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Long-term trends in catchment organic carbon and nitrogen exports from three acidified catchments in Nova Scotia, Canada

T. A. Clair · I. F. Dennis · R. Vet · H. Laudon

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Abstract We sampled two streams in southwestern Nova Scotia from 1983 to 2004 and one stream from 1992 to 2004 for total organic carbon (TOC) and nitrogen (TN) in order to investigate if changes in catchment exports could be determined over the sampling periods, and if so what were the controlling factors. We first show that early TOC measurements underestimated concentrations due to analytical shortcomings and then produce a correction to adjust values to more accurate levels. Our trend results showed that TOC concentrations decreased in the two streams with the longest record, from 1980 to 1992 when acid deposition to the area decreased most rapidly, and have remained constant since then. TOC exports only decreased at one site over the total sampling period. As expected, we also measured seasonal changes in exports, with the autumn period showing TOC and TN exports as high as during spring snowmelt. We found that only 24% of deposition N is

exported from the larger catchments, most of it in organic form, while the smallest catchment exported 16%. We also show a constant increase in TN from 1994 to the present at all three sites sampled. Our results do not support the hypothesis that reductions in sulfur acidification lead to increases in catchment organic carbon mobilization to streams.

Keywords TOC · TN · Streams · Exports · Nova Scotia

Introduction

Freshwater organic carbon (OC) is implicated in a number of lake and river chemical reactions as well as in the global carbon cycle. Freshwater OC can control water acidity (Oliver et al. 1983), metal toxicity (Horne and Dunson 1995), and can protect plankton from ultraviolet radiation (Kaczmarska et al. 2000). Moreover, rivers and streams transfer large amounts of carbon from terrestrial catchments into estuaries and oceans and thus play an important role in marine ecological processes (Opsahl and Benner 1997) and the global carbon cycle (Hope et al. 1994).

Recent work has suggested that there is a consistent increase in OC exports from many river catchments in Europe and North America. Worrall et al. (2004) showed dissolved organic carbon (DOC) concentration increases at a large number of lakes and rivers in the United Kingdom (UK) though they were

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unable to ascribe a cause to these changes. Findlay (2005) also reported increases in DOC exports from the Hudson River in New York State, USA. He theorized that increases in N deposition may be modifying soil organic chemistry, producing more refractory DOC which is then exported from catchments.

Another theory attempting to explain the measured DOC increases was proposed by Evans et al. (2006) who suggested that decreases in acid deposition could be responsible for the DOC increases measured in the UK streams and lakes over the last 10 years. They propose that decreases in sulfur deposition lead to increases in soil organic carbon solubility and thus to increased release to surface waters. Roulet and Moore (2006) have taken a larger view of the issue of DOC changes and have pointed out that it is unlikely that only one factor controls DOC production, and that organic carbon exported from catchments are caused by inter-linked, multiple processes which are more difficult to quantify.

Organic nitrogen (ON) is closely linked to OC, as it also originates from degraded plant matter. As acid nitrogen deposition can be a large component of total rainfall chemistry, and as it is involved in a large number of biological processes it is thus important to know how much is transferred out of catchments, and the factors that may control this transfer.

Because of the role of organic C and N in so many ecological and geochemical processes, it is important to assess how concentrations and exports change over time and to get a better understanding of their controlling factors. In this study we measured trends in organic C and N concentrations and exports from catchments located in a cool temperate region of eastern Canada. We analysed stream chemistry data from three sites, collected over a 26 year sampling program (1980–2005) at Kejimikujik National Park (KNP), located in southcentral Nova Scotia, Canada. The region's surface waters drain abundant wetlands and many streams and lakes have high OC concentrations. Sulfur deposition in this region has decreased by approximately 45% since the early 1980's, while nitrogen deposition has remained relatively unaltered (Clair et al. 2002). If there were changes, then we attempted to understand if these could be related to changes in climatic variables or to the reductions in acid sulfur deposition which have occurred in the study area.

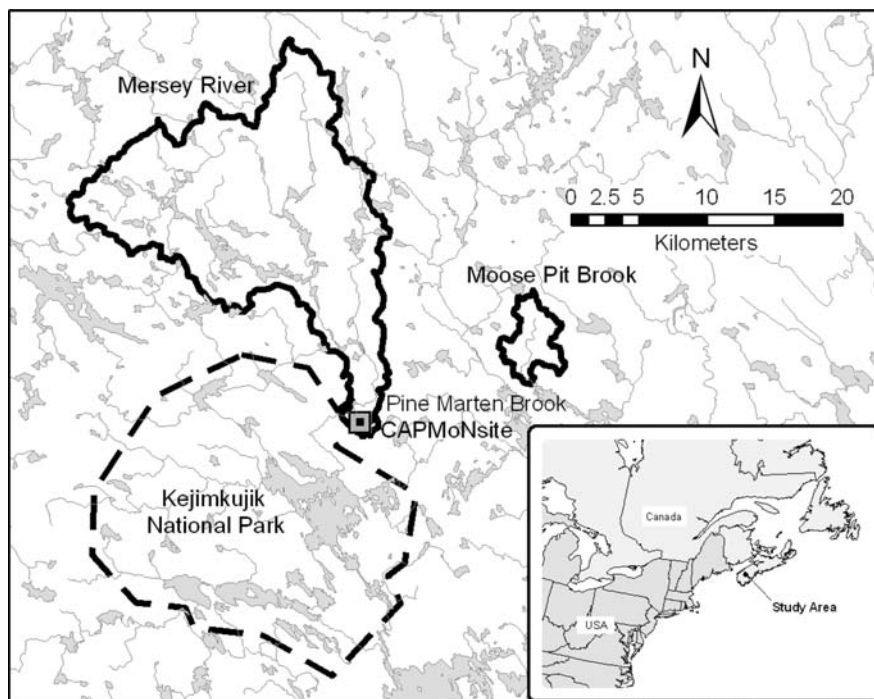
Study area

We sampled three streams located in the KNP area of southwestern NS (Fig. 1). The Mersey River (MR) is a 4th order river, draining a 297 km² area which is mostly composed of coniferous forest with some hardwood stands. Moose Pit Brook (MPB) is a 1st order, 17 km² basin with a forest type similar to the Mersey's. Pine Marten Brook (PMB) drains a 1.3 km² area composed of mixed hardwood and conifer stands. The basins are little influenced by human activity, though some logging is carried out in the MR and MPB catchments. A paved secondary highway crosses the Mersey River catchment 1 km above the sampling site. The bedrock in this region is either granite or slate, both of which are resistant to weathering, thus resulting in low buffering capacity of the catchment soils. Because of recent glaciation (~15 k years), soils are generally thin (<1 m average) and provide poor plant growing conditions (Yanni et al. 2000a).

KNP is in a region with a cool, temperate climate with mean annual precipitation during the study period of 1,352 mm (Fig. 2), 56% of which occurred between November and April. Annual snow amounts averaged 169 mm water equivalents, approximately 18% of total precipitation. Total measured runoff averaged 960 mm per year, so that approximately 30% of precipitation was lost through evapo-transpiration processes. Because of the sites' proximity to the Atlantic Ocean, rain also occurs during the winter when soils are frozen and snow covered (Laudon et al. 2002).

Wetlands occupy less than 1% of the surface area in the basins (Yanni et al. 2000a), but as they are mostly located along stream edges, they cause mean annual stream DOC concentrations values of 10.0 mg l⁻¹ in MPB, 7.0 at MR and 5.4 at PMB (Table 1). Titrated Gran alkalinity values are often negative at both sites suggesting excess acidity during much of the year (Clair et al. in press). ANC calculated as the difference of the base cations from the acid anions (ANCC) is always positive however, demonstrating the importance of natural organic acidity in these systems. Mean annual stream pH values are low (4.9 at MR, and 4.6 at MPB, and 5.4 at PMB), though there are large seasonal and daily fluctuations driven by changes in the hydrology.

Fig. 1 Locations and relative sizes of the study catchments



Methods

Water sampling and analyses

Samples were collected weekly or better at MR from 1980 and weekly at MPB from June 1983 at hydro-metric gauges operated by the Meteorological Service of Canada (MSC). MSC uses best-fit Stage-Discharge curves to produce flow data. The goal is to have the flow data within $\pm 5\%$ of the S-D curve which is validated through multiple discreet discharge measurements during various hydrological conditions. Weekly sampling was begun in June 1992 at the PMB site where daily runoff was estimated using the For-HyMod hydrological model (Yanni et al. 2000b). The modeling results for the Kejimikujik area are nearly identical to gauge readings on a monthly basis, though high flow events are sometime underestimated (Yanni et al. 2000b).

In order to better evaluate catchment processes, we estimated organic C and N exports on a water year basis, from June to May. Weekly water chemistry values were linearly interpolated between sampling dates and the calculated values multiplied by the measured or estimated daily discharge (Q) to produce daily ion exports (Cohn et al. 1989). These

were normalized to surface area and summed to produce monthly and annual export values. Clair and Jeffries (1992) compared ion export calculations using daily data MR collected in the mid-1980's and simulated the weekly sampling and extrapolation approach and found that weekly sampling overestimated exports by less than 2% over a 2 year period. We therefore assumed that the sampling and extrapolation methods we used were adequate for the task.

Water samples were analyzed using standard procedures at the Environment Canada laboratory in Moncton, New Brunswick. The laboratory is accredited through the Environment Canada Acid Precipitation program intercalibration, as well as through the Canadian Environmental Analytical Laboratory Association (CAEL). Water samples were not filtered, as our experience in these waters showed that particulate matter usually contributed $<5\%$ of organic C and N. The results thus reported are as total organic carbon (TOC) and total nitrogen (TN), though we consider them roughly equivalent to dissolved organic carbon (DOC) and dissolved organic nitrogen (DON). Nitrate was analysed by ion chromatography. Total N was estimated since 1994 using an in-line H_2SO_4 digestion unit followed by UV oxidation with

Fig. 2 (a) Kejimikujik annual precipitation and mean temperature over study period and (b) Annual runoff at the typical Mersey River, as well as S deposition

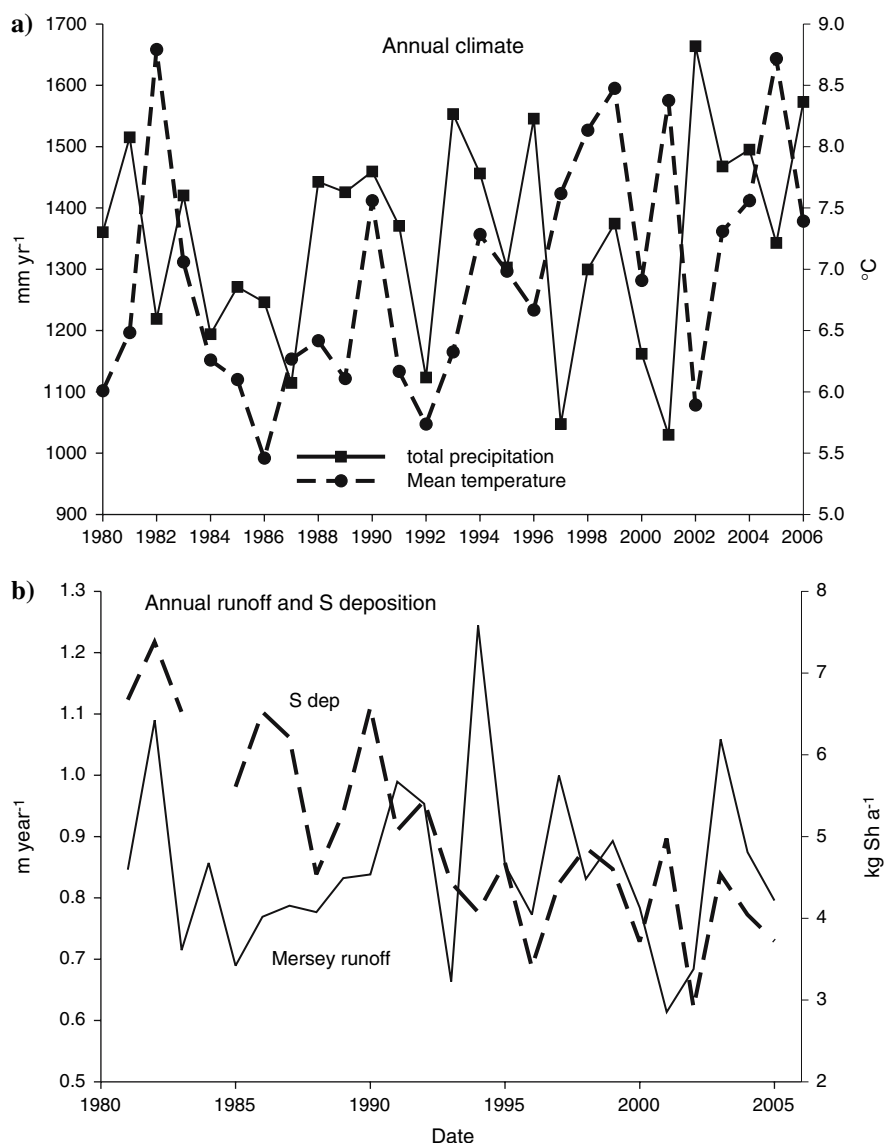


Table 1 Catchment runoff, as well as TOC and TN concentrations and exports

	Mean annual runoff	Mean TOC concentration	Mean annual TOC export	Mean TN concentration	Mean annual TN export
	m	mg l ⁻¹	kg ha ⁻¹ year ⁻¹	mg l ⁻¹	kg ha ⁻¹ year ⁻¹
Mersey	0.85 ± .14	10.7 ± 1.8	84.4 ± 23.8	0.11 ± .09	0.82 ± .21
Moose Pit	0.83 ± .13	17.7 ± 2.4	115.6 ± 30.0	0.12 ± .04	0.78 ± .16
Pine Marten	0.86 ± .21	7.5 ± 3.4	54.5 ± 15.8	0.09 ± .05	0.41 ± .28

TOC data include values uncorrected for the method underestimate from 1982 to 1994. TN concentration and export values are from 1994 to 2005 only

colorimetric analysis of the oxidized and other residual nitrate present. TN was analyzed pre-1994, but values did not pass strict quality control criteria and were thus not used. Trends for TN were therefore only analyzed for the 1994–2005 period when we had dependable data.

The analysis of TOC was also associated with some uncertainty. Before 1994, TOC was analyzed using an automated UV-persulfate wet oxidation method which was shown to underestimate concentrations in seawater (Sharp et al. 1993). This issue was addressed for freshwaters in a method comparison study by Koprivnjak et al. (1995) who showed that the wet oxidation method used by the Environment Canada laboratory underestimated DOC concentrations. Using samples from MR, amongst other sites, Koprivnjak et al. (1995) found that Kejimikujik area samples analyzed using wet combustion methods before March 1995 consistently underestimated TOC by approximately 28% (standard deviation, $\sigma = 8\%$) compared to newer high temperature combustion (HTC) methods (Fig. 3). TOC analyses were therefore changed to a Shimadzu HTC instrument in 1995, in order to produce more accurate data. We then corrected pre-March 1995 values upwards by 28% based on the Koprivnjak et al. (1995) inter-comparison. This correction ensured that underestimated data collected earlier in the study did not

unduly bias the trend assessment by showing unrealistically low TOC exports in the first half of the study. In order to ensure a lower bias caused by the correction factor in our analysis, we also tested the whole data series where the corrected data were reduced by 8% (one standard deviation error reported by Koprivnjak et al. 1995).

There was little inorganic N measured in these stream waters as more than 90% of samples had no measurable NO_3^- (at 0.02 mg l^{-1} detection limit) and no NH_4^+ was ever measured above the detection level of 0.01 mg l^{-1} . Ammonium analyses were thus discontinued early in the program. Because of the inorganic N levels being below detection levels, we found it unacceptable to estimate TON amounts by subtracting NO_3^- and NH_4^+ from TN. We therefore proceeded with the assumption that TN was roughly equal to TON in our interpretation, with the caveat that actual TON values will be slightly lower than those reported as TN.

Sampling precipitation

Wet, dry and total (i.e. wet plus dry) sulfur and nitrogen deposition fluxes were estimated for the study period by the Canadian Air and Precipitation Monitoring Network (CAPMoN) based on measurements at the KNP site. Precipitation amounts and major ion concentrations in precipitation were made daily for all major ions. Wet deposition was calculated as the product of the monthly total precipitation depth times the precipitation-weighted mean precipitation concentration (Vet et al. 1998). DOC was analyzed in precipitation earlier in the program and was found to be at levels too low for detection.

The CAPMoN dry nitrogen deposition measurements were made daily using 3-stage filter packs that measured aerosol NO_3^- as well as gaseous HNO_3 concentrations (Sirois and Vet 1988). Monthly dry deposition fluxes were calculated as the product of an estimated monthly-mean dry deposition velocity times the monthly-mean measured air concentration of each ionic species. A meteorologically-driven resistance model (Brook et al. 1999) was used to estimate the monthly-average dry deposition velocities based on the land use types and aerodynamic resistances calculated at the site. The dry deposition flux of total oxidized N was calculated as the sum of the gaseous HNO_3 and particle NO_3^- fluxes.

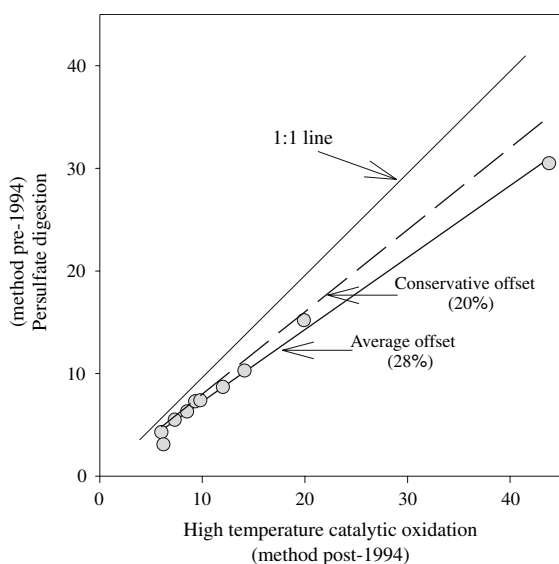


Fig. 3 TOC method intercomparison between older wet reduction and newer high temperature combustion method

Trend analysis

Trend analysis for annual atmospheric deposition, temperature, precipitation, TOC and TN exports and concentrations was done using a modified non-parametric Seasonal Kendall analysis (Loftis et al. 1991). When trends were noted, their slope was calculated from monthly TOC and TN values (Helsel and Hirsch 1992). Trends were analyzed using weekly data for TOC and TN concentrations, while export trends were done on the monthly summed data.

Ehrman and Clair (1995) showed that opposing short-term trends could often be measured within long-term data sets in MR. In order to see if this was still the case with our data set, we analyzed the data two ways. First, we tested for trends for the whole series (Mersey 1980–2005; Moose Pit 1983–2005; Pine Marten 1991–2005) for each site. We then divided the two longest data sets into two parts, based on the TOC analytical method (Mersey 1980–1995 and 1996–2005; Moose Pit 1983–1995 and 1996–2005). Using this approach, we were able to study TOC trends without having to correct for the methodological change, as the methods were internally consistent.

We also tested to see how the use of the TOC correction factor would affect the long term trend results. We therefore tested the whole data series for trends, combining the uncorrected data (to 1995) with the HTC method (post-1995). We then tested the whole series with the pre-1995 data corrected upwards by 28%.

Results

Background conditions

The three catchments showed distinct TOC concentrations and export levels. MPB had the highest concentrations and exports with a mean annual (uncorrected) concentration of 17.7 mg l^{-1} (Table 1). MR mean concentration was 10.7 mg l^{-1} , with PMB having the lowest values (7.5 mg l^{-1}). Despite their TOC concentration differences, TN values were very similar in MPB and MR, at 0.12 and 0.11 mg l^{-1} while PMB values were lower at 0.09 mg l^{-1} . TN exports reflected the concentration values (Table 1).

Mean annual TOC exports (using data corrected for the method underestimate) were 92.5 kg ha^{-1}

($\text{SD} \pm 17.7$) for MR, $129.1 (\pm 22.6)$ for MPB and $55.6 (\pm 14.7)$ for PMB, showing the relative importance of wetlands in each catchment for the production of organic matter (Table 1). The relationship between runoff and TOC generation varied between sites with MPB almost consistently showing the greatest annual TOC yield of the three and PMB the least.

Nitrogen exports from both MR and MPB were 24% of deposition, while only 16% of deposited N was exported from PMB (Table 1). Over the 12 year period for which we had dependable data, there were no significant differences in TN exports between MR and MPB, even though MR TOC export was 27% lower than MPB. Exports averaged $0.82 \text{ kg ha}^{-1} \text{ year}^{-1} (\pm 0.21)$ from 1994 to 2005 at MR and 0.78 at MPB (± 0.16), while PMB exported $0.56 \text{ kg ha}^{-1} \text{ year}^{-1} (\pm 0.17)$ over the same period. N export patterns were similar at the MR and MPB catchments, suggesting similar N processing by their soil-plant systems. The greater N retention in PMB suggests that the soil-plant assemblages more efficiently processed N deposition.

Annual precipitation (Fig. 2a), which controls runoff and thus is a major factor in exports, averaged 1.34 m and showed no trend between 1980 and 2005. Nor did it show any trends when it was divided into two time windows: 1980 to 1995 and from 1996 to 2005. The stability in precipitation was reflected in runoff, as there were no trends detected at the two measured sites (Fig. 2b) either overall or in the two time windows used. Mean annual runoff was 0.85 and 0.83 m at the gauge sites and 0.86 from the modeled catchment (Table 1).

Over the 25 year period, the temperature increased in the study region by 0.07°C per year ($p = 0.006$), though this trend was not measurable when the data set was split into two (Fig. 2a, Table 2). The temperature increase therefore seems to have been gradual, but highly significant over the complete study period.

Acid deposition showed a very strong decrease of $0.12 \text{ kg ha}^{-1} \text{ year}^{-1}$ ($p = 0.002$) over whole the study period (Fig. 2b). An assessment of trends of the two time windows however, shows that most of the reduction in deposition occurred from 1980 to 1995 ($-0.43 \text{ kg ha}^{-1} \text{ year}^{-1}$, $p = .03$) with no detectable change after that period. Overall, the area has then been affected by a significant reduction in sulfur

Table 2 Concentration and export trend analysis results for the three sites

	TOC				TN			
	Uncorrected concentration	Corrected 28% concentration	Corrected 20% concentration	Uncorrected export	Corrected 28% export	Corrected 20% export	Concentration	Export
Mersey	mg l ⁻¹ year ⁻¹	mg l ⁻¹ year ⁻¹	mg l ⁻¹ year ⁻¹	kg ha ⁻¹ year ⁻¹	kg ha ⁻¹ year ⁻¹	kg ha ⁻¹ year ⁻¹	mg l ⁻¹ year ⁻¹	kg ha ⁻¹ year ⁻¹
1980–2005	ns	-0.1, $p = 0.04$	-0.04, $p = 0.05$	ns	-0.08, $p = 0.02$	-0.05, $p = 0.05$	No data	No data
1980–1994	-0.25, $p = 0.06$	Not applicable	Not applicable	ns	Not applicable	Not applicable	No data	No data
1995–2005	ns	Not applicable	Not applicable	ns	Not applicable	Not applicable	+0.0031, $p = 0.015$	ns
Moose Pit								
1983–2005	ns	-0.25, $p = 0.008$	-0.15, $p = 0.05$	ns	ns	ns	No data	No data
1983–1994	-0.58, $p = 0.05$	Not applicable	Not applicable	ns	Not applicable	Not applicable	No data	No data
1995–2005	ns	Not applicable	Not applicable	ns	Not applicable	Not applicable	+0.003, $p = 0.002$	+0.003, $p = 0.01$
Pine Marten								
1991–2005	ns	ns	ns	ns	ns	ns	No data	No data
1995–2005	ns	Not applicable	Not applicable	ns	Not applicable	Not applicable	+0.0026, $p = 0.005$	ns

The TOC columns are for uncorrected 1980–1994 concentrations as well as 1980–1994 values corrected by 28% and by 20%. The TN columns are for concentrations and exports. The values in boxes indicate the slope and direction of a significant trend and the p value indicates the significance level of the slope. ns indicates no significant slope

deposition, a slight increase in annual temperatures and no change in precipitation and runoff.

TOC and TN trends

Statistical analysis showed that over the study period, TOC concentrations showed no trends in MR and MPB when the 1980–1995 uncorrected data was used (Table 2, Fig. 4). When the completed data set was analyzed, including corrected pre-1995 values, as well as the more conservative correction (average offset minus one standard deviation) +28% and +20%, respectively, negative TOC concentration trends were estimated for the whole sampling period at MR ($-0.1 \text{ mg TOC l}^{-1} \text{ year}^{-1}$, $p = 0.04$) and MPB (-0.25 , $p = 0.008$) (Table 2, Fig. 5). When we only assessed trends from 1980 to 1995, where only one consistent analytical method was used, and thus no ambiguity from a method change, decreasing trends of -0.25 and $-0.58 \text{ mg TOC l}^{-1} \text{ year}^{-1}$ ($p = 0.06$ and 0.05) were measured at the two sites. No concentration trends were measured from 1996 to 2005 at any site. The PMB series was too short to provide any trends in TOC concentration data.

Analysis of TOC export trends revealed a different story. As with concentrations, no trends were detected in TOC exports using uncorrected data at any site (Fig. 6a, Table 2). Use of the average correction factor showed significant TOC export trends in only MR over the whole data record ($-0.08 \text{ kg TOC ha}^{-1} \text{ year}^{-1}$, $p = 0.02$). When divided into 1980–1995 and 1996–2005, no trends were measurable at MR. There were no trends measured in the other two catchments over their complete or partial time series (Table 2).

From 1994 to 2005, TN concentrations increased by $+0.003 \text{ mg l}^{-1}$ ($p = 0.015$) at MR, $+0.003 \text{ mg TN l}^{-1}$ ($p = 0.002$) at MPB and also by 0.003 mg l^{-1} ($p = 0.005$) at PMB (Fig. 7). TN exports on the other hand, showed no trends at MR and PMB during the time series, and showed a significant increase of $0.003 \text{ kg TN ha}^{-1} \text{ year}^{-1}$ at MPB (Fig. 6b).

Our analysis showed large seasonal differences in TOC yields between the sites (Fig. 8a). Two TOC export peaks were evident at the three sites, in the autumn during fall rains and in the spring during snow melt period. In the fall, the smaller two catchments (PMB and MPB) exports peaked in November, while the much larger MR peaked in December, due

to the summation of a large number of smaller catchments within the larger one. The fall peaks are due to high rainfall amounts which usually occur in this region during November. In the winter-spring period, PMB peaked in March, while the other two sites peaked in April and the catchment summation effect did not seem to be as important when soils were frozen. Over the course of the year, TOC export amounts were somewhat similar at the three sites during baseflow periods from June to August. The greatest TOC yield differences occur between the sites in the late summer and during fall, when rain washes out soil organic matter which was made available during the warm summer months. Monthly TN exports showed the same patterns as TOC (Fig. 8b).

Discussion

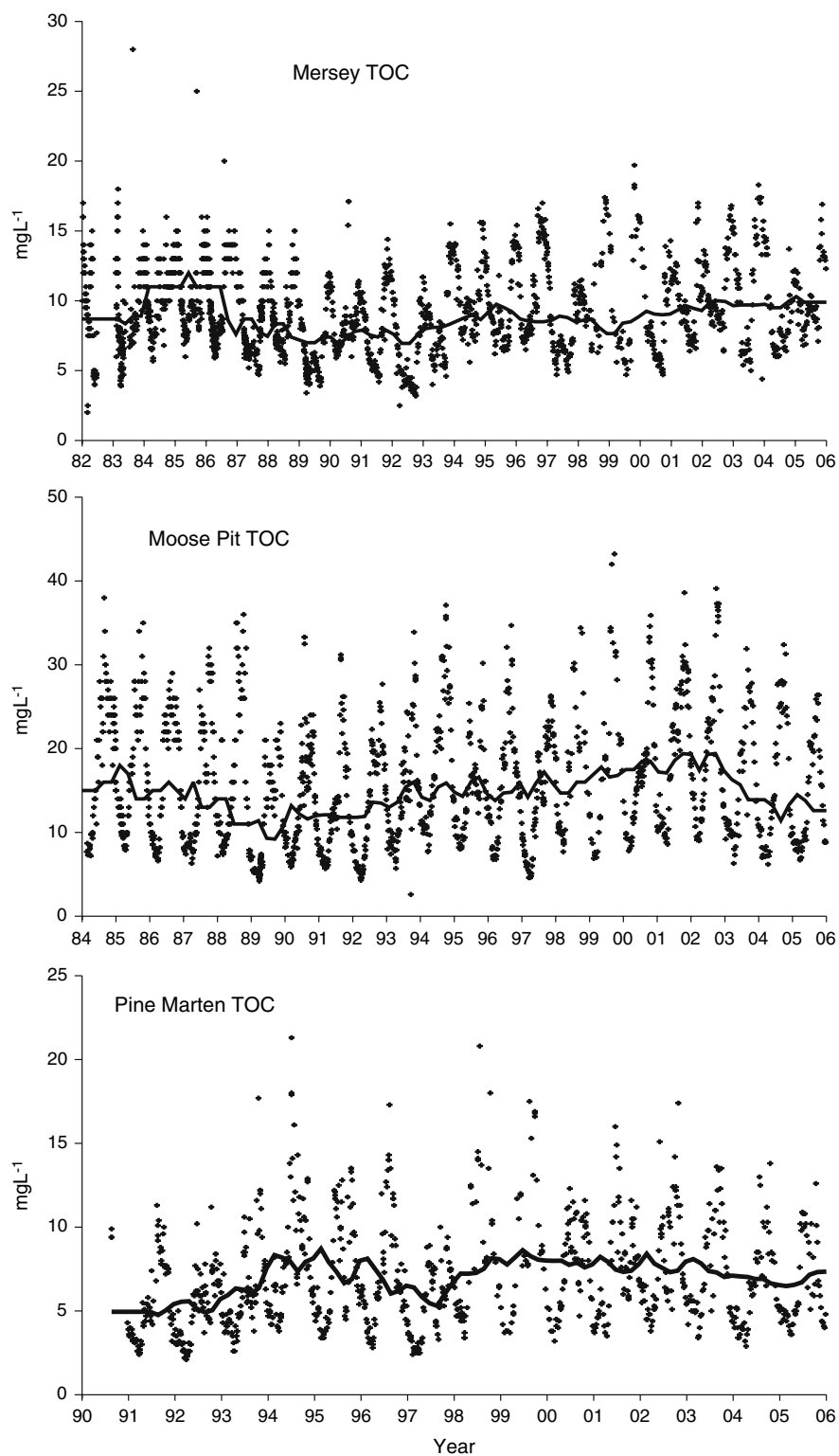
Total organic carbon

Moose Pit Brook exported 23% more TOC per hectare than the Mersey River and 55% more than PMB over the study period. These export differences can be ascribed mostly to the influence of wetlands and thus soil carbon which is controlled by topography (Aitkenhead-Peterson et al. 2005; Clair et al. 1994). Our measured TOC exports were high compared to smaller streams from other regions in temperate North America. MR and MPB export values are higher than those reported by Campbell et al. (2004) as well as those measured by Cronan et al. (1999) for a number of New England streams and by Hinton et al. (1997) for central Ontario.

We report on trends from 25, 22 and 13 year continuous TOC records and an 11 year TN data set. We identify the fact that we faced a problem of interpretation of the statistical results because of changes in TOC analytical methodology. We were able to correct the early, inaccurate data using a published approach (Koprivnjak et al. 1995), but the use of this correction did not affect our conclusion that TOC concentrations in our study streams decreased in the early part of the study. The use of the correction does tend to make an assessment of long-term (>20 years) more questionable however.

When splitting the data into two time windows, within which consistent analytical approaches were used (i.e. no data correction), we show a measurable

Fig. 4 TOC concentration at the Mersey River (top), Moose Pit Brook (middle) and Pine Marten Brook (bottom) (no correction of pre-1995 data). Dark line is the smoothed median



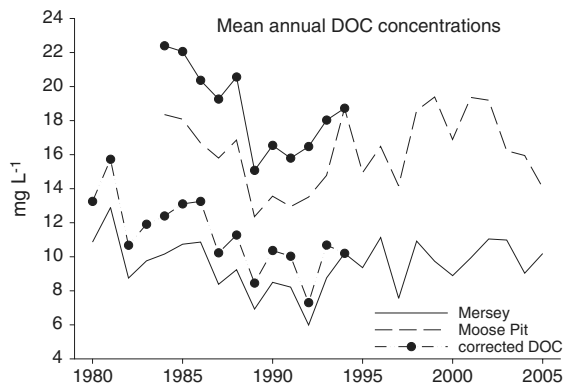


Fig. 5 Smoothed TOC concentration median lines showing the difference caused by the 28% correction factor for pre-1995 data

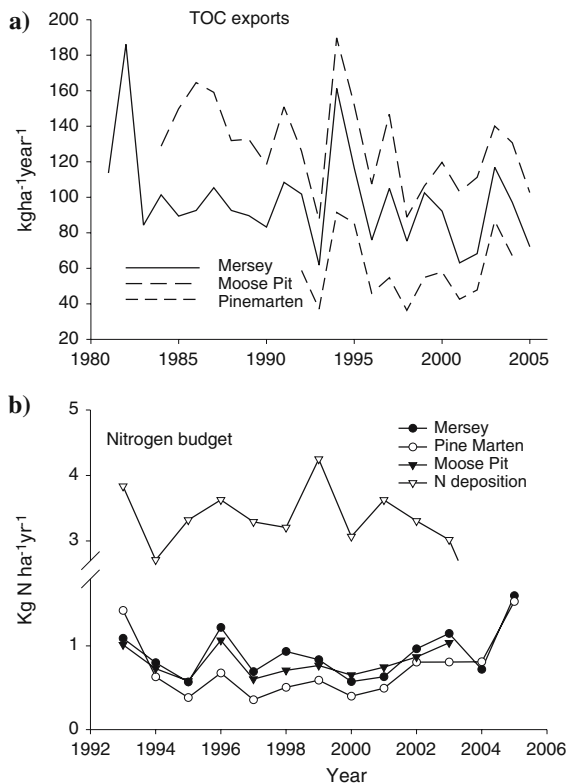


Fig. 6 Annual TOC (a) and TN (b) exports at the three catchments. Total N deposition is also plotted in (b)

decrease in TOC concentrations from 1980 to 1995 at both MR and MPB. We were not able to detect any TOC trends from 1995 to 2005 at any site, suggesting that some equilibrium had been achieved after recovery from an earlier disturbance. These data therefore show that the TOC concentration decreases happened

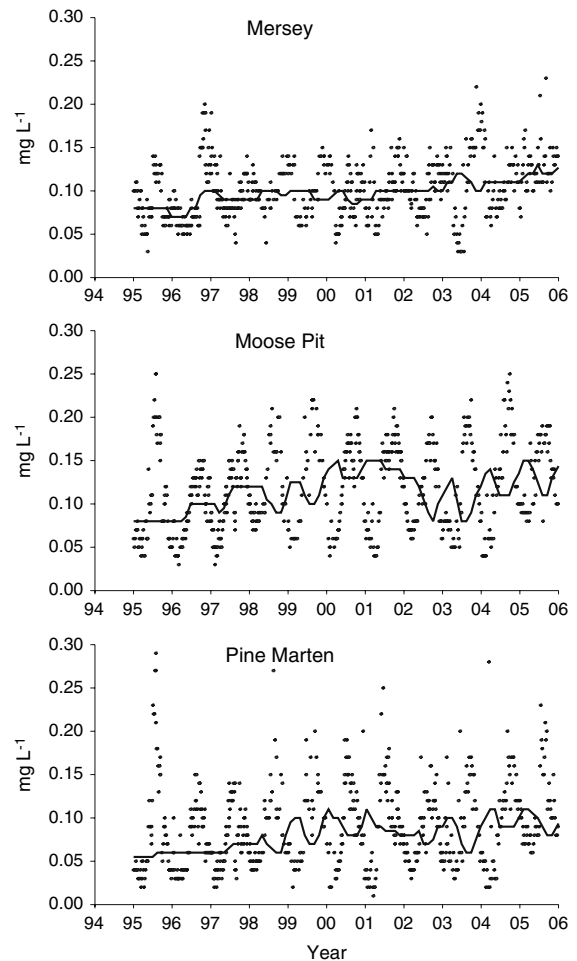


Fig. 7 1994–2005 TN concentrations at the study sites. Dark line is the smoothed median

in the 1980s when most of the acid deposition reduction occurred. The lack of trends from 1995 to the present at MR and MPB, as well as the lack of any TOC trends at PMB suggests that TOC concentrations have been stable over the past decade. This result contradicts the hypothesis that a decrease in sulfur driven acidification would lead to an increase in TOC, as the opposite result happened at the time of greatest deposition decrease at the two catchments with long data sets.

The decrease in TOC concentrations measured at two of the three catchments was only translated into a decrease in TOC export at the MR catchment from 1980 to 2005, which was calculated using a combination of corrected and HTC data (Table 2). No detectable TOC export trends were measured at any other site or time period. When the effect of runoff is

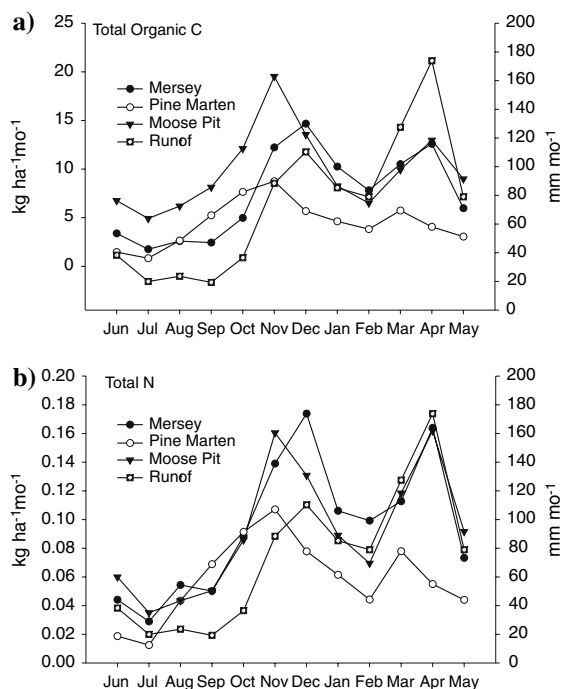


Fig. 8 Monthly TOC and TN exports at the Mersey and Moose Pit sites compared to Mersey runoff

factored into the export correction, it seems that whatever caused the decrease in concentration did not affect the annual flushing out of organic carbon from MPB, even though MR showed significant trends. It could be that the addition of runoff into the equation increases the variability in the data set, making the detection of trends more difficult.

Because of changes in laboratory methodology in Europe and North America, there seem to be very few long-term DOC data sets available made using a consistent method. For example, the longest sets reported by Worrall et al. (2003) were actually made using water colour measurements to which a correction factor based on statistical relationships between it, and modern DOC was made and acknowledge the difficulties inherent in this approach. Findlay (2005) also corrected values to measure DOC trends in the Hudson River of New York State (USA). He used a low temperature, wet oxidation method from 1988 to 1993 and a HTO method after that time. He inter-calibrated the instruments for a full year, corrected the earlier data and then showed an increasing DOC export trend with his corrected data. Both these examples, plus ours serve the point that some compromises and corrections are needed when assessing long-term

DOC trends, but that the approaches have to be strictly documented.

Worrall et al. (2003, 2004) found that of the 169 United Kingdom river sites for which they had historical data, 77% showed increases in TOC concentrations, while 23% showed no changes. They found that they could not correlate the TOC increases with annual precipitation and acidification, but were able to find some links with increases in summer temperature and the increasing frequency of drought. Evans et al. (2006) however, argue that changes in DOC solubility caused by decreasing sulfur deposition may be the cause of the concentration increases. However, another study (Palmer et al. 2004) found that DOC concentrations in Hubbard Brook (NH, USA) forest soils decreased concurrently with decreases in acidification, which should lead to decreases in stream DOC, similar to those that we measured.

A changing climate, as hypothesized by Worrall et al. (2004) is another potential cause of long-term TOC export change. Clair et al. (1994) and Schiff et al. (1998) show that as a rule, the greater the water flow through a catchment, the greater will be its export of organic C and N. This concept is also supported by models which successfully predict soil DOC generation and transfer to streams (e.g. Futter et al. 2007; Hornberger et al. 1994) using temperature and moisture as variable inputs. As in much of temperate North America and Europe, there are large inter-annual changes in precipitation in Nova Scotia (Fig. 2), but no long-term trend in this variable was noted at KNP. The small increase in annual mean temperature over the whole of the study period could play a role in increasing TOC formation by increasing plant and microbial activity, but this could not be seen in our data. Nevertheless, our TOC concentration trends contradict the Evans et al. (2006) hypothesis suggesting increasing TOC with decreases in S deposition.

The analysis of what controls TOC formation and transfer from soils into streams, is complex and is probably driven by more than one factor, as was pointed out by Roulet and Moore (2006). We hypothesize that changes in climate are the most likely driving force for our TOC concentration trends in the early part of our record, even though no statistical link could be made. It is clear however, that a better understanding of factors driving TOC exports will require more in-depth analysis of the soils themselves

as well as the use of models such as INCA-C (Futter et al. 2007) to determine what processes are most relevant in the catchment soils.

TOC (and TN) exports were seasonally variable as there were two export peaks coinciding with autumnal water flushing and spring snowmelt (Fig. 8) with the two export pulses being roughly equivalent. A more thorough assessment of the fall period than we were able to produce, may be key in understanding what controls potential long term changes in exports and concentrations as organic matter flux is mostly controlled by plant decomposition and soil water changes in the summer. Spring pulses on the other hand are mostly determined by the volume of snowmelt waters washing the catchment soils (Agren et al. 2007), so that long-term changes in TOC exports not caused by increases in winter-spring runoff will have to be driven by summer processes. High C and N export levels in the fall as well as in the spring have been documented for temperate regions. The KNP seasonal pattern is similar to what was reported by Cronan et al. (1999) for catchments in northern Maine, by Hinton et al. (1997) in central Ontario and by Laudon and Bishop (2002) in central Sweden.

Total nitrogen

TN export values at MR and MPB tracked each other very closely despite the differences in TOC exports from these two catchments (Fig. 6). They did not track runoff as closely as did TOC, and did not mirror N deposition patterns. Twenty four percent of the total deposited N was exported from either MR or MPB, decreasing to 16% for PMB. Ito et al. (2005) show that landscape features, hydrologic flowpaths, and retention in ponded waters, regulate the loss of N solutes through drainage in catchments in northern New York State watershed ecosystems, and this is clearly the case with our sites.

Kejimikujik TN concentrations results showed identical, significant, increasing trends at all three streams from 1994 to 2005. MPB also showed TN export increases over that period. These results were not matched by increases in TOC, nor could they be related to changes runoff or precipitation, but may be related to the small increase in temperature measured at Kejimikujik. This increase cannot be easily explained by the information we have at hand, but

may be an important indicator of changing ecosystem function and needs to be followed up.

Our study catchments export comparatively little N compared to other parts of North America. In north-eastern North America in particular, measured N exports were four times greater in Vermont than our mean value of $1.1 \text{ kg ha}^{-1} \text{ year}^{-1}$, though N deposition was also four times greater than at KNP (Campbell et al. 2004). Similarly, Boyer et al. (2002) measured N exports of $3.2\text{--}4.0 \text{ kg ha}^{-1} \text{ year}^{-1}$ from catchments in nearby northern Maine, USA. Goodale et al. (2000) reported DON exports of $0.7 \text{ kg ha}^{-1} \text{ year}^{-1}$ from sites in central New Hampshire, but these were accompanied by NO_3^- values of $1.4 \text{ kg ha}^{-1} \text{ year}^{-1}$, so that their TN values were roughly twice those of KNP.

Our results and those of the other studies support the work of Perakis and Hedin (2002) and Petrone et al. (2007) who suggest that most N loss from unpolluted catchments is in the organic form, as opposed to inorganic which is more prevalent under heavily polluted conditions. Wright et al. (2001) also confirm this supposition, as they find that nitrate concentrations in stream waters were related to the amount of N deposition at the catchment. They found that sites receiving less than $10 \text{ kg N ha}^{-1} \text{ year}^{-1}$ deposition have low stream water NO_3^- concentrations, whereas sites receiving $>25 \text{ kg N ha}^{-1} \text{ year}^{-1}$ usually have elevated levels.

On a larger scale, our values are also lower than most of those reported by Lewis (2002) for undisturbed regions of the United States. The only sites with lower values were located in desert catchments, greatly different from the forested conditions of Nova Scotia. Our low TN export results resemble those from the Muskoka region of Ontario, where catchments only exported 20% of the atmospheric N input (Watmough and Dillon 2004) and from Québec where 29% of N was exported of which 67% was in organic form (Duchesne and Houle 2006).

The fate of the N not exported in streams or rivers is clearly of interest and may have some bearing on whether or not N acidification could become a problem to this region in the future. Campbell et al. (2004) found that softwood forests of the northeastern USA are N limited, so that moderate N deposition will not lead to further acidification (except under snowmelt conditions). Moreover, nitrogen

may also be denitrified in catchment soils and thus lost from the system as N_2 gas without contributing to the acidification of the system. Van Breemen et al. (2002) suggest that in the northeastern US catchments, 51% of anthropogenic N is denitrified to N_2 , 20% is exported in water, and the remaining is lost through food and wood exports. Howarth et al. (2006) also propose that denitrification might probably more important in northern watersheds than in southern ones. Though our TN export and concentration results are quite low, they are not unusually so when placed in a larger context.

Conclusions

We show that reductions in TOC concentrations have occurred in catchments of SW Nova Scotia from 1980 to 1995. Since 1995, concentrations have remained stable, contradicting the hypothesis of increasing C with decreasing acid sulfur deposition. We also show that these concentration trends have been matched by TOC exports at one of the two sites with the longest record, though that result is dependent on acceptance of an analytical correction factor. We also show that TN concentrations increased significantly and identically at all three of our sampling sites from 1994 to the present.

Approximately 24% of deposition N in our study region is exported as TN in the two largest streams and 16% in the smallest. Our data and the reports we cite, suggest that the missing N is most likely being denitrified to N_2 and/or incorporated into plant matter. We cannot ascribe the measured changes in concentrations or exports to climatic causes, probably due to the great variability inherent in year-to-year hydrological changes caused by fluctuating precipitation and temperatures. Better assessment of the causes of the change will need in-depth sampling and analysis of soils and the use of soil carbon models.

Finally, though there are measurable trends in concentrations at the sites, these are not always matched by changes in exports which are probably better indicators of catchment organic matter processing. The reasons for the lack of correlation between concentrations and export trends may be because of the extra statistical noise created by the inclusion of runoff in the calculation of exports.

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