Modeling dissolved organic carbon mass balances for lakes of the Muskoka River Watershed

E. M. O'Connor, P. J. Dillon, L. A. Molot and I. F. Creed

ABSTRACT

Changes in the flux of dissolved organic carbon (DOC) into and out of lakes are important to the biogeochemistry of aquatic environments. The ability to estimate or model DOC fluxes and concentrations in lakes and other surface waters is of great benefit for investigations of aquatic systems. Spatial attributes of catchments were derived using GIS techniques and combined with published DOC mass balance models from 20 small study catchments and seven lakes to estimate DOC concentrations for hydrologically connected lakes (i.e. connected by surface or ground waters) of the Muskoka River Watershed, a large tertiary watershed (904 lakes) in southern Ontario. Predicted DOC concentrations were very dependent on the method used to estimate wetland area. When a Rapid Assessment Technique (RAT) was used to estimate wetland area, predicted and observed DOC concentrations were linearly related. Most of the DOC residuals were $< 1\,\mathrm{mg\,L^{-1}}$. Inclusion of riparian wetlands or small lakes in the contributing catchments resulted in a slight improvement of model predictions, but not beyond the variability of the model. Model predictions of DOC were reasonable (according to model fit and residuals), especially considering it was a regional-scale study, but substantial variability was still unaccounted for. Applying the model to other regions with similar landscapes (i.e. other watersheds on the Precambrian Shield in North America and Nordic countries) is feasible.

Key words | dissolved organic carbon, fluxes, mass balance model, Precambrian Shield, wetland

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INTRODUCTION

Dissolved organic carbon (DOC) is a critical component of all freshwater aquatic ecosystems. Changes in the flux of DOC into and out of lakes are important to the biogeochemistry of natural systems because DOC concentrations influence water chemistry parameters and the physical environment, including optical and thermal properties. For example, light penetration into surface waters is changed (Scully & Lean 1994; Molot & Dillon 1997; Lean 1998), which affects primary productivity and heat storage (Perez-Fuentetaja *et al.* 1999). Some trace metals, trace organics and nutrients bind to DOC; their export to lakes is affected by DOC export (Mierle & Ingram 1991) as is their toxicity (Driscoll *et al.* 1995). The ability to estimate or model DOC fluxes and concentrations in lakes and other surface waters is of great benefit for investigations of aquatic systems.

The principal source of DOC to streams, rivers and lakes found in boreal ecosystems is the catchment (Rasmussen *et al.* 1989), particularly wetlands within the catchment (Eckhardt & Moore 1990; Koprivnjak & Moore 1992; Clair *et al.* 1994). Wetlands are areas where the pedology and ecology is changed because the groundwater table is at, close to or above the ground surface, at least periodically (Price & Waddington 2001). Poor drainage and subsequent soil saturation of wetlands leads to accumulation and anaerobic decomposition of natural organic material; eventually DOC is leached into streams (Tan 2003).

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There are four main classes of wetlands in Ontario: swamps, marshes, bogs and fens (Maltby 1986). Swamps are at least seasonally flooded and contain woody plants. Marshes are either saturated or seasonally flooded with water from sources other than direct rainfall (groundwater seepage, stream runoff) and contain grasses and herbaceous plants. Both swamps and marshes may contain appreciable quantities of peat, though marshes in general do not accumulate peat. Bogs are acidic, accumulate peat and are fed by rainfall. Fens are alkaline, accumulate peat and are fed by groundwater. All four classes of wetlands contain deep organic soils that serve as terrestrial sources of DOC to aquatic systems.

The average annual concentration of DOC in streams and lakes has been related to the proportion of wetland area in the catchment (Dillon & Molot 1997*a*; Gergel *et al.* 1999; Creed *et al.* 2003, 2008). However, DOC is also contributed from other terrestrial portions (i.e. forest soils) of the catchment. DOC in soil water percolates through the upper organic soil horizon to the lower horizon and then over bedrock to surface waters. Both horizons contribute DOC to streams through diffuse runoff but the upper soil horizon contributes more because of higher DOC concentrations in the soil water. In the lower horizon, most DOC is mineralized to DIC (dissolved inorganic carbon) (Futter *et al.* 2007).

Models can be used to analyze and explore scientific problems and identify knowledge gaps in processes, rates and parameters. They can be based on a system that has reached steady state, even if there are short-term fluctuations or if the system underwent changes in the past. At steady state, inputs equal outputs and the total pool of a given element inside a compartment of the environment does not change. In reality, few catchment studies conform strictly to steady-state conditions; nonetheless steady-state models are useful to gain insight into biogeochemical processes on an average annual basis.

In previous studies, Dillon & Molot (1997*a*) developed an empirical DOC catchment export model based on peatland area and Dillon & Molot (1997*b*) developed a steady-state lake retention model for Precambrian Shield lakes using measured DOC inputs and outputs. In this study, these two models are used in conjunction with a Geographic Information System (GIS) to estimate DOC concentrations for lakes in the Muskoka River Watershed (MRW), a large tertiary watershed in south-central Ontario, Canada. The GIS based "Lake DOC Model" uses empirical and semi-empirical parameters that describe the variation in DOC retention among lakes within the watershed and uses a spatially explicit tracking system for monitoring DOC movement from DOC production within catchments, to consumption of some of the DOC within a lake, to export of the remaining DOC to downstream lakes and/or rivers. DOC is tracked through each lake in a watershed until its eventual loss at the river mouth.

It is important to have a useful approach to large-scale DOC modeling that incorporates some of the heterogeneity of catchments without becoming overly complicated (Gergel *et al.* 1999). While some processes may become simplified, these simplifications (and/or generalizations) allow for DOC modeling of large watersheds that may suggest hypotheses for future studies. Our model contains these qualities as it links easily determined catchment characteristics with empirical models to estimate DOC budgets.

The goal of this study is to predict DOC concentrations in a series of lakes of the MRW using a mass balance model based on a published relationship between wetland to catchment area ratios and measured DOC fluxes, published DOC loss rates in lakes via sedimentation and degassing to the atmosphere, and hydrology. Specific objectives were to: (1) extend the steady-state integrated catchment-lake models of DOC fluxes in peat-dominated catchments created by Dillon & Molot (1997*a*,*b*) to include hydrologically connected headwater and non-headwater catchments (i.e. connected by surface or ground waters); (2) use the extended model to estimate DOC concentrations for all lakes in the MRW; (3) compare these estimates against observations of DOC concentrations in some lakes in the MRW; (4) evaluate the consistency of the Lake DOC Model across the MRW; (5) perform sensitivity analysis on the model and (6) examine relationships between wetland estimates and lake DOC concentrations.

METHODS

Study area

The Muskoka River Watershed (MRW) is a tertiary watershed located in south-central Ontario, Canada

(Figure 1), within the southern Boreal Ecozone of the Precambrian Shield. The watershed extends across portions of the Districts of Muskoka and Parry Sound and the County of Haliburton. The catchment area is over 5000 km^2 with 904 lakes that drain into the southeastern side of Georgian Bay of Lake Huron. The MRW is composed of three drainage systems: the North and South Branches of the Muskoka River and the Lower Muskoka sub-watershed. The Muskoka River is 210 km long, descending 345 m in elevation.

The MRW is underlain by Precambrian metamorphic plutonic and volcanic silicate bedrock. Topography varies from the rugged highlands of Algonquin Provincial Park in the northeast to rocky knolls and ridges interspersed with thin sandy till in the lower portions of the watershed.

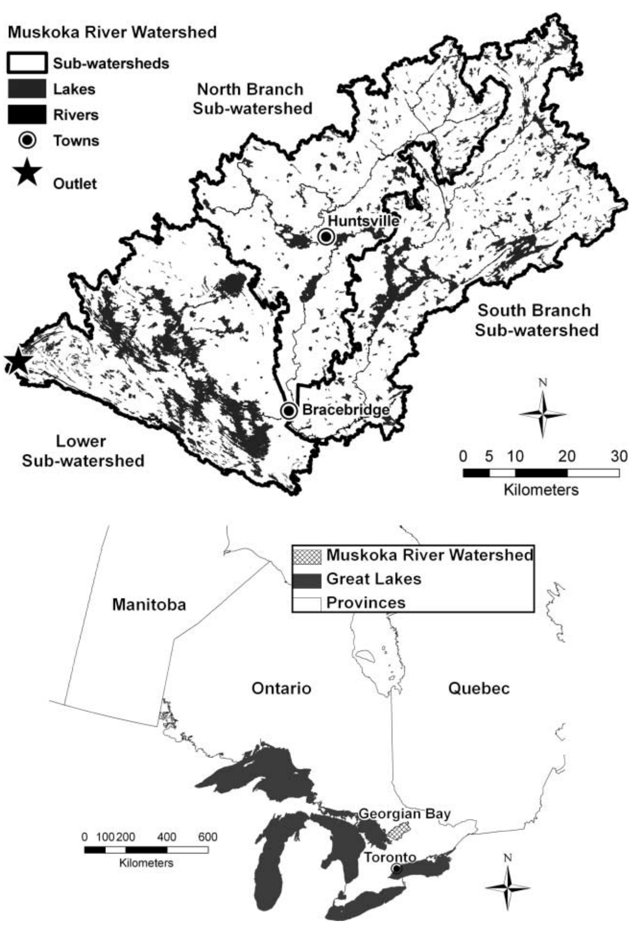

Figure 1 | The Muskoka River Watershed (MRW) (above) and its location in Ontario, Canada (below). The MRW contains three major drainage basins, which drain into Georgian Bay.

Deeper sand, silt and clay deposits exist in the central valleys and southwest portion, supportive of farm pasture fields. Forests are often dense and include mixed hardwood (maple, birch and oak) and coniferous species (spruce, white and red pine, balsam fir, tamarack and hemlock). The area was extensively logged around the beginning of the 20th century but has not had significant logging since then. Of the 150,000 people populating the MRW, two-thirds are seasonal residents.

The MRW receives an average annual precipitation of about 1,000 mm, including 300 mm of snowfall. Long-term average catchment runoff (measured and interpolated) in the region is 504 $mm\,yr^{-1}$ (ranging from 354–596 $mm\,yr^{-1}$). Schiff *et al.* (1998) stated that most of the Precambrian Shield forested catchments contain wetlands; 10% of the total area of the MRW is wetlands. Lakes cover 15% of the MRW surface area, with 60% of the lakes in headwater reaches. The average surface area of the lakes is 80 ha (ranging from 5 to 12,000 ha). For this study, 904 lakes of the MRW and their catchments were used for modeling the mass balances of DOC.

DOC and other chemistry data were available from the Inland Lakes Database (ILDB; Ontario Ministry of the Environment (MOE)) (Table 1). Based on this database, alkalinity data indicate that 77% are softwater lakes that are poorly buffered ($< 75\,\mu eq\,L^{-1}$ calcium carbonate ($CaCO_3$)), whereas 6% are hardwater lakes that are strongly buffered ($> 150\,\mu eq\,L^{-1}$ $CaCO_3$). Total phosphorus (TP) data indicate that 60% of the lakes are oligotrophic (low nutrient status; $TP < 10\,\mu g\,L^{-1}$), 35% are mesotrophic (moderate nutrient status; $10\,\mu g\,L^{-1} < TP < 20\,\mu g\,L^{-1}$) and 5% are approaching eutrophic status (high nutrient status; $20\,\mu g\,L^{-1} < TP < 26\,\mu g\,L^{-1}$). Most of the lakes sampled have relatively high sulfate levels (for Shield lakes), reflecting the fact that these are lakes impacted by acid rain (Eimers *et al.* 2004). Up to 20% of the lakes have sodium (Na) or chloride (Cl) levels $> 2\,mg\,L^{-1}$, probably a result of application of road salt within the watershed.

Model structure

The Lake DOC Model is comprised of catchments listed in rows and spatial and budget parameters listed in columns of a spreadsheet. Parameters are connected using

Table 1 | Summary of chemistry concentrations for sampled lakes of the Muskoka River Watershed

Chemical parameter	N	Range	Median	Unit
DOC	285	1–14	4.5	$mg\,L^{-1}$
pH	318	4.5–7.4	6.1	
Alkalinity	317	0–974	42	$\mu eq\ CaCO_3\ L^{-1}$
Conductivity	318	18–150	30	$\mu S\ cm^{-1}$
Sodium	280	0.4–12	0.8	$mg\,L^{-1}$
Chloride	171	0.1–19	0.5	$mg\,L^{-1}$
Sulphate	288	3.6–10.5	7.0	$mg\,L^{-1}$
Total phosphorus	193	3–26	9	$\mu g\ L^{-1}$

mathematical operations entered as formulae into the cells of the spreadsheet. Any time new data is entered into the model (e.g. new wetland data), the model automatically updates other parameters. Table 2 lists each parameter in the model, including its formula and data source. Spatial and budget parameters are described below.

Spatial parameters

Catchment boundaries for the region were digitally delineated using an Enhanced Flow Direction grid (EFDir, 10 m resolution, version 2.0.0) and the Water Resources Information Program (WRIP) toolbox (Ontario Ministry of Natural Resources (OMNR)) within ArcGIS (Environmental Systems Research Institute Inc. (ESRI), Redlands, CA). The EFDir is a grid representing surface flow directions determined using (1) a flow directed stream network; (2) a hydrographic layer (i.e. water body boundaries from the Natural Resources and Values Information System (NRVIS)); and (3) a 10 m DEM derived from 1:10,000 Ontario Base map (OBM) digital data (horizontal precision of ±10 m and a vertical reliability of ±5 m). Flow directions are consistent with the deterministic eight-direction (D8) algorithm described by O'Callaghan & Mark (1984) and Jenson & Domingue (1988). Compared to regular flow direction grids derived using only a DEM, the EFDir grid

Table 2 | Key parameters and coefficients used in the Lake DOC Model to compute DOC concentrations in lakes (i.e. modeled DOC concentrations ($mg\,L^{-1}$; DOC_m) $= 0.001(L_c(q_s + v_l)^{-1} + L_u(q_s + v_u)^{-1})$ (Dillon & Molot 1997b)

	Parameter	Symbol	Formula or source	Units
Spatial	Lake area	A_o	NRVIS	m^2
	Whole catchment area (including lake)	A_w	NRVIS	m^2
	Catchment area (excluding lake)	A_d	$A_w - A_o$	m^2
	Total wetland area in A_d	wet_t	NRVIS or RAT*	m^2
	Upland area	A_{upl}	$A_w - (A_o + wet_t)$	m^2
	Total wetland area in A_d		$100\ wet_t A_d^{-1}$	%
Budget	DOC export†		261 wetland% + 2390	$mg\,m^{-2}\,yr^{-1}$ [uses m^2 of A_d]
	DOC input		DOC export × A_d	$mg\,yr^{-1}$
	DOC loading	L_c	DOC input × A_o^{-1}	$mg\,m^{-2}\,yr^{-1}$ [uses m^2 of A_o]
	Runoff‡	Q	MOE	$m\ yr^{-1}$
	Lake discharge§	q_s	(upstream water + runoff × A_w)A_o^{-1}	$m\ yr^{-1}$
	Loss coefficient (lake)§	v_l	3	$m\ yr^{-1}$
	Loss coefficient (upstream lake)‖	v_u	3	$m\ yr^{-1}$
	DOC output *via* the outflow		$A_o\ q_s\ DOC_m \times 1000$	$mg\,yr^{-1}$
	DOC load from upstream lakes	L_u	(Σ DOC output from upstream lakes) A_o^{-1}	$mg\,m^{-2}\,yr^{-1}$ [uses m^2 of A_o]
	Water from upstream lakes		Σ $(q_s A_o)$ of upstream lakes	$m^3\,yr^{-1}$

NRVIS = Natural Resource and Values Information System; RAT = Rapid Assessment Technique; MOE = Ontario Ministry of the Environment.
*Hogg et al. (2002).
†Dillon & Molot (1997a).
‡Cummings-Cockburn and Associates.
§Dillon & Molot (1997b).
‖Estimated from v_l.

has this benefit of using photogrammetrically mapped, flow directed hydrology so that known hydrology is accurately represented and honoured during watershed delineation. The data layers and WRIP toolbox were the most up-to-date versions available from the OMNR in Peterborough, Ontario as of September 2007.

The WRIP toolbox delineates catchment boundaries by identifying land surfaces that slope towards the outflow point of each lake (i.e. pour point). The Water Virtual Flow layer contains a continuous stream network through the region (i.e. virtual streams within lakes are included in order to determine the flow direction through lakes). The stream network contains numerous "arcs" or lines, each containing an arrowhead at the "to-node" (i.e. the direction the stream is flowing to). Pour points were selected by intersecting lake outlines and to-nodes of virtual stream arcs (Figure 2).

Wetland areas within each catchment were identified and used to calculate the per cent wetlands for each catchment (Table 2). Two different methods were used for estimating wetland areas and the effect of these different methods on the Lake DOC Model were assessed. The first method used to estimate wetland areas was based on NRVIS data. A "Water Feature Area" GIS layer, derived from 1:10,000 OBM digital data, was used to obtain lake and wetland areas. The GIS layer contained surface water features identified as either wetland or other water features (lakes, rivers and reservoirs (including flooded areas)). Wetlands and lakes were put into separate GIS layers; the lake GIS layer included reservoirs but excluded rivers. OBM data originated from photogrammetric compilations of aerial photography (1:30,000) which were captured

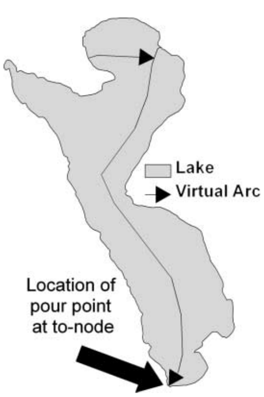

Figure 2 | Pour points for catchment delineation were selected by intersecting lake outlines and to-nodes (arrow head) of virtual stream arcs.

between 1977 and 1996. Some hydrologic features may have been created or modified since the original date of the aerial photograph.

The second method used to estimate wetland areas was based on data compiled by the Rapid Assessment Technique (RAT) (Hogg *et al.* 2002). The RAT wetland mapping method was developed for the Southern Ontario Land Resource Information System (SOLRIS) and was applied to the District of Muskoka as a pilot project, and then applied to the County of Haliburton and the Districts of Parry Sound and Algoma. RAT generates maps of wetlands using existing GIS layers combined with recent remote sensing imagery. Swamp and marsh areas were identified by training LANDSAT imagery with the field-surveyed Evaluated Wetland layer developed by the OMNR. The boundaries of these resultant wetlands were refined and/or confirmed using both a 1:50,000 quaternary geology "peat/muck" layer interpreted from aerial photographs and a topographic index of potential wetness derived using upslope contributing area. In the NRVIS wetland GIS layer, shallow emergent marshes (<2 m in depth) may have been mistaken for open waters during wet periods in early spring or late autumn on aerial photographs. RAT uses a Normalized Difference Vegetation Index (NDVI) derived from summer LANDSAT imagery to flag marsh areas. RAT also improves estimates of wetland areas by detecting swamps under canopy. Canopy type is often used to determine wetlands from aerial photography (as in NRVIS), but pre-leaf deciduous trees may render forested swamps undetected. RAT overcomes this potential problem by identifying swamps under canopies using corner reflectance (microwave energy that penetrates the canopy, then reflects from wetland surfaces beneath and again from tree trunks, and finally towards a radar detection system; Richards *et al.* (1987)) combined with topographical and hydrological data. Additional hardwood wetlands were added from 1:10,000 Forest Resource Inventory (FRI) generated from aerial photography. All wetlands were modeled into a final dataset for each region (e.g. Parry Sound).

Using GIS, the RAT wetlands for the model were merged together from three RAT datasets (County of Haliburton, Districts of Parry Sound and Muskoka) obtained from Ducks Unlimited Canada (Barrie, ON, Canada). This layer was clipped using the MRW boundary. The RAT wetland data covered all but 3% of the MRW; for this gap NRVIS wetlands were merged with the rest of the RAT wetlands to create complete coverage of the MRW. For the rest of the document, this merged layer is referred to as RAT wetlands.

Catchment boundaries were delineated for NRVIS lakes larger than 5 ha ($n = 904$). Smaller lakes may consume DOC through settling into the sediment and photochemical mineralization (Kothawala *et al.* 2006) or they may accumulate and export carbon similarly to wetlands. Neither NRVIS or RAT wetlands included open water features (e.g. small lakes). To assess the role of small lakes on DOC export, model trials were run with and without small lakes. When included, lakes smaller than or equal to 5 ha were treated as wetlands.

Budget parameters

In this study, the models used to determine DOC export to lakes and DOC concentration within lakes were developed previously by Dillon & Molot (1997*a*,*b*). These models were extended to include DOC loading from upstream to downstream lakes within the MRW.

The concentration of DOC (DOC_m; mg C L^{-1}) of each lake was estimated using the combined DOC loadings (mg m^{-2} yr^{-1}) from the surrounding catchment and upstream lakes (L_c and L_u, respectively), each divided by the sum of lake discharge, q_s (m yr^{-1}) and either the loss coefficient for the lake, v_l (m yr^{-1}), or for the upstream lakes, v_u (m yr^{-1}) (Equation (1)). The details of these variables are described in the paragraphs below:

$$DOC_m = 0.001[L_c(q_s + v_l)^{-1} + L_u(q_s + v_u)^{-1}] \quad (1)$$

Dillon & Molot (1997*a*) calculated DOC export (mg m^{-2} yr^{-1}; using catchment surface area) as a function of the percentage of peatland (i.e. not including beaver ponds) in gauged portions of a lake's catchment with available long-term data. When developing lake DOC budgets, Dillon & Molot (1997*b*) assumed that gauged and ungauged catchments within the total catchment area of a lake had a similar percentage of peatland. The DOC export equation of Dillon & Molot (1997*a*) and NRVIS- or RAT-based wetland area (m^2) of the catchment area surrounding each lake were used to calculate the annual DOC export on a catchment area basis (mg m^{-2} yr^{-1}) and DOC loading on a lake area basis, L_c (mg m^{-2} yr^{-1}) (Table 2).

Lake discharge, q_s (m yr^{-1}; Table 2) in the model was calculated as the combination of water contributed to a lake from: (1) catchment runoff; (2) the difference between precipitation onto and evaporation from the lake surface and (3) water entering from lakes directly upstream, if applicable (i.e. if the lake was not a headwater).

Catchment runoff to each lake, Q (m yr^{-1}; Table 2), was interpolated from runoff contour maps. These maps were created using runoff measurements of some lakes (runoff measurements completed by Cummings-Cockburn and Associates in 1991), a 1-min by 1-min map grid created through GIS (MOE), and historical water survey records of Canada. Runoff values from the contour map were assumed to be the difference between precipitation, P (m yr^{-1}), onto a lake's surrounding catchment and evapotranspiration, ET (m yr^{-1}), from the catchment. For the difference between P and evaporation, E (m yr^{-1}), for lake surfaces, E was approximated by ET as there was no measure of evaporation from lakes; therefore the difference between P and E was equal to Q (Equations (2) and (3)). As a result, q_s for headwater lakes was calculated in the model using Equation (4):

$$q_s = [(\mathrm{P} - \mathrm{ET})A_d + (\mathrm{P} - \mathrm{E})A_o]A_o^{-1} \quad (2)$$

$$q_s = [Q(A_d + A_o)]A_o^{-1} \quad (3)$$

$$q_s = [Q(A_w)]A_o^{-1} \quad (4)$$

where A_d is the catchment area (m^2) excluding the lake, A_o is the lake area (m^2) and A_w is the catchment area (m^2) including A_o.

Water entering a lake was assumed to be the same quantity that leaves through the lake outflow; thus, q_s was the same for input and output. Water flowing out of a lake was equal to the lake's q_s multiplied by its A_o; and this was the volume of water the upstream lake contributed to a lake directly downstream. For non-headwater lakes, the water flowing in from upstream lakes (m^3 yr^{-1}) was included in Equation (4) (see Table 2).

The loss coefficient, v_l (m yr^{-1}) which estimates DOC lost from the water column through mineralization and burial into the sediments, was estimated by Dillon & Molot (1997*b*) from long-term mass balance data from seven lakes in the region. v_l was based on the result of a relationship between retention (R), the portion of DOC loaded to a lake that is not lost through its outflow, and lake discharge (q_s), for the seven lakes. Therefore a single v_l is applicable to these lakes and has been applied to the lakes of the MRW (Table 2). v_u was assumed to be the same value as v_l in this study because another estimate of v_u was not available from the literature. Theoretically, though, v_u could be less because DOC would be less labile coming from upstream lakes compared to DOC from local catchments and therefore would not be as easily lost from the water column.

DOC travels downstream through lakes connected hydrologically; the advantage of this model is that DOC is routed from upstream to downstream lakes (Figure 3). Annual DOC output from each lake via the outflow ($mg\,yr^{-1}$) was calculated using the modeled lakewater DOC concentration (DOC_m) multiplied by the lake area (A_o) and q_s. DOC output from a lake was assumed to be the same quantity that entered the lake directly downstream (calculated as loading in $mg\,m^{-2}\,yr^{-1}$ according to downstream lake surface area). Therefore loadings from all

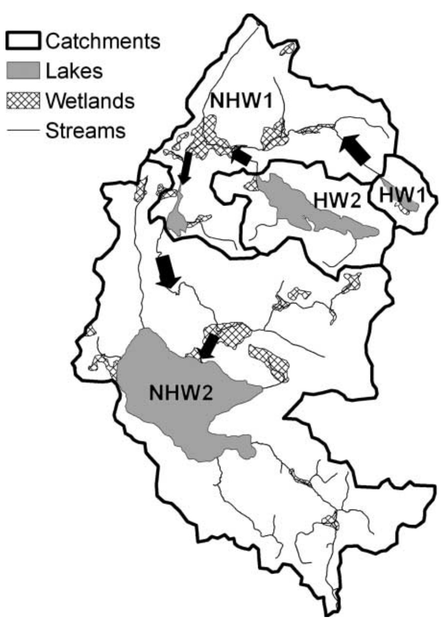

Figure 3 | Example of DOC routed from headwater (HW1 and HW2) to non-headwater catchments (NHW1 and NHW2). Black arrows show direction of route of DOC between lakes. Loading of DOC to headwater lakes is from local catchment; loading of DOC to non-headwater lakes is from local catchment and upstream lakes.

catchments directly upstream (i.e. only the next lake in each chain) of a lake were summed together (L_u), and then also combined with the lake's local catchment loading (L_c), to produce a total loading to a non-headwater lake (Equation (1) and Table 2). The production and/or consumption of DOC in streams as it travels between lakes is an important process (Köhler *et al.* 2002); it was not included in the Lake DOC Model, but will be considered in future research (e.g. using Integrated Catchments Model for Carbon (INCA) (Hanson *et al.* 2004; Futter *et al.* 2007)).

Autochthonous DOC is derived from primary production (including from algae, phytoplankton and macrophytes) within a lake, but it is decomposed rapidly and is believed to make up only a small portion of the DOC in surface waters (Wetzel 2001). Bade *et al.* (2007) quantified the proportions of allochthonous and autochthonous DOC in lakes (in northern Wisconsin and the Upper Peninsula of Michigan) and showed that both sources of DOC to lake ecosystems can be significant. Autochthonous contributions (from algal production) varied between 0 and 55% of total DOC contributions, but a large portion of the lakes had a contribution of less than 10%, suggesting that the allochthonous contribution (from wetlands within surrounding catchments) dominates. A model relating per cent of autochthonous DOC to colour and gross primary production was presented by Bade *et al.* (2007). The per cent contribution of autochthonous DOC increased with increasing chlorophyll-*a*, but decreased with increasing colour. Lakes in the MRW are mostly oligotrophic and therefore it is not expected that the autochthonous DOC contribution would be significant for most lakes. Therefore autochthonous DOC was not included in the model; it was not included in the model developed by Dillon & Molot (1997*b*) either. Atmospheric loading of DOC was negligible and was not included in the model.

Observed DOC concentration data

Measured DOC concentrations (DOC_o) for 285 lakes of the MRW were available from the Inland Lakes Database (ILDB; MOE). These were acquired through extensive studies spanning 25 years in the Muskoka region (1978–2003). The concentrations were averages from either regular sampling events (over many years for some lakes) or irregular sampling events (sometimes representing only one season–usually the ice-free season–and/or one year) (Figure 4). The number of samples was not known for 29 lakes; but of the other 256 lakes, most (96%) had 10 samples or less and the others had 11–77 samples collected. Of the first set (i.e. lakes with 10 values or less), 40% were sampled one time only, 30% were sampled across a range of up to 10 years and 30% were sampled across a range between 10–25 years. Of the second set (i.e. lakes with 11 values or more), 50% were sampled across a range of up to 5 years and 50% were sampled across a range of 18–24 years. To represent lake averages, samples were collected from the deepest part of the lake and throughout the water column during spring and fall turnover or as volume-weighted samples during summer stratification. Water samples were analyzed at the MOE Dorset Environmental Science Centre. Modeled DOC concentrations (DOC_m) were compared to these observed concentrations (DOC_o) to evaluate the success of the model.

Comparison of modeled and observed DOC

Results of the Lake DOC Model (i.e. DOC_m) using NRVIS- or RAT-based estimates of wetlands with and without small lakes were compared to DOC_o. In other model trials, wetland areas that overlapped lake areas (i.e. riparian wetlands) were included. Specifically the wetland datasets and model trial numbers were: (1) NRVIS wetlands; (2) NRVIS wetlands including overlap; (3) NRVIS wetlands + small lakes; (4) NRVIS wetlands including overlap + small lakes; (5) RAT wetlands; (6) RAT wetlands including overlap; (7) RAT wetlands + small lakes and (8) RAT wetlands including overlap + small lakes. The model using RAT wetlands (model trial 5 listed above) was broken down further into (9) headwater catchments only and (10) non-headwater catchments only. As a test of model consistency across all catchments, four subsets of lakes from one model (model trial 5) were randomly selected and results of DOC_m vs. DOC_o were compared amongst the subsets.

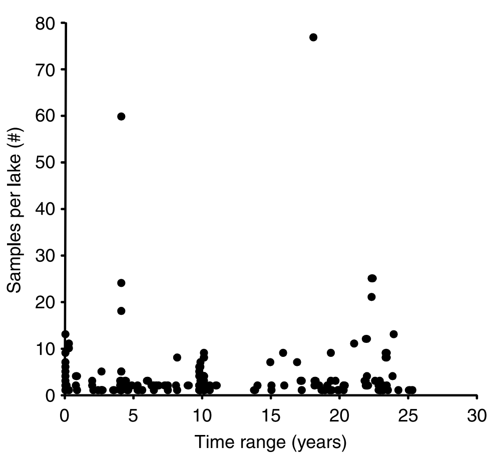

Figure 4 | Scatterplot of the number of DOC samples per lake vs. the time range (in years) over which those samples were collected. Data are from the Inland Lakes Database ($n = 256$, Ministry of the Environment, 1978–2003).

DOC_m from the various model trials were compared to DOC_o using regression analysis (Data Analysis Tools, Microsoft Excel). If a regression had a y intercept that was not significantly different from 0, the regression was rerun with the y intercept equal to 0; the resulting regression equation provided a more straightforward comparison of the slope to 1. Two-tailed t-tests were used to identify whether the slopes of the regressions were significantly different than 1. Regression results from model trials were compared to determine the model with the best fit.

Export equation evaluation

The export equation (from Dillon & Molot 1997*a*) was developed using DOC export and %peatland of gauged subcatchments, but the Lake DOC Model was based on whole catchments (excluding lakes) and RAT-based wetlands. Peatlands were determined using aerial photograph analysis supplemented with field observations to validate the presence of the peatlands (Jeffries *et al.* 1982; Dillon *et al.* 1991); these were different methods from RAT. RAT wetland areas were compared to peatland areas of Dillon & Molot (1997*a*) for the gauged portions of catchments to validate the use of their export equation in the model. Wetland areas determined from peatland and RAT datasets were generally similar for catchments (Figure 5). Beaver ponds were not included in Harp or Crosson catchments by Dillon & Molot (1997*a*) but perhaps were identified as wetland rather than pond by RAT mapping, which would explain why RAT mapping had greater areas for these.

Export equations were developed using DOC export data (from Dillon & Molot 1997*a*) and (A) RAT-based

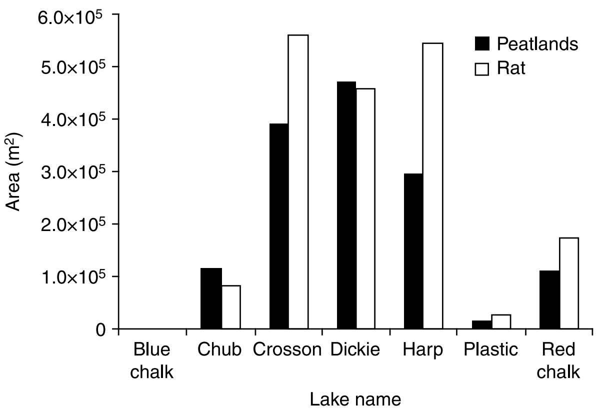

Figure 5 | Comparison of peatland (from Dillon & Molot 1997*a*) and Rapid Assessment Technique (RAT) wetland areas from gauged portions of seven catchments.

wetland areas of gauged sub-catchments (Table 3) or (B) RAT wetland areas of whole catchment areas (excluding lake; DOC export for the ungauged sub-catchments were treated as the weighted average of the gauged sub-catchments) (Table 3). The resultant export equations were used in the Lake DOC Model instead of the export equation from Dillon & Molot (1997*a*).

Sensitivity analysis

Sensitivity analysis was used to determine the sensitivity of the model output (DOC_m) to the input parameters. Parameters that have a strong influence on the output should have as little uncertainty as possible. Sensitivity analysis was performed with Crystal Ball® 7 (Oracle USA, Inc., Redwood City, CA) using Monte Carlo simulations that selected random values from ranges of parameter values and various starting points. Ranges were described by probability distributions that represented the data. Coefficients (e.g. loss coefficient) were given a uniform range covering realistic values. The sensitivity analysis trials were set with a very high number of simulations (i.e. 10^5) but stopped once the program was 95% confident that the mean of the outputs (i.e. the DOC_m calculated from each simulation) was true. The program was also set to acquire DOC_m in a normal range (1–30 mg L^{-1}). During each simulation, rank correlation coefficients between each parameter and the output (DOC_m) were calculated, to provide information on how DOC_m changed with the change in each parameter. By normalizing the coefficient

Table 3 | Results of modeled DOC concentrations (DOC_m mg L^{-1}) compared to observed (DOC_o mg L^{-1}) when various DOC export equations (DOC export (mg m^{-2} yr^{-1}) = $m \times$ wetland (%) + b) were used in the Lake DOC Model. The export equations were developed using DOC export data (Dillon & Molot 1997*a*) and either %RAT-based wetlands of the gauged portion of the catchments (Test A) or whole catchments not including the lake area (Test B). Coefficients of determination (r^2) and standard error of estimates (SEE) outline the strengths of the models. The slope and *y* intercept of DOC_m vs. DOC_o are compared to the ideal 1:1 line with an origin of 0. The *y* intercept was forced through 0 if it was not significantly different than 0

	DOC export vs. %wetland					DOC_m vs. DOC_o						
Test	Wetlands	Equation	n	r^2	p	Equation	n	y intercept = 0 ($p > 0.05$)	Equation y intercept = 0	r^2 ($p < 0.001$)	SEE	Slope = 1 ($t_{0.05(2),300}$)
A	%RAT gauged area	$Y = 147x + 3290$	20	0.37	0.004	$y = 0.75x + 0.90$	285	No		0.54	1.4	No
B	%RAT catchment area	$Y = 310x + 2068$	7	0.60	0.04	$y = 1.04x - 0.36$	285	Yes	$y = 0.97x$	0.50	2.1	Yes

from each input parameter to 100%, the sensitivity of the output to each of the parameters could be compared. Parameters were included in the sensitivity analysis if some part of their calculation was unique and not simply constructed from other parameters. Sensitivity analysis was performed using the entire dataset, but also for a subset of the data that included only headwater lakes.

RESULTS

Modeled DOC concentrations

RAT-based models were better able to predict DOC concentrations of lakes than NRVIS-based models. When NRVIS-based wetlands were used in the Lake DOC Model, the slopes of the relationships between DOC_m vs. DOC_o were much less than 1 (slope of DOC_m vs. $DOC_o = 0.54$–0.58, Table 4). In contrast, when RAT-based wetlands were used in the Lake DOC Model, the slopes were similar to 1 (slope of DOC_m vs. $DOC_o = 0.94$–1.06, Table 4), and a larger proportion of the variability was explained ($r^2 = 0.50$–0.51 compared to 0.36–0.39). Furthermore, the addition of small lakes (<5 ha) as wetlands improved the RAT-based model (slope closer to 1), although variability was increased slightly ($r^2 = 0.50$, Table 4). Small lakes increased wetland area for 580 of the 904 catchments (64% of the lakes), but resulted in only a slight to moderate increase in DOC_m (0–3 mg L^{-1}, median increase of 0.2 mg L^{-1}). The addition of riparian areas (i.e. overlapping wetland/lake areas) improved the RAT-based model according to slope (slope similar to 1) although variability was increased slightly ($r^2 = 0.50$, Table 4). The addition of both small lakes and riparian areas caused the slope to be high. Although the model improved with the addition of small lakes or riparian wetlands, they were not included in further model analyses because their role in DOC export has varied in other studies and their effects on the model were small.

The RAT-based model (model trial 5; Figure 6) was used for further analyses because this model simulated DOC measurements better than NRVIS-based models. Subsets of the DOC data were used in regression analyses to assess model performance on headwater vs. non-headwater lakes (Table 5; Figure 6). The model was better for non-headwater lakes (slope = 1.05, y intercept = 0, $r^2 = 0.50$) than headwater lakes (slope = 0.84, y intercept = 0, $r^2 = 0.54$). The RAT-based model underestimated DOC for headwaters in general, suggesting that there are other sources of DOC that are not accounted for in the model (e.g. autochthonous). The success in predicting DOC of non-headwater lakes suggests that the concepts in the model (i.e. DOC flux between lakes) are generally simulating true fluxes between lakes, although there is still substantial variability. If DOC_m for headwaters were closer to the 1:1 line with DOC_o, then lakes downstream might have DOC_m that are too high. The model should address physical, chemical and biological processing of DOC within lakes and streams.

Table 4 | Effect of different wetland estimates used in the Lake DOC Model on the strength (r^2), significance (p) and standard error of estimate (SEE) of the regression of modeled vs. observed lake DOC (mg L^{-1}) (DOC_m vs. DOC_o, respectively; $n = 285$). Small lakes (<5 ha) treated as wetlands and/or wetlands overlapping lake areas (riparian wetlands) were included in models for several trials. The y intercept was forced through 0 if it was not significantly different than 0

Model trial no.	Wetlands used in model	Equation	DOC_m *vs.* DOC_o y intercept = 0 ($p > 0.05$)	Equation y intercept = 0	r^2 ($p < 0.001$)	SEE	slope = 1 ($t_{0.05(2),300}$)
1	NRVIS wetlands	$y = 0.54x + 0.86$	No		0.38	1.4	No
2	NRVIS wetlands (overlap)	$y = 0.56x + 0.85$	No		0.39	1.4	No
3	NRVIS wetlands + small lakes	$y = 0.57x + 1.00$	No		0.36	1.5	No
4	NRVIS wetlands + small lakes (overlap)	$y = 0.58x + 0.99$	No		0.37	1.5	No
5	RAT wetlands	$y = 0.93x + 0.06$	Yes	$y = 0.94x$	0.51	1.8	No
6	RAT wetlands (overlap)	$y = 1.05x - 0.10$	Yes	$y = 1.03x$	0.50	2.1	Yes
7	RAT wetlands + small lakes	$y = 0.94x + 0.21$	Yes	$y = 0.98x$	0.50	1.9	Yes
8	RAT wetlands + small lakes (overlap)	$y = 1.05x + 0.05$	Yes	$y = 1.06x$	0.50	2.1	No

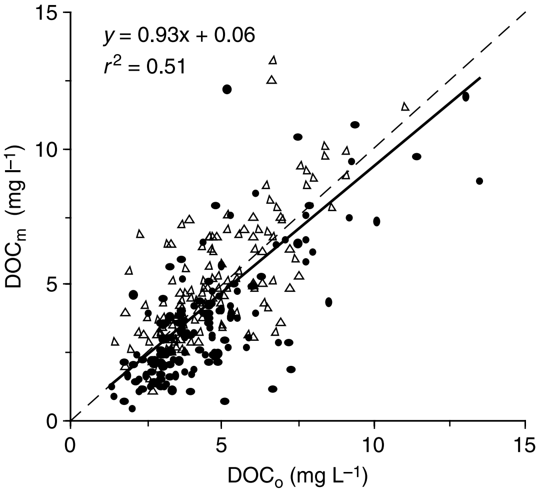

Figure 6 | Modeled DOC concentrations (DOC_m) vs. measured DOC concentrations (DOC_o) for lakes of the Muskoka River Watershed ($n = 285$). The data are divided into headwater (solid circles) and non-headwater lakes (open triangles). Rapid Assessment Technique (RAT) wetlands were used in the model (Model trial 5, Table 4). One-to-one line (dashed) is drawn for comparison to the regression trend line.

Within-model consistency

The results of four subsets of the model that used RAT wetlands (model trial 5) are listed in Table 6. DOC_m vs. DOC_o from three of the four datasets were not significantly different from the 1:1 line. There was a range of r^2 values (0.45–0.65). The ratios of the number of headwater to non-headwater lakes of the subsets were compared; subsets with a higher number of non-headwater lakes compared to headwater lakes produced lower slopes, inconsistent with the previous observation of under-predictions of DOC for headwater lakes. The effects of lake order on the modeled results are not clear. The differences in DOC_m suggest that regionally generalized coefficients in model equations (e.g. DOC export to lakes, DOC mass balances for lakes) and parameters (e.g. percentage of wetland areas) are less efficient for some lakes.

Investigations were carried out to evaluate which catchment characteristics (catchment area, lake area, runoff, lake discharge, headwater, non-headwater and high or low DOC_o) were associated with better model predictions. Most parameters were not significantly correlated with residuals, except for runoff in headwater catchments ($r = 0.35$, $p < 0.001$). No combination of the parameters was related to residuals, in multiple regressions. The medians of the parameters from subsets 1 and 4 (better model fit for latter; Table 6) from within-model tests were compared; subset 4 had slightly higher catchment areas, lake area, runoff and lake discharge. According to these investigations no catchment characteristic was substantially better represented by the model.

Residuals

The frequency histogram of DOC residuals (from model trial 5) in Figure 7 (i.e. $DOC_m - DOC_o$) indicates that these data are not normally distributed (Shapiro–Wilkes test, $W = 0.9$, $p < 0.0001$, $n = 285$). DOC residuals are somewhat positively skewed (skewness = 1.1), because there were fewer positive residuals than negative residuals, which supports the observation that DOC_m were often underestimated (i.e. slope = 0.94, Table 4).

The shape of the peak is leptokurtic (kurtosis = 8.4) and 50% of the residual data are between −1.2 and 0.5: therefore, many residuals are small in absolute value. Infrequent lake sampling may increase scatter in regressions of predicted vs. observed DOC concentrations because observed annual DOC varies whereas the model is long term and steady state. Within-lake annual ice-free DOC concentrations in the Dorset lakes varied significantly over a 28 year period. For example, the difference between minimum and maximum annual DOC concentrations over

Table 5 | Results of regressions of modeled vs. observed lake DOC concentrations (mg L^{-1}) (DOC_m vs. DOC_o, respectively) for headwater and non-headwater lakes of the MRW. The *y* intercept was forced through 0 if it was not significantly different than 0. Rapid Assessment Technique (RAT) wetlands were used in the models (model trial 5, Table 4)

				DOC_m vs. DOC_o				
Model trial no.	**Catchments used in model**	***n***	**Equation**	***y* intercept = 0 ($p > 0.01$)**	**Equation *y* intercept = 0**	**r^2 ($p < 0.001$)**	**SEE**	**Slope = 1 ($t_{0.05(2),120}$)**
9	Headwaters	142	$Y = 0.93x - 0.51$	Yes	$Y = 0.84x$	0.54	1.9	No
10	Non-headwaters	143	$Y = 0.90x + 0.76$	Yes	$Y = 1.05x$	0.50	1.6	Yes

Table 6 | A comparison of regressions of modeled vs. observed lake DOC concentrations ($mg\,L^{-1}$) (DOC_m vs. DOC_o, respectively) using four different subsets of lakes from the Lake DOC Model. The ratio of headwater to non-headwater lakes is listed. The *y* intercept was forced through 0 if it was not significantly different than 0. Rapid Assessment Technique (RAT) wetlands were used in the models (model trial 5, Table 4)

Model subset no.	*n*	HW/NHW	Equation	DOC_m *vs.* DOC_o *y* intercept = 0 ($p > 0.05$)	Equation *y* intercept = 0	r^2 ($p < 0.001$)	SEE	Slope = 1 ($t_{0.05(2),n}$)
1	71	33/38	$Y = 0.75x + 0.53$	Yes	$Y = 0.85x$	0.49	1.6	No
2	62	32/30	$Y = 0.93x + 0.26$	Yes	$Y = 0.98x$	0.55	1.7	Yes
3	87	47/40	$Y = 1.03x - 0.25$	Yes	$Y = 0.99x$	0.45	2.2	Yes
4	65	30/35	$Y = 1.01x - 0.28$	Yes	$Y = 0.96x$	0.65	1.5	Yes

a long time range was $0.8\,mg\,L^{-1}$ in a clear lake (Blue Chalk Lake, $1.63\,mg\,L^{-1}$ in 1988 and $2.50\,mg\,L^{-1}$ in 2003) and $2.8\,mg\,L^{-1}$ in a coloured lake (Chub Lake, $4.25\,mg\,L^{-1}$ in 1983 and 1985, $7.06\,mg\,L^{-1}$ in 2004) (P. J. Dillon, unpublished data). Most of the residuals in Figure 7 were small in comparison to differences in annual variation; thus the model predictions are reasonable (not outside the variation that occurs inter-annually).

Range of concentrations

DOC_o ranged from 1.4 to $13.5\,mg\,L^{-1}$ (median = 4.3 $mg\,L^{-1}$; $n = 285$), whereas DOC_m ranged from 0.3 to $25.4\,mg\,L^{-1}$ (Table 7; median = $4.4\,mg\,L^{-1}$; $n = 904$). The model should not be used to estimate DOC outside the range of DOC_o in which the model was validated (i.e. up to $14\,mg\,L^{-1}$). Of the 285 lakes that had DOC_o, 283 had DOC_m less than $14\,mg\,L^{-1}$. Of the 904 lakes in the MRW, only 32 had DOC_m greater than $14\,mg\,L^{-1}$. Very few lakes were

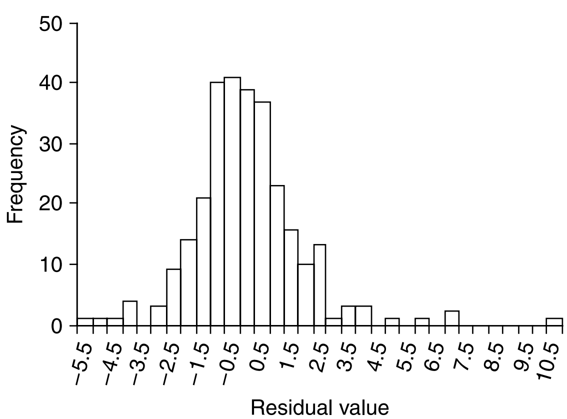

Figure 7 | Frequency histogram of the residuals ($DOC_m - DOC_o$) ($n = 285$). DOC_m is from model trial 5 (Table 4).

outside of the validated modeled DOC range. DOC_m for lakes without measurements should be comparable to those for lakes with measurements because the frequency distributions of DOC_o and DOC_m data were similar in shape (Figure 8).

Export equation evaluation

The results of the Lake DOC Model, using the export equation derived from %RAT-based wetlands in gauged catchment area, were not as good as when the export equation from Dillon & Molot (1997*a*) was used (slopes of 0.75 vs. 0.94, respectively) (Table 3, Test A and Table 4, model 5). When the export equation derived from %RAT of the whole catchment areas was used, there was a better fit between DOC_m and DOC_o, according to slope (0.98) (Table 3, Test B). An export relationship based on RAT wetland areas of the whole catchment would be ideal because it is consistent with the structure of the Lake DOC Model.

Sensitivity analysis

Results of sensitivity analysis performed on the whole model are shown in Figure 9(a). The model output, DOC_m, was most sensitive (−33%) to water inflow from upstream lakes. An increase in water from upstream lakes was associated with a decrease in DOC_m. Alternatively, loading of DOC from upstream lakes and wetland areas had strong positive effects on the model output (32% and 23%, respectively). Water and DOC from upstream lakes are not completely independent of each other and other parameters, though; the sensitivity of the model to these two parameters is at least partly redundant. The lake area contributed some uncertainty to the model output (−4%)

Table 7 | Range of model inputs and outputs using RAT wetland areas (model trial 5, Table 4) and formulas from Table 1

Parameter	Min	Median	Max	Units
Lake area	49,828	126,368	121,074,389	m^2
Whole catchment area (including lake)	122,351	1,445,730	520,173,160	m^2
Whole catchment area (excluding lake)	66,871	1,255,861	399,098,771	m^2
Wetland area per catchment	0	96,892	33,401,776	m^2
Upland area (excluding wetland)	51,145	1,150,307	372,106,371	m^2
Wetland/catchment area (excl. lake)	0	7	91	%
DOC export	2,390	4,233	26,092	$mg\,m^{-2}\,yr^{-1}$
DOC input	160	5,784	1,658,348	$kg\,yr^{-1}$
DOC loading	1,220	32,570	3,613,258	$mg\,m^{-2}\,yr^{-1}$
DOC load from upstream lakes	0	0	26,879,403	$mg\,m^{-2}\,yr^{-1}$
Water from upstream lakes	0	0	2,515,382,416	$m^3\,yr^{-1}$
Runoff	0.354	0.507	0.596	$m\,yr^{-1}$
Lake discharge	1	6	5,729	$m\,yr^{-1}$
Lake DOC concentration (modeled)	0.3	4.4	25.4	$mg\,l^{-1}$
DOC discharge from lake	35	4,798	12,331,679	$kg\,yr^{-1}$

whereas the loss coefficients, export coefficients, catchment area and runoff contributed very small amounts to uncertainty (<2% each). Results of sensitivity analysis performed using only headwater lakes are shown in Figure 9(b). The importance of headwater model parameters increased, but they were similarly ordered to the parameters from the full sensitivity analysis.

DISCUSSION

Large-scale DOC modeling approaches that incorporate the heterogeneity of catchments without becoming overly complicated are needed (Gergel *et al.* 1999). A Lake DOC Model was developed based on previously published relationships between percentage wetlands in catchments and DOC export to lakes (Dillon & Molot 1997*a*), DOC loss rates in lakes via sedimentation and mineralization (Dillon & Molot 1997*b*), and lake water fluxes to predict DOC concentrations in lakes. This model was used to track DOC movement from its source areas within catchments to its export to downstream lakes in the MRW, a large tertiary watershed in south-central Ontario, Canada.

The performance of the Lake DOC Model was sensitive to the method used to estimate wetland areas. Models using NRVIS-based wetlands underestimated significantly DOC concentrations of lakes. Models using RAT (Rapid Assessment Technique) based wetlands resulted in a better fit between modeled and observed DOC concentrations of lakes. Therefore RAT-based wetlands became the subsequent focus of this study.

Model performance was improved slightly by inclusion of small lakes (<5 ha) as wetland areas but not beyond the

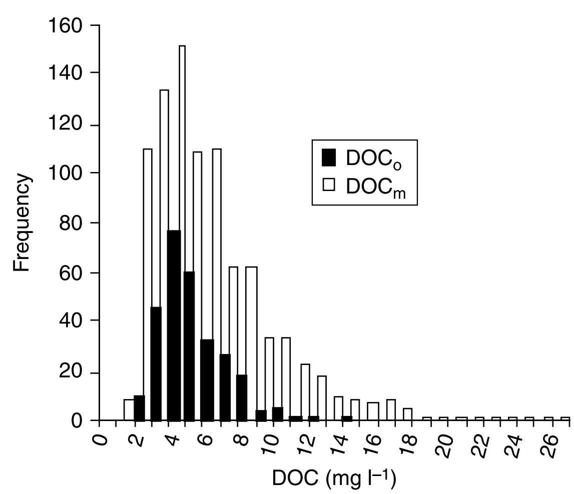

Figure 8 | Distributions of DOC_o ($n = 285$) and DOC_m ($n = 904$) values. DOC_m is from model trial 5 (Table 4).

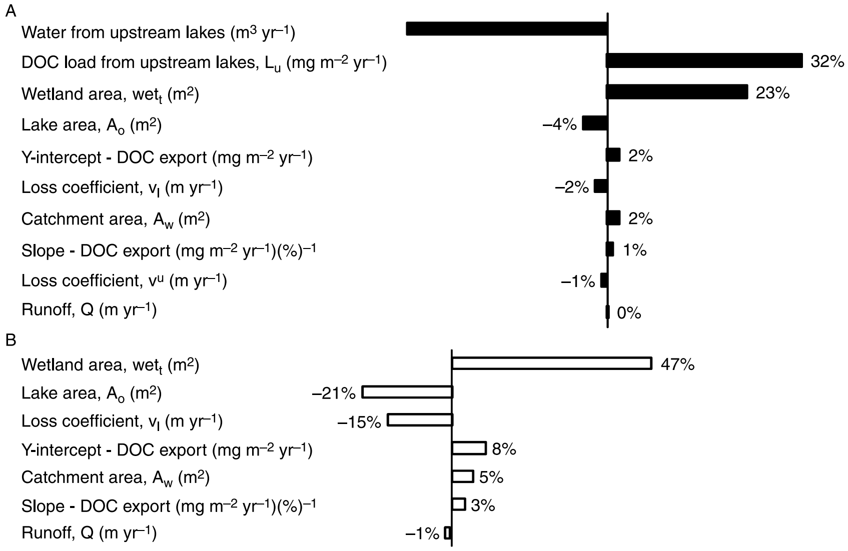

Figure 9 | Results of sensitivity analysis using (a) all lakes and (b) only the headwater lakes. The relative importance of selected parameters in the Lake DOC Model on the output (DOC_m) is indicated by the bars. Model trial 5 (Table 4) was used for the analysis.

differences of slopes and r^2 observed in the results of within-model testing (compare RAT model results with and without small lakes in Table 3 with Table 6). Small lakes may include beaver ponds. Kothawala *et al.* (2006) observed that stream DOC concentrations declined downstream a series of beaver ponds. They suggested that the successional stage of a beaver pond might determine the type and amount of DOC processing, with newer beaver ponds (i.e. open water) functioning as DOC sinks and older beaver ponds (i.e. with characteristics similar to swamps or marshes) functioning as DOC sources. Johnston *et al.* (2008) suggested that there might be a size threshold of small lakes that determines whether they act as a DOC sink or a DOC source to surface waters, although the position of the water table would likely be a better indicator of whether they are DOC sources or sinks. Further research is needed to identify this size threshold and to explore its influence on DOC export models. Model performance was also improved slightly by inclusion of riparian areas adjacent to lakes as wetland areas, but not beyond the differences of slopes and r^2 observed in the results of within-model testing (compare RAT model results with and without overlap in Table 4 with Table 6). While it was inconclusive as to whether small lakes or riparian wetlands contribute DOC to lakes, their impact on model predictions within the MRW was not significant. Including both small lakes and riparian areas over-predicted DOC, though.

The Lake DOC Model did not distinguish among wetland classes. The potential for DOC release (or retention) will vary among wetland types (Johnston *et al.* 2008). The RAT database included information on both wetland area and class for the MRW. However, field campaigns conducted to confirm these wetland characteristics revealed RAT was effective in identifying wetland areas but not necessarily wetland class. A field campaign was conducted by Ducks Unlimited Canada in 2004 to confirm the area and class of RAT wetlands for the County of Haliburton and District of Muskoka. The field campaign data revealed that about 90% of the sampled locations were identified correctly as wetland but there were problems with identification of wetland class. A subsequent field campaign was conducted by Ducks Unlimited Canada in 2005 to confirm the area and class of RAT wetlands for the southern portion of the District of Parry Sound. The data from this field campaign revealed that about 81% of the sampled locations were identified correctly as wetland, but while swamps and marshes were classified correctly as one class (i.e. swamp and marsh were not differentiated), bogs and fens were often misclassified.

Efforts to improve the accuracy of wetland areas and their classification (i.e. marsh, swamp, fen or bog) continue. For example, recent developments in digital terrain analysis of digital elevation models have resulted in significant advances in wetland mapping (e.g. Creed *et al.* 2003, 2008). If these wetland mapping techniques are combined with high resolution optical remote sensing data accurate wetland areas and classes at regional scales may be produced. These and other efforts including the US National Wetlands Inventory are critical for improved modeling of DOC dynamics in tertiary watersheds like the MRW.

Improvements in the Lake DOC Model can be made. This is suggested by the error in model estimates for individual lakes and from the inconsistent model predictions resulting from within-model testing. However, most of the residuals were small for RAT model trials. Some variation could be explained by parameter value inaccuracies, because regional generalizations were made. Other sources of variability could be explained by natural variation in factors that influence DOC export to lakes among catchments (e.g. surface water chemistry, mean catchment slope (Andersson & Nyberg 2008; Nyberg 2008), proximity of wetlands to lakes and streams, wetland type (Kothawala *et al.* 2006; Johnston *et al.* 2008) and forest cover). Additionally, Hudson *et al.* (2003) stated that regional and global-scale anthropogenic stressors cause year-to-year variability in DOC concentrations between lakes and within lakes and Futter *et al.* (2008) suggested that climate-related processes affect DOC concentrations in surface waters.

There is an on-going debate as to the effect of acid deposition on surface water DOC concentrations (Roulet & Moore 2006; Monteith *et al.* 2007). Acid rain is a problem in the MRW. The assumption of "steady state" in the model may not be justified if the MRW is recovering from acid rain. There is little evidence of long-term trends of DOC, though; in fact, the evidence points to patterns which are not unidirectional (Hudson *et al.* 2003). O'Connor (2007) normalized average annual DOC concentrations according to long-term patterns observed in lakes of the MRW to remove the effect of yearly fluctuations. These data were compared to DOC_m from the Lake DOC Model. The long-term fluctuations in the measured data were not a source of variation between DOC_m and DOC_o. Inter-annual changes in DOC concentration are a limitation in the model, but not likely a major one. In lakes, the main effect of acidity on DOC concentration is enhanced photochemical loss below pH 6. Since the median pH is 6.1 (Table 1), about half of the lakes would have loss coefficients $>3.0\,m\,yr^{-1}$ used in the study. The residuals are small (Figure 7) though and the overall impact of acidity in the MRW is not large.

This regional-scale DOC model includes both headwater and non-headwater lakes; the similarity of results of the model for each type of lake illustrates that DOC can be modeled in all lakes. Upstream lakes add large amounts of water and DOC to lakes downstream and are therefore very important in estimations of DOC; sensitivity analysis illustrated this. Total loadings of DOC to non-headwater lakes were higher on average than loadings to headwater lakes. Upstream loads of DOC averaged 50% of the total loads to non-headwater lakes in the model. While the flux of DOC between lakes were important for modeling regional carbon fluxes, illustrated also by sensitivity analysis, these fluxes included substantial uncertainty as they were coarsely estimated from runoff, spatial attributes (i.e. lake and catchment areas) and estimated DOC concentrations of upstream lakes. Future studies are needed to reduce this uncertainty.

Further research is needed to improve parameters and coefficients of regional-scale models. For example, Dillon & Molot (2005) showed that runoff and DOC export were highly correlated in a long-term study of lakes in Dorset, Ontario; runoff needs to be further evaluated for use in the Lake DOC Model. The v_u, loss coefficient for upstream lakes, should likely be less than v_l unlike the equal values used in this study, because DOC should be less labile coming from upstream lakes compared to DOC from local catchments and therefore it should not be as easily lost from the water column. Bade *et al.* (2007) demonstrated that autochthonous DOC contributions to lakes can be significant. Their model used to estimate autochthonous DOC from algae is based on chlorophyll-*a* and color, data that are available for a portion of lakes in the MRW. It would be interesting to include estimates of autochthonous DOC inputs in the Lake DOC Model and assess their effect on predicting DOC concentrations in lakes (particularly those with high phosphorus concentrations).

A large number of export coefficient models have been developed in Canada and Europe for nutrients, phosphorus and nitrogen (Dillon & Molot 1997*a*; May *et al.* 2001; Bowes *et al.* 2005; Paterson *et al.* 2006); other loading studies provide information to continue this work (Winter et al. 2007). The basis for much of the work on eutrophication is the use of nutrient export modeling, and the approach has a long and successful history. The model presented here is the first regional-scale export coefficient model for DOC.

DOC models support ongoing national projects based on key carbon sources, carbon sinks and processes of importance to Canada (Perry 2001). The Lake DOC Model could be used in other parts of the Canada and the world using GIS techniques and region-specific DOC mass balance models. The model is conceptually simple, with minimal parameter input required. The GIS data required are often accessible through government databases. The parameters required are often available through routine monitoring programs. With these minimal data inputs, the model can be used to estimate DOC for other regions, especially with similar landscapes and hydrological and biogeochemical characteristics as the Precambrian Shield in Canada, the USA and Nordic countries.

CONCLUSIONS

A DOC mass balance model called the Lake DOC Model was developed to predict average annual DOC concentrations for lakes within a tertiary watershed with substantial success. Different sets of wetland data were used in an effort to improve the performance of the Lake DOC Model. The regression equation used throughout this study and derived using the output from the Lake DOC Model (DOC_m) and measured DOC concentrations (DOC_o) was: $DOC_m = 0.94DOC_o$, $r^2 = 0.51$, $p < 0.001$. When estimates were compared to observations, the slope of the relationship was nearly 1:1, but there was considerable variability in the relationship. Differences in the estimates of DOC in headwater and non-headwater lakes suggests that the effects of in-stream processing of DOC need to be incorporated in the model. Further research is needed to improve estimation of model coefficients and to incorporate parameters and/or processes not currently included in the Lake DOC Model, perhaps focusing initially on small catchment studies prior to incorporation into the tertiary watershed model.

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