{2}$$

where P and A_D are the catchment perimeter and catchment area, respectively. Geological variables are expressed as a percent of total catchment area (A_D). However, land cover and soil variables are expressed as a percent of total catchment area (A_D) minus the area of the catchment covered by waterbodies (A_W), leaving only the terrestrial catchment area ($A_D - A_W$). We used two different map layers of different categorical resolution to characterize the land cover properties of our catchments. In the first land cover classification, the landscape was broadly defined as vegetated, unvegetated, and water (Base nationale de données topographiques, Natural Resources Canada). The %vegetation derived from this layer is a broad category that includes wooded areas and shrublands but excludes pastureland and agricultural land and wetlands. The nonvegetated land includes pastureland and agricultural land, as well as bare rock (which is rare in our landscape), and therefore, these two categories roughly correspond to "natural" versus "managed" landscapes. We further characterized the landscape using another land cover layer that provided a finer classification (Canada Land Inventory, Natural Resources Canada, http://sis.agr.gc.ca/cansis/publications/maps/index.html), and we derived percent forest, pastureland, wetlands, and mines for each of our catchment. The areas considered as forest included the zones on land cover maps classified as "productive woodland," "nonproductive woodland," and "outdoor recreation," which consisted of forested parks in these catchments. The areas considered as pasture were the zones on land cover maps classified as "improved pasture and forage crops" and "unimproved pastureland and rangeland." To calculate percent wetlands, regions on land cover maps that were coded as "swamp, marsh, or bog" were merged with "wetlands." Land cover categorized as cropland or urban was not present in the studied catchments. Building density is expressed as the number of buildings per square kilometer of terrestrial catchment area. All the above land cover categories are expressed as percent of the terrestrial area in each catchment, whereas %lake is the water area over the total catchment area.

2.4. Statistical Analyses

A principal component analysis was performed on the variables describing topography, land cover, geology, and soil in Table 1 to explore the multiple relationships among variables. They were then offered for inclusion in multiple linear regression models predicting DIC, DOC, and TC exports. The models were built using a mixed stepwise selection process, with $p < 0.05$ as the condition for including a variable in the model. Both %forest and %pasture from land cover maps were excluded from these analyses as they were strongly correlated with the broader category of %vegetation from topographic maps (%forest: positive, $R^2 = 0.73$, $n = 83$, $p < 0.0001$; %pasture: negative, $R^2 = 0.72$, $n = 83$, $p < 0.0001$) and were therefore considered redundant. The interannual variability in DIC and DOC exports was examined for a subset of 32 catchments using a one-way analysis of variance and the Tukey-Kramer post hoc test to find significant differences among three sequential years ($p < 0.05$). Exports for the 32 sites were centered by expressing the export from each site in a given year as the difference relative to that site's average export over the 3 years (2003, 2004, and 2005). This procedure allowed us to examine more robustly interannual differences for streams with very different average export.

3. Results

3.1. Carbon Export

We observed a wide range in export rates of both DIC and DOC across the 83 catchments studied. DIC export was 4.6 g m^{-2} yr^{-1} (average of 2004 and 2005 values) and ranged an order of magnitude, from 1.1 to 11 g m^{-2} yr^{-1} (Figure 1). Similarly, DOC export averaged 5.1 g m^{-2} yr^{-1} over the same period and ranged

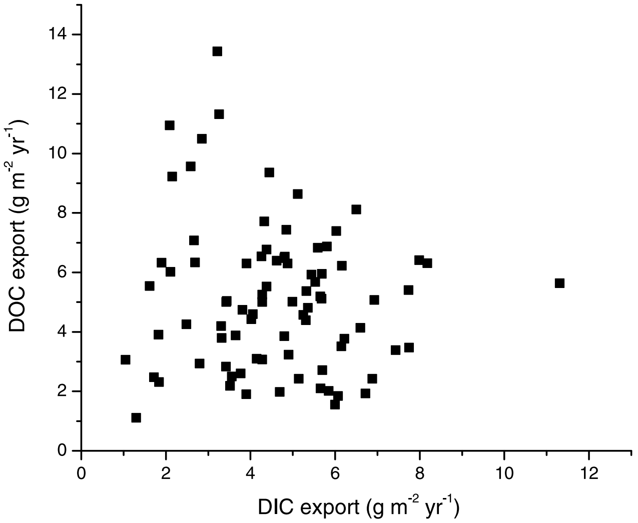

Figure 1. DOC export versus DIC export for the 83 catchments. Exports are expressed as the average of 2004 and 2005 measurements in grams of carbon per square meter of total catchment area per year.

from 1.1 to 13 g m^{-2} yr^{-1} (Figure 1). As a result, TC export averaged 10 g m^{-2} yr^{-1} and ranged from 2.5 to 18 g m^{-2} yr^{-1}. Combining the uncertainty of both discharge and concentration estimates, error propagation calculations suggest that the export values have an associated error of about 25%.

Despite the similar range and magnitude of DIC and DOC exports, there was no significant correlation between the exports of these two C species. The relative contribution of the two dissolved constituents to TC export thus varied considerably among the catchments, with exports from some sites being overwhelmingly dominated by inorganic C and others by its organic counterpart. The ratio of DIC to DOC export ranged 20-fold, from 0.19 and 3.9, averaging 1.1, with 56 of the 83 catchments falling in the range between 0.5 and 2.0. In addition, the range and magnitude of DIC and DOC concentrations (in mg L^{-1}) across the 83 sites were similar (average of 2004 and 2005 values; Table 1), yet there was no relationship between concentrations of these inorganic and organic components for the region.

Overall, there was a significant positive spatial scale effect on C export (Figure 2), such that DIC, DOC, and TC exports increased with catchment size ($\log_{10}(\text{DICexport}) = 0.54 + 0.11{*}\log_{10}(A_D)$, $R^2 = 0.19$, $p < 0.0001$, $n = 83$; $\log_{10}(\text{DOCexport}) = 0.56 + 0.12{*}\log_{10}(A_D)$, $R^2 = 0.16$, $p = 0.0002$, $n = 83$; $\log_{10}(\text{TCexport}) = 0.90 + 0.11{*}\log_{10}(A_D)$, $R^2 = 0.33$, $p < 0.0001$, $n = 83$).

3.2. Factors Influencing Carbon Export

A principal component analysis of DIC, DOC, and TC exports (average of 2004 and 2005 values) as well as topographic and land cover variables demonstrates the large degree of uncoupling between DIC and DOC exports, as these two variables are orthogonal to each other on the summary plot of the first two components (Figure 3). The first two components explained more than 50% of the variance in the data, with component 1 aligning strongly with topographical variables, such as catchment area, slope, and elevation (34%), and component 2 aligning more with land cover variables, such as %vegetation and %wetlands (18%).

The position of DIC and DOC exports at 45° to the axes reveals that the export of either C component is related to a combination of the topographical variables of component 1 and the land cover variables of component 2. Not surprisingly, TC export was intermediate between DIC and DOC exports. The multiple linear regression models presented in Table 2 thus incorporate a combination of topography and land cover variables and explain 34%, 62%, and 53% of the variance in DIC, DOC, and TC exports, respectively. Both DIC and DOC exports were positively related to total catchment area (as shown in Figure 2). BSI and %vegetation both had a significant negative effect on DIC export but a significant positive effect on DOC export. In addition, building density (a measure of human influence) was positively related to DIC export, whereas wetlands were positively related to DOC export. Finally, the presence of lakes in the catchment had a negative effect on DOC export but none on DIC export. Variables describing geology (as either general rock formation or surface material type) and soil type did not contribute significantly to predicting C export. As mentioned in section 2.4, %forest and %pasture were not offered in the stepwise model-building process, because of their strong correlation with %vegetation.

An examination of the sums of squares associated to each variable in the multiple regression models allows us to determine the relative influence of topographical and land cover variables on C export (Figure 4).

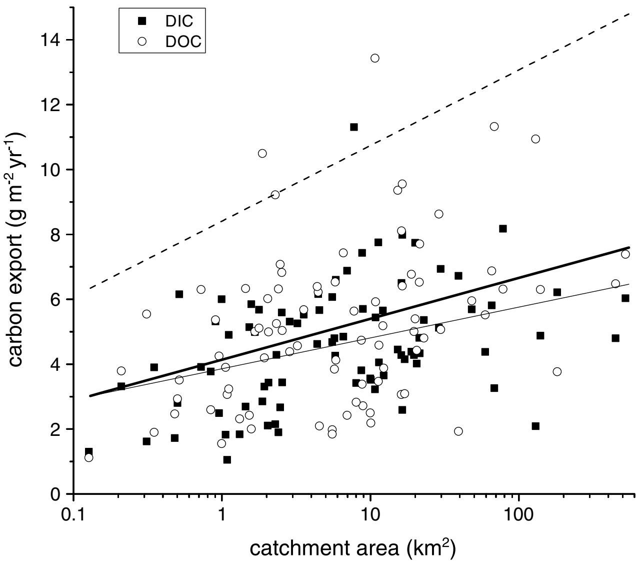

Figure 2. Carbon exported as DIC (solid squares) and DOC (open circles) in g m^{-2} yr^{-1} for the 83 catchments, average of 2004 and 2005 measurements, as a function of total catchment area. Significant correlations with catchment area are shown for DIC export (thin line), DOC export (thick line), and TC export (dashed line, points not shown).

The topographical variables (catchment area and BSI) were slightly more important than the land cover variables (%vegetation and building density) in predicting DIC export, with topography and land cover explaining 19% and 15% of the variability, respectively. In contrast, land cover variables (% vegetation, %wetland, and %lake) were more important than the topographical variables (catchment area, BSI, and slope) in predicting DOC export, land cover, and topography explaining 44% and only 18% of the variability in the DOC model, respectively. In terms of TC export, the topographical variables (catchment area and slope) and land cover (%wetland) explained roughly the same amount of variation (24% versus 29%, respectively).

The positive relationship of catchment size with both DIC and DOC exports resulted in an overall positive effect of catchment size on TC export (Table 2). In contrast, the opposing effects of BSI and %vegetation on DIC and DOC exports canceled each other out, and as a result, these variables had no overall impact on TC export. The positive effect of %wetland and the negative effect of slope on DOC export were strong enough to influence overall TC export, despite their lack of influence on DIC export.

3.3. Interannual Variation in Carbon Export

The preceding results were based on the average C export for 83 basins in 2004 and 2005; however, we also examined interannual variation in C export from 2003 to 2005 for a subset of 32 basins. Continuous measurements from 13 weather stations in the study area reveal that 2005 was the warmest and wettest year, with 1°C higher annual mean air temperature, and 71 mm and 290 mm more precipitation than in 2003 and 2004, respectively (Table 3). This is also reflected by 2005 showing the highest and most variable mean daily discharge at the gauged Trois-Lacs and Waterloo sites. For each of the 32 sites, we calculated an average export over 3 years and then examined how individual years differed from this 3 year average. DIC exports were significantly higher in 2005 than in 2004 and in 2003, with average DIC exports for the 32 basins of 6.8, 5.2, and 5.3 g m^{-2} yr^{-1} in 2005, 2004, and 2003, respectively (analysis of variance (ANOVA), $R^2 = 0.59$, $p < 0.0001$, $n = 96$, Tukey-Kramer $p < 0.0001$) (Figure 5). DOC exports were also significantly higher in 2005 than in 2004 and 2003, with average DOC exports for the 32 basins of 6.1, 5.0, and 5.2 g m^{-2} yr^{-1} in

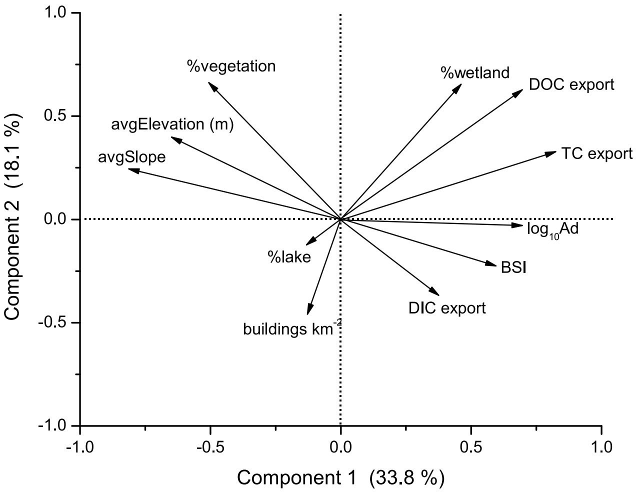

Figure 3. Principal component analysis of DIC, DOC, and TC exports (average of 2004 and 2005 values) and key topographic and land cover variables for the 83 catchments.

Table 2. Multiple Linear Regression Models Predicting DIC, DOC, and TC Exports in g m^{-2} yr^{-1a}

		DIC		DOC		TC	
	Parameter	Estimate	p value	Estimate	p value	Estimate	p value
Topography	Catchment area (km^2)^b	1.069	$<$**0.0001**	0.672	**0.0323**	1.412	**0.0002**
	Average elevation (m)		0.7584		0.2181		0.6454
	Average slope (°)		0.2418	−0.271	**0.0041**	−0.266	**0.0066**
	BSI	−2.088	**0.0201**	2.705	**0.0068**		0.8220
Land cover	%vegetation	−0.038	**0.0017**	0.061	**0.0003**		0.5486
	%wetland		0.8931	0.530	$<$**0.0001**	0.690	$<$**0.0001**
	%lake		0.3783	−0.139	**0.0002**		0.0601
	Buildings per km^2	0.036	**0.0116**		0.4498		0.8632
	Intercept	9.914	$<$**0.0001**	−3.423	0.1072	9.731	$<$**0.0001**
R^2		0.34		0.62		0.53	

[a] Estimates of coefficients and corresponding p values are given for all variables offered during the stepwise selection process. Variables were included in the model if $p < 0.05$ (in bold) and the corresponding R^2 values are shown ($n = 83$ for each).
[b] Catchment area is log10 transformed.

2005, 2004, and 2003, respectively (ANOVA, $R^2 = 0.31$, $p < 0.0001$, $n = 96$, Tukey-Kramer $p < 0.0001$) (Figure 5). As a consequence, TC exports were also significantly higher in 2005 than in 2004 and in 2003, with average TC exports for the 32 basins of 13.6, 10.7, and 11.0 g m^{-2} yr^{-1} in 2005, 2004, and 2003, respectively (ANOVA, $R^2 = 0.67$, $p < 0.0001$, $n = 96$, Tukey-Kramer $p < 0.0001$). There was no interannual difference between exports in 2003 and 2004 for any C species.

4. Discussion

The C exports and DIC/DOC export ratios that we measured for these 83 basins in southern Québec are well within the range of values found in the literature. Our range of DOC export (1.1 to 13 g m^{-2} yr^{-1}) is in very good agreement with that estimated by *Eckhardt and Moore* [1990] in roughly the same area (1 to 18 g m^{-2} yr^{-1}). The average DOC export of 5.1 g m^{-2} yr^{-1} corresponds to the midrange of DOC exports reported for Atlantic Canada (1.6 to 12.4 g m^{-2} yr^{-1}) [*Clair et al.*, 1994], for forested landscapes in southeastern Canada (0.9 to 13.7 g m^{-2} yr^{-1}) [*Creed et al.*, 2008], or for forested watersheds in other temperate regions of North America (0.3 to 41.7 g m^{-2} yr^{-1}) [*Hope et al.*, 1994] and very similar to the average DOC export of the 6 g m^{-2} yr^{-1} reported for wet temperate regions by *Meybeck* [1993]. Similarly, our DIC export range of 1.1 to 11 g m^{-2} yr^{-1} and average of 4.6 g m^{-2} yr^{-1} were well within the range of riverine exports found in Europe (0.5 to 67.8 g m^{-2} yr^{-1}) [*Hope et al.*, 1994], although they were slightly higher than those found in Atlantic Canada (0.04 to 4.19 g m^{-2} yr^{-1}, average 0.71 g m^{-2} yr^{-1}) [*Clair et al.*, 1994] and were much higher than those found in central Ontario (0.81 to 1.69 g m^{-2} yr^{-1}, average 1.12 g m^{-2} yr^{-1}) [*Dillon and Molot*, 1997]. As for TC export, our range of 2.5 to 18 g m^{-2} yr^{-1} and average of 10 g m^{-2} yr^{-1} agree well with TC export from North Atlantic rivers in the United States (3.7 to 15 g m^{-2} yr^{-1}, average of 7.2 g m^{-2} yr^{-1}) [*Stets and Striegl*, 2012] but are lower than TC exports from European rivers at similar latitudes (e.g., TC exports for the Adige, Danube, and Po Rivers, which were 16.7, 12.4, and 30.1 g m^{-2} yr^{-1}, respectively) [*United Nations Environment Programme*, 2003].

The decoupling between DIC and DOC exports that we observed in our systems (Figure 1) has also been observed in other regions, leading to variations in DIC/DOC export ratios both within and across regions. In this regard, our DIC/DOC export ratio varied widely across catchments (from 0.2 to 3.9) and the overall mean of 1.14 was much higher than published DIC/DOC ratios in Atlantic Canada (0.01 to 0.86, average 0.13) [*Clair et al.*, 1994] and central Ontario (0.13 to 0.32, average 0.27) [*Dillon and Molot*, 1997]. This interregional difference is largely attributable to differences in the amount of wetlands and carbonate rocks, which relate to the production of soil DOC and DIC, respectively. Atlantic Canada and central Ontario are lithologically dominated by volcanic and granitic rocks, respectively, whereas most of our study area is underlain by carbonaceous sedimentary rocks [*Paradis and Lavoie*, 1996], which contribute more DIC by weathering. In addition, most of the catchments studied in Atlantic Canada are located on islands where the soils are poorly developed, thereby producing less DIC from soil respiration. Furthermore, the study area in central Ontario has more wetlands (up to 25%) than ours (up to 9%), which contribute more DOC and further lower the DIC/DOC ratio.

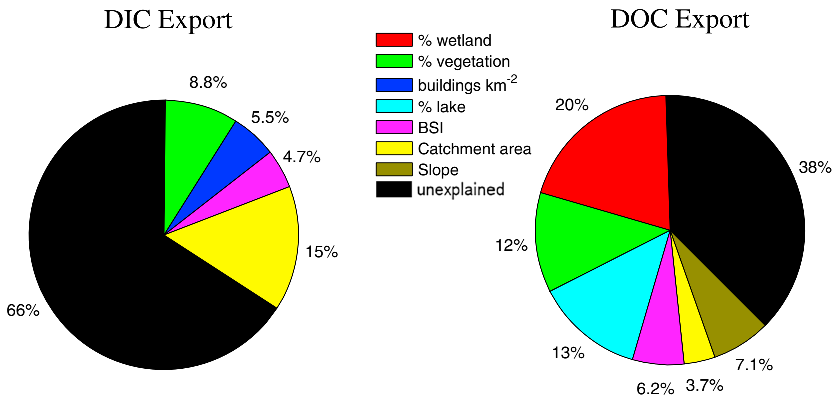

Figure 4. Variance partitioning in the multiple linear regression models of DIC and DOC exports, showing the percentage of variability explained by each component variable and the remaining variability, unexplained by the models.

We designed this study to maximize spatial coverage and environmental gradients, while still capturing at least some of the seasonal variability in riverine discharge and C concentration. Discharge is without doubt the most variable of these two components, but we were able to reconstruct the annual discharge pattern by relating our point measurements to a continuous discharge record in one of study streams ($n > 600$ point measurements). This approach is effective to capture both the total runoff from each stream and the main features of the annual hydrographs. With regard to the temporal variability in C concentrations, we examined the mean-variance relationship for DIC and DOC concentrations, by plotting the variance of all concentration measurements at a given site in a given year, V, versus the mean concentration for that site in that year, X. Combining the 32 sites sampled in 2003 with the 83 sites sampled in 2004 and 2005, there were a total of 198 site years for which we could compare the variance to the mean. Applying the resulting mean-variance equations ($V_{\mathrm{DIC}} = 0.032{*}X_{\mathrm{DIC}}^{2.49}$, $R^2 = 0.51$, $p < 0.0001$, $n = 198$; $V_{\mathrm{DOC}} = 0.019{*}X_{\mathrm{DOC}}^{2.62}$, $R^2 = 0.67$, $p < 0.0001$, $n = 198$) following *Cattaneo and Prairie* [1995] allowed us to determine that no more than four samples per year were required to obtain a mean concentration for a given site with a precision of 20%. As we visited each site 4–7 times per year, the mean concentration calculated for any site should have an error of 20% or less, thereby confirming the adequacy of our sampling strategy. Carbon concentrations are less temporally variable than nutrients such as N and P [*Moatar and Meybeck*, 2007; *Birgand et al.*, 2011], and a similar precision was obtained by *Birgand et al.* [2011] for total dissolved carbon sampled monthly in a forested catchment. With our experimental design, we found more variability in carbon export among sites than within a year at a single site, which allowed us to explore the drivers of carbon export across catchments of differing topographical and land cover characteristics.

4.1. Drivers of Terrestrial Carbon Export to Aquatic Systems

While topography and land cover together explained only 34% of the variability in DIC export, they explained 62% of the variability in DOC export, clearly illustrating that DIC and DOC exports are controlled by different

Table 3. Local Climate, Gauged Daily Discharge as Well as Discharge, and DIC and DOC Concentrations Measured in Situ at the 32 Sites in 2003, 2004, and 2005

	2003	2004	2005
Annual mean air temperature (°C)[a]	5.0	5.1	6.0
Annual precipitation (mm)[a]	1245	1026	1316
Mean (SD) of mean daily discharges at Trois-Lacs ($m^3\ s^{-1}$)[b]	13.4 (18.7)	12.7 (15.9)	15.6 (23.9)
Mean (SD) of mean daily discharges at Waterloo ($m^3\ s^{-1}$)[c]	0.57 (0.77)	0.62 (0.81)	0.68 (0.97)
Mean (SD) measured in situ discharge ($m^3\ s^{-1}$)	NA	0.30 (0.59)	0.59 (1.4)
Mean (SD) DIC concentration ($mg\ L^{-1}$)	8.7 (4.0)	8.9 (4.7)	9.8 (5.4)
Mean (SD) DOC concentration ($mg\ L^{-1}$)	8.3 (3.7)	8.2 (4.0)	8.7 (4.7)

[a] Data from http://climate.weatheroffice.gc.ca.
[b] Data from https://www.cehq.gouv.qc.ca/suivihydro/graphique.asp?NoStation=030101.
[c] Data from https://www.cehq.gouv.qc.ca/suivihydro/graphique.asp?NoStation=030343.

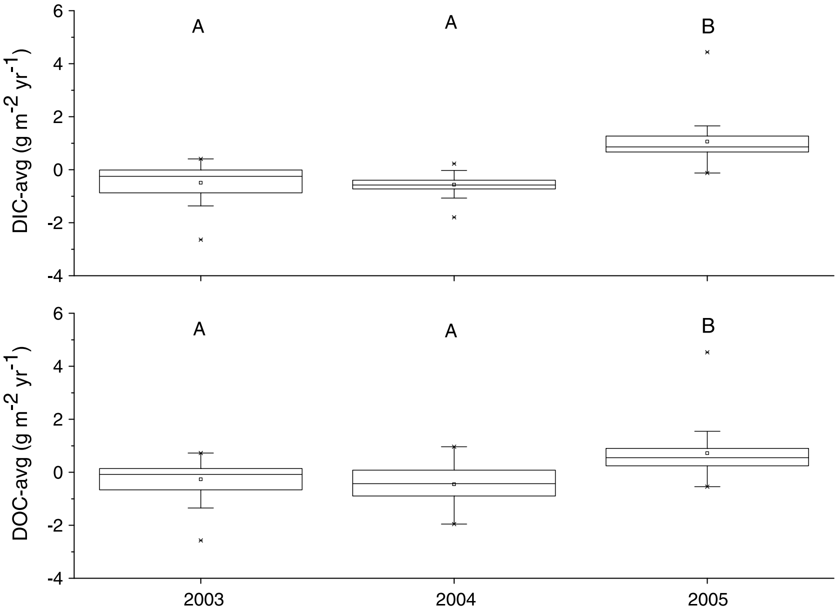

Figure 5. Interannual variation in DIC and DOC exports for 32 basins. For each site, export is reported as the difference between the export in the given year and the 3 year average export for that site (in g m^{-2} yr^{-1}). The mean difference is the small square within the larger 75th percentile box, with 95th percentile whiskers, a median line, and asterisks for maximum and minimum values. Different letters within a panel indicate significant differences among years (one-way ANOVA and Tukey-Kramer post hoc test).

biogeochemical processes. Furthermore, whereas land cover and topography were equally important in determining DIC export (explaining 15% and 19% of the variability, respectively), land cover was clearly a stronger driver of DOC export than was topography (explaining 44% and 18% of the variability, respectively). These results support our hypothesis that a combination of underlying topographical features and potentially more dynamic land cover features are involved in determining the various forms of C exported.

Despite these differences, there was one driver that was common to all forms of C export, whether DIC, DOC, or TC: catchment area was positively related to all forms of C export, either alone (Figure 2) or in combination with other effects in multiple linear regression models, explaining 15%, 4%, and 16% of the variability in DIC, DOC, and TC exports, respectively (Table 2 and Figure 4). This is in contrast to the finding of *Ågren et al*. [2007] that small headwater catchments export the most terrestrial DOC, in a comparison of 15 subcatchments in Sweden ranging in size from 0.03 to 22 km^2. It is difficult to explain why catchment area should play a role in how much C is exported per square kilometer. We found no significant relationship between carbon concentration (DIC, DOC, or TC) and catchment area ($p > 0.05$, $n = 83$, using the average of 2004 and 2005 concentrations for each site and using either terrestrial or total catchment area). This is inconsistent with the positive relationship with DOC concentration reported by *Inamdar and Mitchell* [2006] and the negative relationship with DOC concentration reported by *Wolock et al*. [1997]. Thus, the ultimate driver is likely hydrology, and in this regard, we find a relatively strong positive relationship between catchment size and runoff (parameters) and also with catchment elevation. The reasons underlying this positive relationship are not clear but could be related to shifts in land cover patterns with catchment size. In particular, there was a trend for larger catchments to have less forest and vegetation cover and higher proportion of agricultural lands, and it has been suggested that runoff actually increases with deforestation and human-induced landscape alternations [*Allan*, 2004; *Maetens et al*., 2012].

4.1.1. Drivers of DIC Export

After catchment area, %vegetation in the watershed was the second most important factor determining DIC export, with less vegetated basins exporting more DIC. This agrees with previous work that has shown that deforestation or conversion of natural vegetation into pasture increases DIC export from the landscape, either when comparing DIC export across basins [*Baker et al*., 2008; *Rantakari and Kortelainen*, 2008; *Regnier et al*., 2013] or when following DIC export within a basin as its land cover changes over time [*Raymond and Cole*, 2003; *Yan et al*., 2013]. There are several processes that can explain the observed pattern between %vegetation

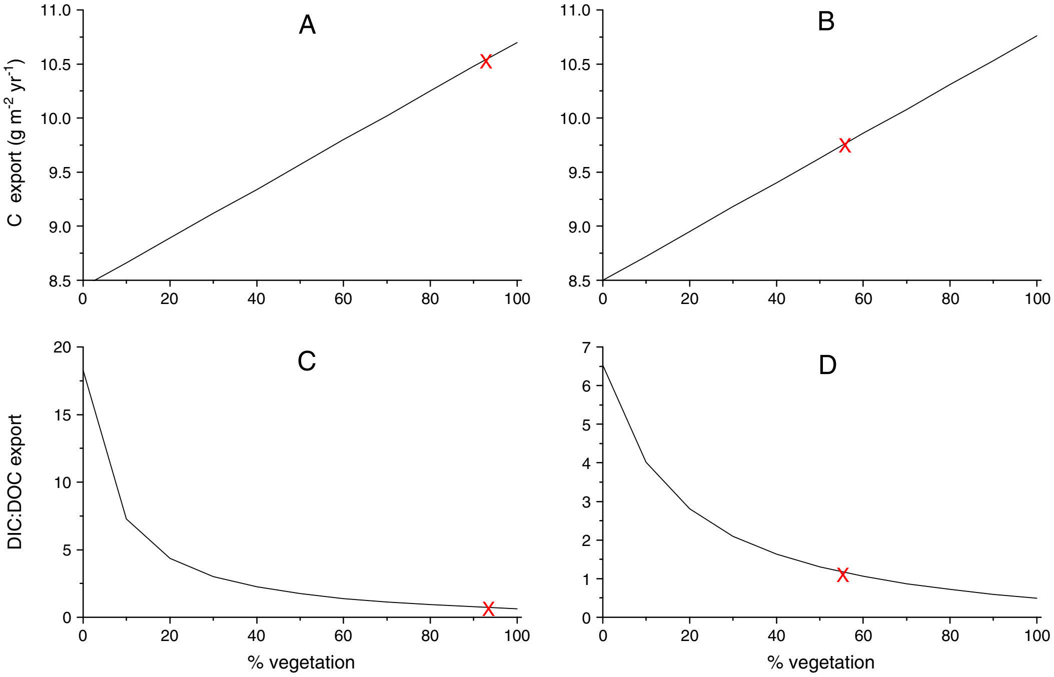

Figure 6. Carbon export as the sum of DIC export and DOC export in g m^{-2} yr^{-1} and the DIC/DOC export ratio versus %vegetation for two example watersheds, (a and c) an inflow to Lac d'Argent and (b and d) an inflow to Roxton Pond. The current vegetation coverage of the catchment is indicated by a red cross in each panel.

and DIC export. In our study region, unvegetated areas often corresponded to pasturelands which, in comparison with forest soils, tend to have higher soil respiration rates [*Smith and Johnson*, 2004; *Kellman et al.*, 2007], leading to elevated soil CO_2 and greater weathering potential [*Likens*, 2010; *Bayon et al.*, 2012]. Previous studies have shown that replacing forest species with forage or farm crops results in a decrease in the soil C/N ratio, leading to a more rapid mineralization of soil organic matter and litterfall, thus increasing groundwater DIC and soil CO_2 [*Marland et al.*, 2004; *Hedley et al.*, 2009]. Moreover, deforestation, due to agriculture or pasture, can intensify weathering [*Likens*, 2010; *Bayon et al.*, 2012], thus releasing more bicarbonate and carbonate ions into river water. Therefore, reducing the vegetation coverage and/or shifting land uses to agricultural or residential may increase DIC export by increasing soil respiration rates and weathering.

In addition, C geochemistry and water chemistry in river systems are dependent largely on lithological variability in carbonate/silicate-dominated terrains [*Amiotte-Suchet et al.*, 2003; *Zhang et al.*, 2009]. Our study area is located in the transition region between the Humber and Dunnage zones, underlain by carbonate-rich and noncalcareous siliceous sedimentary rocks and mafic volcanic rocks associated with marine sediments, respectively. Particularly, in the Humber zone there are the world's largest asbestos mine and several talc mines [*Castonguay and Tremblay*, 2003], both of which are hydrous magnesium silicates that are often associated with carbonates and easily hydrolyzed to release HCO_3^-. The fact that 9 of the 10 catchments with DIC export of more than 6.6 g m^{-2} yr^{-1} are in the Humber zone (except the stream outflowing Lake Nick) further highlights the importance of carbonate and silicate rocks in controlling riverine DIC export from the catchment. DIC export also increased with building density. Buildings and their residents are not point sources of DIC, but higher building density usually results in land clearing and road construction, causing an anthropogenic increase in erosion and therefore DIC export from soils. This positive effect is strongly supported by previous studies [*Daniel et al.*, 2002; *Barnes and Raymond*, 2009; *Zeng et al.*, 2011].

Basin shape index, BSI, also played a significant role in controlling DIC export. The greater the departure from a circular basin (BSI $>$ 1.0), the less DIC is exported. This negative relationship may be due to hydrological pathways being more convoluted in basins with more complex shapes. For example, circular catchments are more prone to flooding than elongated ones [*Waugh*, 1995; *Rasool et al.*, 2011], leading to higher erosion and flushing out of various forms of terrestrial DIC.

4.1.2. Drivers of DOC Export

The two variables that explained most of the variation in DOC export were %lake and %wetland. Basins containing more lakes exported less DOC, which highlights the role of lakes as sinks of terrestrially derived organic matter [*Larson et al.*, 2007]. Temperate and boreal lakes accumulate large amounts of terrestrial C in their sediments [*Ferland et al.*, 2012; *Tranvik et al.*, 2009] and also decompose and emit a portion of this terrestrial DOC as CO_2 and CH_4 [*Larson et al.*, 2007; *Dinsmore et al.*, 2013]. Although the catchments in this study did not contain many wetlands (maximum 9% coverage), wetlands still played a role in shaping DOC export, as has been reported for other regions [*Eckhardt and Moore*, 1990; *Dillon and Molot*, 1997; *Huntington and Aiken*, 2013]. These two land cover variables are susceptible to anthropogenic and climate change through drainage, damming, and changes in the hydrologic regime. Therefore, changes to the amount and extent of wetlands and lakes in a watershed will affect two important sources and sinks of DOC and thus the movement of terrestrial C into the aquatic system and the atmosphere.

We found that DOC export was also correlated with %vegetation and BSI, but the direction of the correlation was opposite of that for DIC export, highlighting the independent nature of DOC and DIC exports (Figures 1 and 3). Although the presence of vegetation lowered DIC export, it increased DOC export in these basins, which agrees with previous work [*Meyer and Tate*, 1983; *France et al*., 1996]. The positive relationship between DOC export and %vegetation reflects the fact that most riverine DOC is ultimately derived from land vegetation (via direct litter input and leaching) and soils (via microbial activity, root exudation, leaching, and erosion of organic matter) [*Spitzy and Leenheer*, 1991]. The influence of BSI on DOC export was opposite to that on DIC export, with elongated more complex high BSI basins exporting more DOC than round, less complex low BSI basins. Similarly, *Pacific et al*. [2010] showed that a more elongated basin often has a higher ratio of riparian to upland area and can export more DOC to river systems. As mentioned above, larger catchments exported more C, but in this region, larger watersheds were also characterized as having a lower average slope ($R^2 = 0.17$, $p = 0.0001$, $n = 83$) and lower average elevation ($R^2 = 0.08$, $p = 0.0080$, $n = 83$), although these correlations are weak. Once entered into a multiple regression with catchment area as a factor, elevation had no effect on C export; however, watersheds with a flatter average slope exported more DOC and TC, independent of the effect of catchment size. Gentler slopes facilitate wetland formation, leading to more DOC production and export [*D'Arcy and Carignan*, 1997], and also have longer water residence times, allowing more time for soil DOC to leach into soil water and neighboring waterways [*Hazlett et al*., 2008; *DeCatanzaro and Chow-Fraser*, 2011].

4.1.3. Drivers of TC Export

We were able to explain 53% of the variation in total C export using two topographical variables, catchment area and slope, and one land cover variable, %wetland. The positive effect of catchment area on both DIC and DOC exports results in a similar influence on TC export, likely through its effect on discharge, as discussed above. The negative effect of slope on DOC was strong enough to result in a negative effect on TC export, explaining 8% of its variability, despite the lack of a relationship between slope and DIC export. Similarly, the effect of increasing TC export with increasing wetland coverage arose solely because of the important role of wetlands in controlling DOC export, as wetlands did not play a role in DIC export. This land cover feature of the catchment explained 29% of the variability in TC export. In contrast, although BSI and %vegetation played important roles in both DIC and DOC exports, they acted in opposite directions on the two C species, and as a result, they had no overall impact on TC export. As we observed for DIC and DOC exports, TC export is influenced by a combination of topographic and land cover effects, explaining 24% and 29% of its variability, respectively. Because the drivers of DIC export and DOC export are quite different, the model of TC export provides a simplified summary of what influences the movement of terrestrial C to aquatic systems, while hiding the complexity of what influences the movement of individual C species.

Despite there being evidence in the literature for the effect of soil type and geology on C export, these factors did not emerge as significant drivers in our watersheds. We used maps of geology and soil to divide the catchments, based on areal percentages (Table 1), into three mutually exclusive categories of rock type (intrusive, sedimentary, and volcanic) as well as three mutually exclusive categories of surficial deposits (rock, till, and mud) and five mutually exclusive categories of soil (brunisolic, gleysolic, regosolic, podzolic, and organic). We found one potential model of DIC export that incorporated the percent coverage of sedimentary rocks and rocky surficial deposits, but it is unclear why DIC export would decline with increasing presence of sedimentary rocks and rocky surficial deposits. In addition to explaining only a marginal 4% more of the variability in DIC export than the model in Table 2, it required removing BSI as an effect and removing one outlier site, and so this model was considered less appropriate for these catchments. There were no potential models for DOC or TC export that incorporated geology or soil. In summary, we did not find that geology or soil type played very important roles in controlling DIC, DOC, and TC exports from the landscape.

4.2. Influence of Land Cover on the Forms of Carbon Exported

Although vegetation coverage did not play a significant role in total C export, it did have an impact on the actual nature of this export. We used the models in Table 2 to project total C export and its partition into DIC and DOC exports, under scenarios of changing land use in terms of %vegetation, for two of our basins (Figure 6). In the case of the basin that drains into Lac d'Argent, which currently has 92% vegetation coverage, reducing the vegetation coverage to 40%, for example due to agriculture or urbanization, would result in an 11% decrease in C export from the basin (as DIC + DOC) (our test using DIC + DOC, instead of DIC + 1.1*DOC, as TC export showed the same result, although the coefficients are slightly different) but a threefold increase in the DIC/DOC export ratio, from 0.8 to 2.2. The reduction in vegetation coverage would thus cause a shift in this basin from a system that exports most of its terrestrial C as DOC to a basin that exports mostly DIC. Conversely, for an inflow of Roxton Pond, which currently drains a watershed that is 57% vegetated, increasing the vegetation coverage to 100% would result in only a 9% increase in C export, while the DIC/DOC export ratio would be reduced to half, from 1.1 to 0.5 (Figure 6). In this case the watershed would shift from exporting equal amounts of DIC and DOC to exporting mainly DOC. Land use change that modifies vegetation coverage, such as deforestation or reforestation, would therefore have a modest effect on total C export but would greatly alter the form of C exported. Although deforestation is widely regarded as one of the most common anthropogenically driven land cover changes, especially in developing countries [*Nagendra*, 2007], many of the temperate regions in eastern North America and western Europe have been undergoing reforestation due to a decline in agriculture [*Rudel*, 1998; *Intergovernmental Panel on Climate Change*, 2013]. As DOC and DIC are processed differently in aquatic systems, changes in the form of terrestrial C exported will lead to changes in the fate of this C, with DOC being more likely to be mineralized and released to the atmosphere as CO_2 and CH_4 than DIC, which may be transported downstream in a more conservative manner. To summarize, reductions in vegetation coverage will shift the C export to favor the inorganic rather than the organic forms of C, potentially leading to the terrestrial C being transported further downstream rather than being released to the atmosphere through biological processes in the aquatic system.

4.3. Interannual Variation in Carbon Export

The differences in C export observed in 32 basins over three consecutive years were likely driven by interannual variations in temperature and precipitation, causing interannual variations in stream discharge (Table 3). Export of both DIC and DOC was about 25% higher in 2005 (at 6.8 and 6.1 $g\,m^{-2}\,yr^{-1}$, respectively) relative to 2003 and 2004 exports (Figure 5). In terms of temperature and precipitation, 2005 was a warm, wet year and 2004 a dry year, as compared to a relatively average 2003. This resulted in the mean daily discharge at the Trois-Lacs gauged site being higher and more variable in 2005 than in the two preceding years (ANOVA $p = 0.0063$, $n = 1096$, 2003 = A, 2004 = AB, 2005 = B). Similarly, at the Waterloo gauged site, mean daily discharge was higher and more variable in 2005 (ANOVA $p = 0.0004$, $n = 1096$, 2003 = A, 2004 = B, 2005 = B). Discharge was therefore significantly higher in 2005 than in 2003, and this likely drove the differences in C export, a pattern that has been previously reported [*Dillon and Molot*, 2005; *Dinsmore et al*., 2013]. As C export is the product of discharge and C concentration per unit catchment area, we also examined interannual variability in concentration. Average DIC and DOC concentrations were highest in 2005 (Table 3), yet there were no significant differences in concentration among years. In other words, variation in C concentration across the 32 sites was more important than variation across the 3 years. Interestingly, at the scale of the individual site, we found a negative effect of discharge on DIC concentration within 31 of our 83 sites (dilution effects; outlined in section 2.2), yet at the regional scale, the highest discharge year (2005) was associated to the highest average DIC concentrations and the highest average DIC export from all sites combined. We suggest that transient increases in runoff and discharge within a catchment may not necessarily lead to increased DIC release from soils, and this may explain the local dilution effects that we sometimes observed. However, a systematic increase in overall precipitation and temperature, and the associated sustained increased in runoff and discharge, may act to increase overall DIC and DOC export on an annual scale.

5. Conclusions

With this study, we not only quantify both DIC and DOC (and therefore TC) exports from a diverse set of temperate watersheds covering 1160 km^2 but also reveal that the topographic and land cover features of this landscape do not influence DIC exports in the same way as they influence DOC exports, yet interannual changes in the climate of the region have a similar impact on both DIC and DOC exports. Since the export of inorganic and organic C is regulated by different factors, the total C export from these temperate watersheds represents an emergent property of the landscape that cannot be derived from either the DIC or DOC export alone. We further show that topography is slightly more important than land cover in explaining the variance in DIC export, whereas land cover is much more important than topography in terms of DOC export. We also show that interannual differences in precipitation and temperature lead to differences in discharge, which in turn influences both DIC and DOC exports, such that regional climate shifts that affect the hydrologic regime will also influence C exports from these catchments.

Carbon export from terrestrial to aquatic ecosystems is controlled by biogeochemical processes that are influenced by both the underlying topography of the watershed and the overlying land cover, which is subject to changes due to natural and anthropogenic drivers. Among the land cover variables that were drivers of C export, building density, %vegetation, and %wetland are easily and frequently impacted by human activities, thus changing the magnitude and composition of riverine C export. The proportion of lakes and wetlands in the landscape plays a role in determining DOC export, highlighting the role of these inland waters, respectively, as sinks and sources of terrestrially derived organic matter. We suggest that human activities or climatic shifts that modify the vegetation cover of these temperate basins will impact not only the total C exported from the basin but more importantly will strongly influence the DIC/DOC export ratio. This has consequences in terms of both the fate of this C and its impact on the receiving aquatic systems, as DOC is more susceptible than DIC to burial in the sediments and degassing to the atmosphere as CO_2 or CH_4. Although we show that topographic variables such as basin area, slope, and shape influenced C export in this study, these features of the landscape are stable relative to the land cover, implying that anthropogenic impacts would be the driving forces for changes in C export.

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