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A SPATIALLY EXPLICIT WATERSHED-SCALE ANALYSIS OF DISSOLVED ORGANIC CARBON IN ADIRONDACK LAKES

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Abstract. Terrestrial ecosystems contribute significant amounts of dissolved organic carbon (DOC) to aquatic ecosystems. Temperate lakes vary in DOC concentration as a result of variation in the spatial configuration and composition of vegetation within the watershed, hydrology, and within-lake processes. We have developed and parameterized a spatially explicit model of lake DOC concentrations, using data from 428 watersheds in the Adirondack Park of New York. Our analysis estimates watershed loading to each lake as a function of the cover type of each 10 $\times$ 10 m grid cell within the watershed, and its flow-path distance to the lake. The estimated export rates for the three main forest cover types were 37.7–47.0 kg $C \cdot ha^{-1} \cdot yr^{-1}$. The four main wetland cover types had much higher rates of export per unit area (188.4–227.0 kg $C \cdot ha^{-1} \cdot yr^{-1}$), but wetlands occupied only 11%, on average, of watershed area. As a result, upland forests were the source of ~70% of DOC loading. There was evidence of significant interannual variation in DOC loading, correlated with interannual variation in precipitation. Estimated net in situ DOC production within the lakes was extremely low ($<$1 kg $C \cdot ha^{-1} \cdot yr^{-1}$). Many of the lakes have large watersheds relative to lake volume and have correspondingly high flushing rates. As a result, losses due to lake discharge generally had a larger effect on lake DOC concentrations than in-lake decay. Our approach can be readily incorporated within a GIS framework and allows examination of scenarios such as loss of wetlands, alterations in forest management, or increases in conserved areas, as a function of the unique configuration of individual watersheds.

Key words: Adirondack Park; dissolved organic carbon; DOC; lakes; likelihood estimation; watershed loading; watershed models; wetland vs. upland loading.

Introduction

One of the largest mass fluxes from terrestrial to aquatic ecosystems is the movement of dissolved organic carbon (DOC) (Schlesinger and Melack 1981). DOC is a complex mixture of molecules typically dominated by humic and fulvic acids that can be highly colored, and consequently light absorbing (McKnight et al. 1985). Lakes and streams receiving large inputs of DOC may appear brown in color. The variation in DOC concentrations among aquatic ecosystems can be large. For example, a survey of 1469 lakes in the Adirondack Park of New York, USA revealed that DOC concentrations ranged from $<$0.2 to 36 mg/L (Kretser et al. 1989). Such differences are associated with variation in important physical, chemical, and biological properties. Lakes rich in DOC have limited penetration of solar radiation, especially UV radiation (Morris et al. 1995). This affects photosynthesis, mixing, heat budgets, and oxygen concentrations (Jackson and Hecky 1980, Fee et al. 1996, Snucins and Gunn 2000). DOC also binds metals and phosphate, altering bioavailability (Shaw et al. 2000, Maranger and Pullin 2002). DOC is typically a weak acid and influences pH, particularly in systems with low buffering capacity (Driscoll et al. 1994). DOC is also associated with the bioaccumulation of toxins such as mercury in fish (Driscoll et al. 1995*a*).

The movement of solutes like DOC from terrestrial to aquatic ecosystems is often characterized in terms of area-weighted exports from watersheds or loadings to receiving waters. These models traditionally represent inputs for a year either as an average value for a watershed area or as some function of land-cover type (Reckhow and Simpson 1980, Soranno et al. 1996). Most empirical models of DOC (e.g., Rasmussen et al. 1989, Kortelainen 1993, Houle et al. 1995, D'Arcy and Carignan 1997) have not considered spatially explicit data, leaving open questions about how different cover types contribute to and how exports from different areas are affected by distance from the receiving waters

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(Gergel et al. 1999). The models must also consider in-lake transformations and losses from the system. Many current models do not utilize mass balance but instead transform inputs via ''retention'' factors to predict concentration (e.g., empirical phosphorus models; see Reckhow and Chapra [1983]). This approach does not explicitly consider washout, burial in sediments, or chemical and biological processes that degrade or transform materials in the lake. Adding additional terms to models, however, creates the need for additional parameter estimation and its associated uncertainty.

In this study, we develop and parameterize a mass balance model of dissolved organic carbon (DOC) concentrations in lakes using data on the spatial configuration of land cover types, lake properties, and hydrologic variables for the watersheds of 428 lakes in the Adirondack Park of New York. The watersheds are primarily forested, with little agricultural land. Roughly half of the study area is in protected wilderness, with forests that have never been logged or were only lightly logged over a century ago. The region has extensive wetlands (~11% of watershed area), many of which fringe the extensive network of streams and lakes.

Our study had two general goals. First, we sought to develop a spatially explicit model to examine questions about landscape heterogeneity and the sources of loading of DOC to lakes. For example, hydrologic studies indicate that watershed areas prone to saturation are critical DOC source areas (e.g., Boyer et al. 1997). This suggests that spatial heterogeneity in land cover interacts with hydrological flow paths to influence DOC loading. Second, we sought to develop a modeling approach for large-scale regional assessment that facilitates quantitative analysis of the relative importance of different land use and land cover types among watersheds, effects of cumulative impacts, and sensitivity of systems to changes in loading. Increasingly, management agencies are developing extensive spatial databases of the type presented in this paper, and require methods of analysis that allow projection of both the immediate and cumulative impact of human activities and long term environmental change.

We used the model to estimate the export of DOC from different land cover types and the effects of distance from a source area to the lake on the net loading of DOC to the lake. We assessed the likelihood of alternative versions of the mass balance model to test hypotheses about both watershed loading and in-lake processes. For example, we compared models with alternative formulations for in-lake degradation of DOC as a function of depth, contributions from wetlands, and alkalinity.

METHODS

Study area

There are over 2750 lakes greater than 0.2 ha in size with a total surface area of ~100 000 ha in the 2 400 000-ha Adirondack Park (Kretser et al. 1989). Regional surveys of Adirondack lakes have highlighted their diversity in biological and chemical properties (e.g., Linthurst et al. 1986, Landers et al. 1988, Kretser et al. 1989, Baker et al. 1990, Driscoll et al. 1994, 1995*b*). The region is also characterized by abundant wetlands that are critical habitat for a significant percentage of the area's biodiversity (Davis 1988, Curran 1990). Adirondack lakes and wetlands are embedded in watersheds dominated by a relatively unbroken landscape of upland forests that are either protected public lands (~45%) or managed as commercial forests.

A spatially explicit, mass-balance analysis of lake DOC

Our analyses are based on the principles of mass balance, in which variation in DOC concentration can be understood as a balance between total inputs to the lake, primarily from the surrounding watershed, and net losses, primarily as a result of in-lake processes and output in lake discharge. In the formal terms of a difference equation,

$$\mathrm{DOC}_{t+1} = \mathrm{DOC}_t + \mathrm{Inputs}_{t\rightarrow t+1} - \mathrm{Degradation}_{t\rightarrow t+1} - \mathrm{Discharge}_{t\rightarrow t+1} \quad (1)$$

where DOC is measured as a concentration (g C/m^3), and inputs and losses are scaled to a predefined time interval (e.g., a year). Inputs to the lake are assumed to be independent of in-lake DOC concentration, while losses are assumed to be proportional to in-lake DOC concentration. This results in a predicted steady-state when DOC concentration reaches a level where losses balance inputs. Our analysis is designed to predict average, mid-summer concentrations within individual lakes. Studies have shown significant year-to-year variability in mid-summer averages, often with significant regional synchrony (e.g., Pace and Cole 2002). This is incorporated in the model through additional terms that account for effects of interannual variability in climate and hydrology on nutrient loading and lake discharge.

Inputs.—There are three major allochthonous inputs of DOC to lakes: (a) atmospheric deposition, (b) streams that carry DOC exported from upstream lakes and their associated watersheds, and (c) inflowing streamwater and groundwater from wetlands and upland areas within the immediate watershed. In addition, there is in situ production of DOC within lakes. For the purposes of our model, we assume that both in situ DOC production and atmospheric deposition of DOC directly to the lake are linearly proportional to lake surface area (SA, in m^2), so we combine these two sources into a single, net lake surface area input (SAI, in g C/m^2).

We consider the watershed of a given lake as a grid of source areas of fixed size (10 × 10 m), in which each source area is classified as a discrete cover type based on vegetation, drainage, and land use. Inputs arise from grid cells and move along flow paths that conceptually include both overland and groundwater flow, until they reach surface water (either the lake shore or streams feeding into the lakes). The model does not discriminate between overland vs. groundwater flow, but instead lumps them as ''ground'' flow, as distinct from ''stream'' flow inputs to the lake. In the simplest model, total annual input (g) of DOC to the lake is specified by

$$\text{Inputs} = (\text{SAI} \times \text{SA}) + \sum_{j=1}^{M} \lambda \times \text{ULE}_j + \sum_{i=1}^{N} \text{Export}_c e^{-\alpha_c D_i^{\beta_c}}. \quad (2)$$

ULE is the export (in g) from $j = 1 \ldots M$ upstream lakes, and λ is the average proportion of upstream lake export that is not lost through processing within a stream before it reaches the downstream lake. For the sake of simplicity, λ is assumed to be independent of stream length. Export_c is the export (in g) of the ith grid cell (0.01 ha) of type c within the immediate watershed. The fraction of the export that reaches the lake (i.e., loading) is specified by an exponential loss as a function of the flow-path distance (D_i) from the grid cell to the lake. The loss function is flexible enough to accommodate a wide range of shapes according to the estimated parameters α and β. Loss of DOC along the flow path is assumed to occur because of a several processes, including (a) decomposition, (b) sedimentation and mineral complexing in soils and sediments along the flow path, and (c) loss to deep groundwater.

Eq. 2 is, in effect, a simple additive model of nonpoint inputs in which each unit area of the watershed is a potential source, and the amount of DOC from each source area that reaches the lake is a declining function of the distance of the source area from the lake. In this simplest model, loss along a flow path that originated from an upslope source area does not depend on the nature of the cover type through which DOC moves.

Boyer et al. (1996) have shown that overland flow from nearshore areas with saturated soils is a proximate source of significant DOC loading from uplands. A ''topographic index'' (Beven and Wood 1983) based on the slope of a grid cell and the upslope contributing area is frequently used to identify areas prone to saturated soil conditions. We calculated the topographic index (TI) for each grid cell in the study region to explore whether the index would improve our predictions of watershed-scale inputs. We tried several model variants incorporating TI in our mass-balance model, but none of the variants improved the fit, so the results are not presented. Some of the information contained in TI is already incorporated in our model in a different form, since areas with high TI values are generally occupied by wetlands, and our wetland data layers allow us to take that into account.

Interannual variability in DOC loading.—The lakes in our data set were sampled in midsummer of one of four years (1984–1987). In each year, the sampled lakes were widely distributed across the region and well stratified across watershed characteristics such as lake size and flushing rate. Nonetheless, lakes sampled in 1986 had a significantly higher DOC concentration than lakes sampled in the other three years. In a separate study, Pace and Cole (2002) examined temporal variation of DOC in a set of Michigan lakes and found a high degree of synchrony. Years with high midsummer DOC concentrations were associated with higher-than-normal runoff in spring and early summer. On this basis, we incorporated a term in our model to allow for interannual variation in total DOC loading from within the watershed. 1984 was set as a benchmark, and the analysis then estimated the variation in total within-watershed loading for the three other years (1985–1987) needed to account for the observed interannual variation in lake DOC concentration.

Losses.—Losses of DOC from the lake are conceptually separated into (1) lake discharge and (2) within-lake losses. Loss via lake discharge is estimated from flushing rates based on data on runoff from within the immediate watershed, lake morphometry, and discharge from upstream lakes. Degradation of DOC in aquatic systems is actually an amalgamation of processes that include direct photodecay, microbial degradation, and flocculation/sedimentation (Wetzel 2001, Molot and Dillon 1997). Following previous studies (Engstrom 1987, Dillon and Molot 1997), we combine these processes into a single decay constant:

$$\text{Degradation} = k \times \text{volume} \times \text{DOC}. \quad (3)$$

Combining Eqs. 1–3, at steady state,

$$\text{DOC} = \frac{(\text{SAI} \times \text{SA}) + \sum_{j=1}^{M} \lambda \times \text{ULE}_j + \sum_{i=1}^{N} \text{Export}_c e^{-\alpha_c D_i^{\beta_c}}}{\text{volume}(k + \text{flushing rate})}. \quad (4)$$

We also considered alternative formulations of within-lake losses that were related to three factors: (a) lake depth (Rasmussen et al. 1989, Dillon and Molot 1997), which could be expected to reduce decay, (b) the proportion of watershed DOC loading from wetlands, which could be expected to increase decay because of higher loading of more labile DOC from wetlands (Engstrom 1987), and (c) lake acid neutralizing capacity (ANC), which could be expected to increase decay (Reche et al. 1999). All three factors have been shown to influence rates of degradation of DOC in lakes, as a result of different mechanisms (see *Results*). Specifically, for the set of 355 headwater lakes, we tested alternate models in which k in Eq. 4 was replaced by one of the following equations:

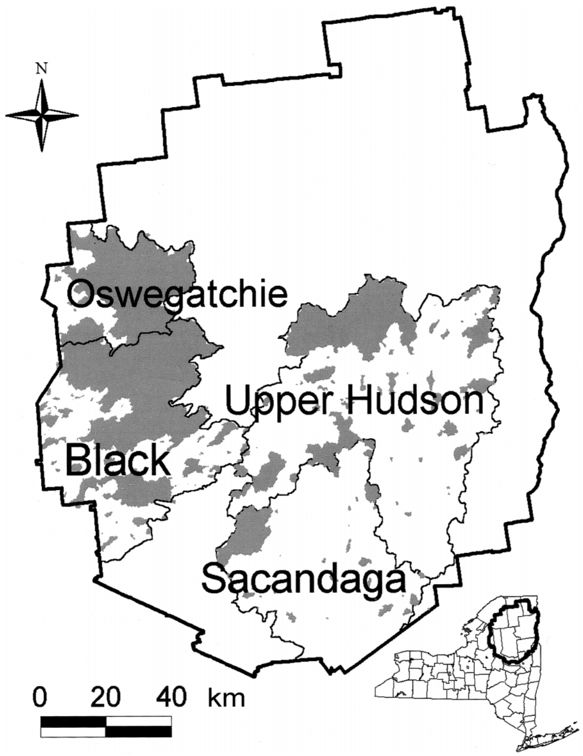

FIG. 1. The Adirondack Park, with the outlines of the Oswegatchie, Black, Sacandaga, and Upper Hudson River drainages within the park, and the distribution of the 610 watersheds within these drainages for which ALSC sampled lake DOC. The locator map shows the location of the park within New York State.

$$k = k' \exp^{(-A \times \text{depth})} \tag{5a}$$

$$k = k' + A \times (\text{Wetland loading, \%}) \tag{5b}$$

$$k = k' + A \times \text{ANC}. \tag{5c}$$

Watershed data sources

Data for this study come from several sources. Between 1984 and 1987 the Adirondack Lake Survey Corporation (ALSC) sampled 1469 lakes within the boundaries of the park (Kretser et al. 1989). The wetlands and forests for the major river drainage systems in the park are being mapped and classified by the Adirondack Park Agency (APA) (Roy et al. 1997, Primack et al. 2000). As a companion to the wetlands mapping program, APA has also assembled an extensive set of GIS-referenced data layers on the physical and biological characteristics of the watersheds in those drainages (Roy et al. 1997, Primack et al. 2000).

To date, watershed data are available for four major river drainages in the park: the Oswegatchie River, the Black River, the Sacandaga River, and Upper Hudson River (Fig. 1). Within these drainages, 610 lakes were sampled for DOC by ALSC. Each lake was sampled twice (spring and summer or summer and fall) during this period for a spectrum of physical, chemical, and biological variables including DOC, with roughly equal numbers of lakes sampled in each year. All summer lake sampling was conducted from late July to early August of each year (Kretser et al. 1989).

We analyzed two categories of watersheds. First, we considered only headwater lakes—those that had no upstream ponded waters over 1 ha in size. This allowed for an initial examination of model results without the complication of inputs from upstream lakes. A second analysis included all lakes (n = 610). A total of 182 of the 610 lakes could not be used in our analyses, for a variety of reasons. Twenty-two lakes were dropped because they were downstream from very large reservoirs that would constitute a large, unmeasured input of DOC. Twenty-five ''lakes'' were dropped because they were actually emergent marshes rather than open water, or had a mean depth <1 m. One hundred twenty-five lakes had ponds >1 ha in size upstream for which there were no ALSC DOC data available to estimate downstream exports. We were unable to produce acceptable watershed delineations for 10 of the lakes that were in areas of very low relief. In most of these cases, the 10 m resolution digital elevation model (DEM) produced watershed boundaries that split parts of wetlands bordering the lake into adjacent watersheds. Of the 428 remaining lakes, 355 were headwater lakes.

Wetlands.—APA has identified and mapped all wetlands within the Oswagatchie, Black, Sacandaga, and Upper Hudson drainages (Roy et al. 1997, Primack et al. 2000). Wetlands were delineated from 1:40 000 scale United States Geological Survey (USGS) National Aerial Photography Program color infrared imagery taken in the mid-1990s and 1:58 000 scale USGS National High Altitude Photography Program color infrared imagery taken in the mid 1980s, as described in Roy et al. (1996) and Primack et al. (2000). The classification was based on National Wetlands Inventory (NWI) techniques (Cowardin and Golet 1995) and identified the dominant and subordinate strata in each wetland, along with modifiers for hydrology and disturbance (by beavers, etc.). For our purposes, we lumped the wetlands into seven major groups: emergent marshes (EM), typically dominated by cattails and sedges; deciduous shrub swamps (DSS), dominated by speckled alder (*Alnus incana* ssp. *rugosa*) and willows (*Salix* spp.); broadleaved evergreen shrub swamps (BESS), primarily bogs dominated by a variety of ericaceous shrubs; needle-leaved evergreen shrub swamps (NESS), typically bogs dominated by stunted black spruce (*Picea mariana*); deciduous forest swamps (DFS), typically dominated by red maple (*Acer rubrum*); conifer forest swamps (CFS), dominated by red spruce (*Picea rubens*), black spruce, or balsam fir (*Abies balsamea*); and ''dead tree'' swamps (DTS), in which most of the canopy trees were dead, usually as a result of beaver activity (Roy et al. 1996, Primack et al. 2000). In order to keep the number of parameters in the model to a manageable number, we did not further divide these groups based on the estimated frequency and duration of flooding.

Forests.—The APA also mapped and classified upland forests in the four drainages using LANDSAT 5 Thematic Mapper imagery (Roy et al. 1997, Primack et al. 2000). The classification delineated forests into four major cover types (deciduous forests, coniferous forests, mixed deciduous/coniferous forests, and mixed deciduous/open forests), and two nonforest cover types (''deciduous/open'' vegetation with a mix of herbaceous and young woody vegetation, and ''open vegetation'' for areas dominated by nonwoody vegetation). The much coarser resolution of forest cover types was, in part, dictated by the nature of the remote sensing analysis. However, previous studies suggest that this is an appropriate level of resolution for characterizing the effects of variation in forest composition on inputs of DOC to lakes (e.g., D'Arcy and Carignan 1997). We combined the two ''mixed'' forest types into a single type, giving us five upland vegetation types: deciduous forest (DF), mixed forest (MF), conifer forest (CF), deciduous/open vegetation (DO) and open vegetation (OV) (which included most residential and developed areas).

Roads.—For watersheds that contained roads, we used a road data layer compiled by the APA, and assigned a width to each road category: 10 m for local and town roads; 20 m for secondary state highways, and 30 m for primary state highways. Roads were assumed to have no DOC export. Roads can have significant impact on hydrologic flow paths, particularly for overland flows (Tague and Band 2001). Many of the watersheds in our study are in roadless wilderness areas, and roads were rare in the study area in general, so we did not attempt to incorporate the effects of roads on flow paths.

Watershed delineation.—We delineated the watershed for each lake using GIS software (ArcView 3.1, ESRI, Redlands, California, USA), combined with our own scripts. Ten-meter resolution DEM data were downloaded from the Cornell University Geospatial Data Information Repository (CUGIR; available online).[7] These data were imported into ArcView and merged into one grid data layer. An ArcView script (Spatial.DEMFill) was used to remove sinks from the grid layer. The ALSC field manual was used to identify lakes for which DOC was measured. These were extracted from the photo-interpreted GIS wetlands data layer and converted to grid format. The contributing area above each lake was calculated using the ArcView command ''watershed'' on the sink-free DEM data. The resulting watersheds were verified using the APA delineation from USGS topographic maps.

Stream networks.—Part of the watershed delineation procedure requires the calculation of a flow-direction map. These data were used to calculate a flow-accumulation map. This was, in turn, used to create the stream network by applying a threshold to identify cells with high accumulated flow. Results were compared to USGS topographic maps to give a reasonable approximation to the mapping of perennial streams. This method alone did not generate stream networks that corresponded to USGS maps in both steep and flat areas. Different thresholds could be selected that optimized for one at the expense of the other, but not both. We developed another procedure that weighted upstream cells according to the landscape type. Unsaturated areas were given a weight of 1, whereas saturated areas were given a weight of 50. This, combined with a stream threshold of 5500, resulted in an acceptable approximation of the USGS-mapped streams. The stream vector coverage was converted to a grid layer with a width of 10 m (the minimum resolution of our grid data layers).

Flow-path distances.—Flow-path lengths were calculated from each point (i.e., 0.01-ha grid cell) in each watershed to the drainage lake using ArcView's ''flowlength'' command. ''Flowlength'' calculates the flow-path length using the flow direction map from each point to the outlet at the lake edge.

Compiled watershed data sets.—For the 428 watersheds in our final data set, we classified each 10×10 m grid cell into either a nonsource area (lakes, streams, and roads) or one of the 12 wetland or upland cover types, based on the GIS data layers. For each cell, we used the 10-m resolution digital elevation model to calculate flow-path distance to the lakeshore. Data from the ALSC surveys provided the midsummer lake DOC concentrations, lake volume, and lake flushing rate (based on watershed runoff calculations) (Kretser et al. 1989). In order to increase the speed of the iterative process used to estimate model parameters, for each cover type in each watershed we calculated the average flow-path distance to the lake for all cells of that cover type in each of 20 distance classes for the headwater watersheds or 26 distance classes for the analysis of all 428 lakes (which included larger watersheds). The sizes of the distance classes were chosen to provide more precise discrimination of flow-path distances near the lake (starting at 10-m intervals), and increased in size with greater distance from the lake. Thus, rather than integrate across all grid cells in each watershed (the summation terms for watershed loading in Eq. 4), we summed across the 20 or 26 distance classes, using the mean flow-path distance for grid cells in that class.

Parameter estimation through inverse modeling and maximum likelihood methods

Our analysis is a form of inverse modeling using a spatial regression in which lake DOC concentration is the dependent variable, and the independent parameters are (1) lake volume and surface area, (2) lake flushing rate, (3) the cover type and distance from lake for each of the grid cells in the immediate watershed, and (4)

[7] URL: ⟨http://cugir.mannlib.cornell.edu/index.html⟩

TABLE 1. Percentages of headwater lakes ($n = 355$) and all lakes ($n = 428$) in seven lake types based on classification by the Adirondack Lake Survey Corporation (Kretser et al. 1989).

Lake type	Headwaters	All lakes
Carbonate influenced	7.3	6.8
Salt impacted	7.6	7.5
Flow seepage	5.9	5.6
Mounded seepage	6.5	5.6
Thick till drainage	6.2	6.3
Medium till drainage	12.1	11.7
Thin till drainage	53.0	55.4

the year the lake was sampled (as a categorical variable). The basic model in Eq. 4 requires $3(n + 5)$ parameters where n is the number of cover types, for a total of 41 parameters given 12 cover types. The parameters are analogous to regression coefficients. We solve for the parameter estimates that maximize the likelihood of the observed lake DOC concentrations, using simulated annealing (Goffe et al. 1994), an iterative, global optimization procedure. Residuals were assumed to be normally distributed. The analysis was done with software written by the first author using Delphi (Borland International, Scotts Valley, California, USA) for a PC running Windows (Microsoft, Redmond, Washington, USA).

Statistical analyses

We compared alternate models with different numbers of parameters using likelihood-ratio tests (LRT) (Hilborn and Mangel 1997). This tested the significance in improvement (if any) in likelihood of a model due to the incorporation of additional parameters. Under principles of parsimony, we accepted a simpler model (i.e., with fewer parameters) if it did not have a significantly lower likelihood. For alternate models with the same number of parameters, no significance tests were necessary: parsimony dictated choosing the model with the highest likelihood. We calculated asymptotic 95% support limits (analogous to traditional confidence intervals) for each of the parameters by holding all other parameters at their maximum likelihood value, and then systematically increasing or decreasing the parameter of interest until the likelihood of the resulting model was significantly worse (at a 5% alpha level) than the maximum likelihood model. The fit of a model was evaluated using three metrics. Bias was evaluated by fitting a linear regression (without intercept) to the observed vs. predicted DOC data: a slope of 1 indicates an unbiased model. Overall goodness of fit was evaluated using R^2, and the predictive power of the model was evaluated using root mean squared error (RMSE).

RESULTS

Lake and watershed characteristics

The Adirondack Lake Survey Corporation (ALSC) developed a classification system that characterizes lake chemistry in relation to soils and lake drainage patterns. More than half of the lakes in our data set were classified by ALSC as thin-till drainage lakes (Table 1), reflecting the dominant lake type in this region of thin, postglacial soils. The remainder of the lakes were spread among a series of categories including medium till drainage, thick till drainage, mounded seepage, flow seepage, carbonate influenced, and salt impacted (Table 1). We examined the residuals of our models to see if there was variation related to lake type, but did not find any clear patterns. In general, the sample of 355 headwater lakes was characterized by only slightly smaller watershed area, lake area, lake volume, and mean depth than the entire sample of 428 lakes (Table 2). The median watershed area of the 355 headwater lakes was 72 ha, with a median lake area of 6 ha and a median mean depth of 2 m (Table 2). The average relative cover of the 12 vegetation types was similar for both the entire data set and the subset of headwater watersheds (Table 3). Upland vegetation covered 90% of the headwater watersheds, on average, with the three forest types combined covering 84% of the area, while the remaining two upland cover types and the seven wetlands occupied only 16% of the total area of the headwater watersheds (excluding open water in the lakes and streams). Individual watersheds varied dramatically in the relative cover of any of the vegetation types (Table 3). For example, there were watersheds where either conifer forest swamps or needle-leaved evergreen shrub swamps (e.g., shrubby black spruce or balsam fir) covered more than 80% of the watershed (Table 3).

Likelihood estimation of model parameters

The analysis produced unbiased fits to the data (i.e., slope of regression of observed vs. predicted $\cong$ 1.0),

TABLE 2. Watershed and lake basin attributes for the sample of headwater lakes ($n = 355$) and the total sample of all lakes ($n = 428$).

	Watershed area (ha)		Lake area (ha)		Lake volume (1×10^3 m^3)		Mean depth (m)	
Attribute	Headwaters	All lakes	Headwaters	All lakes	Headwaters	All lakes	Headwaters	All lakes
Mean	130.77	385.58	10.91	15.06	0.367	0.568	2.46	2.59
Median	71.63	101.71	5.98	7.13	0.102	0.125	2.00	2.10
Minimum	0.97	0.97	0.32	0.32	0.003	0.003	0.40	0.40
Maximum	1444.58	40 205.80	145.07	188.49	14.540	14.540	15.20	15.20

TABLE 3. Percent cover of upland and wetland vegetation in the watersheds of the sample of 355 headwater lakes and the total sample of all lakes (n = 428).

Vegetation cover type	Relative cover		Median cover		Maximum cover	
	Headwaters	All lakes	Headwaters	All lakes	Headwaters	All lakes
Upland vegetation						
Deciduous forest	30.20	30.56	25.9	26.3	84.5	84.5
Mixed forest	41.67	39.15	39.2	38.9	94.2	95.8
Conifer forest	12.13	13.04	7.4	7.8	93.0	92.9
Deciduous/open	1.73	1.49	0.0	0.0	56.0	55.9
Open uplands	4.36	4.78	1.4	1.9	67.7	67.7
Average total upland cover	90.09	89.02				
Wetlands						
Emergent marsh	0.67	0.75	0.0	0.0	22.0	35.6
Deciduous forest swamp	1.01	0.67	0.0	0.1	17.1	17.0
Conifer forest swamp	4.43	5.07	2.4	3.0	79.9	83.7
Dead tree swamp	0.16	0.17	0.0	0.0	15.1	15.1
Deciduous shrub swamp	1.99	2.77	0.4	1.2	58.8	58.3
Broadleaved evergreen shrub swamp	0.70	0.61	0.0	0.0	56.5	56.5
Needle-leaved evergreen shrub swamp	0.85	0.93	0.0	0.1	96.9	96.9
Total area (ha)	42 172	199 207				

Note: Relative cover is the percentage of the total area of all watersheds occupied by a given vegetation type; median and maximum cover reflect variation in percent cover of a given vegetation type among the sample of watersheds.

explaining 55% of the variation in DOC for the 355 headwater lakes (Fig. 2), and 48% of the variation in the larger sample of 428 lakes. Root mean squared error (RMSE) was 2.49 for the headwater lakes model, and 2.75 for the 428 lakes.

Loading of DOC from wetland and upland cover types.—Our analyses estimate both the total annual export of DOC from different watershed cover types (in kg C·ha^{-1}·yr^{-1}), and the proportion of that export that reaches the lake, as a function of distance from the lakeshore. Export of DOC to headwater lakes from the three upland forest cover types was remarkably similar (37.7–47.0 kg C·ha^{-1}·yr^{-1}), and did not decline significantly with distance of the source area from the lakeshore (Fig. 3). Similarly, export to headwater lakes from four of the main wetland cover types—conifer forest swamps, deciduous shrub swamps, broadleaved evergreen shrub swamps, and needle-leaved evergreen shrub swamps—was similar (188.4–227.0 kg C·ha^{-1}·yr^{-1}), and did not decline significantly with distance from the wetland to the lake (Fig. 3). Export from these four wetland cover types was roughly five times higher on a per unit area basis than from the three forest types. Many studies indicate that phosphorus loading to lakes is dominated by erosion and overland flow from nearshore and riparian areas (e.g., Soranno et al. 1996). In contrast, our analyses indicate that these watersheds are well ''plumbed'' for flow of DOC to lakes, and that in contrast to the variable source area concept for water flow (Hewlett and Hibbert 1967), major wetland and forest types throughout the watersheds are important as source areas for DOC.

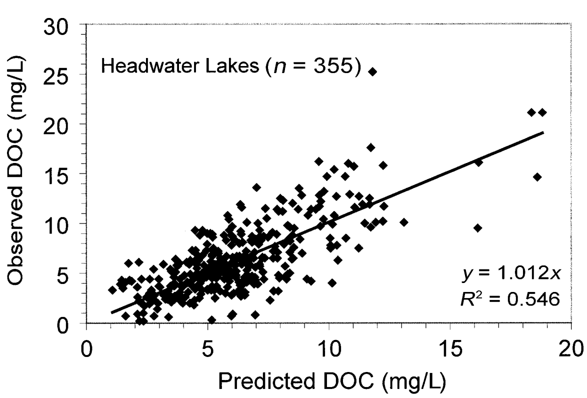

FIG. 2. Observed lake DOC concentrations (mg/L) for the 355 headwater lakes vs. concentrations predicted by the basic model. The line is a linear regression through the origin, to test for bias in the model (slope = 1 for an unbiased model).

The remaining five cover types (two upland types and three wetland types) showed very steep declines in loading of DOC with distance from the shores of headwater lakes (Fig. 3). The two upland types represent forests recently disturbed by either logging or natural disturbance (the ''deciduous/open'' category), or areas in which forests have been converted to other land cover types, primarily lake-shore development (the ''open vegetation'' category). In both of these cases, effective DOC loading to the lakes was negligible from source areas more than 200 m from the lakeshore. The three remaining wetland types—emergent marshes, deciduous forest swamps, and dead tree swamps (primarily the margins of recent beaver ponds), are generally found immediately adjacent to either the lakeshore or a stream leading into the lake, but our analysis suggests that source areas of these wetland types far away (>500 m) or upstream from the lake make a much smaller contribution of DOC to the lake than areas immediately adjacent to the lake.

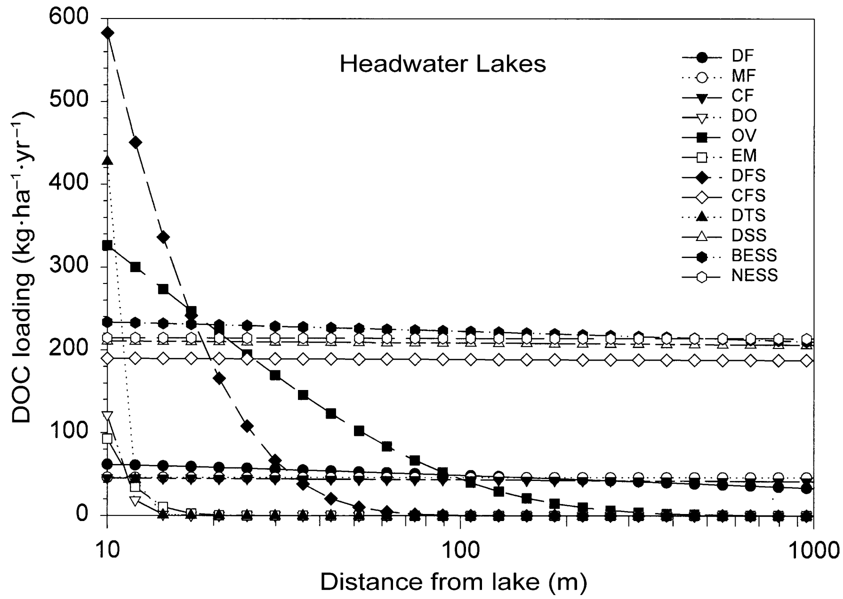

FIG. 3. Predicted DOC loading to headwater lakes (kg C·ha^{-1}·yr^{-1}) as a function of distance from the lake for the 12 upland and wetland cover types. Cover-type codes: DF, deciduous forest; MF, mixed forest; CF, coniferous forest; DO, deciduous/open upland vegetation; OV, open upland vegetation; EM, emergent marsh; DFS, deciduous forest swamp; CFS, coniferous forest swamp; DTS, dead tree swamp; DSS, deciduous shrub swamp; BESS, broadleaved evergreen shrub swamp; NESS, needle-leaved evergreen shrub swamp.

Spatial vs. nonspatial models of DOC loading.—A simpler, nonspatial model for the headwater lakes that assumed no distance decay in loading (i.e., estimating $Export_c$ but fixing all $\alpha_c = 0$) was a significantly worse fit to the data (labeled as ''reduced model—no distance decay'' in Table 4). We also tested an intermediate-complexity model of the headwater lakes that assumed no distance decay for the three upland forest types and the four wetland types that showed little decline in loading (Fig. 3), while fitting a simple exponential decay for the remaining five cover types (i.e., varying α_c, but fixing $\beta_c = 1$). This model was not a significantly worse fit (likelihood-ratio test), and required estimation of 19 fewer parameters (labeled as ''reduced model—five types vary'' in Table 4).

For the data set combining headwater and downstream lakes ($n = 428$ lakes), the nonspatial model was only a slightly worse fit to the data ($R^2 = 46.1\%$ vs.

TABLE 4. Comparison of the likelihood and goodness of fit (R^2 and slope of the regression of observed DOC on predicted DOC) of the full model (basic model: total distance) and alternate models for the headwater lakes and all lakes, combined.

Model	No. lakes	No. parameters	Likelihood	R^2	Slope	P†
Headwater lakes						
Basic model: total distance	355	41	−818.67	0.551	1.012	···
Basic model: ground distance	355	41	−823.13	0.538	0.999	0.003
Basic model: stream distance	355	41	−832.52	0.509	1.005	0.000
Basic model + depth	355	42	−814.92	0.555	0.994	0.023
Basic model + wetland loading	355	42	−816.11	0.551	1.001	0.077
Basic model + ANC‡	348	42	−782.53	0.542	1.003	0.067
Reduced model: no distance decay	355	17	−838.26	0.498	0.997	0.035
Reduced model: five types vary	355	22	−824.60	0.530	1.011	0.920
All lakes						
Basic model: total distance	428	29	−1040.21	0.477	0.995	···
Reduced model: no distance decay	428	18	−1046.16	0.461	0.996	0.453

Notes: For models with more parameters than the full model, a significant likelihood-ratio test indicates that the alternate model is a significant improvement in likelihood. For simpler models with fewer parameters, a nonsignificant likelihood-ratio test indicates that the simpler model is not a significantly worse predictor of variation in lake DOC.

† P values of likelihood-ratio tests comparing alternate models to the full model.

‡ Likelihood-ratio test calculated from full model with $n = 348$.

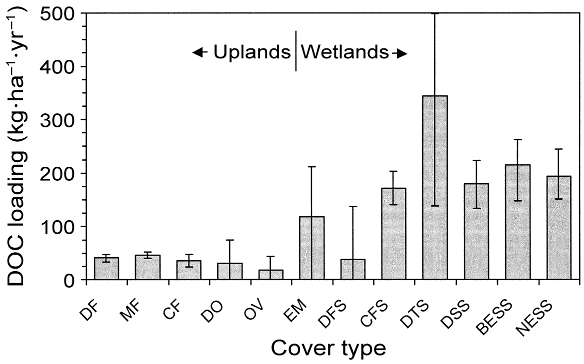

FIG. 4. Predicted DOC loading (kg $C·ha^{-1}·yr^{-1}$) to the sample of all lakes (n = 428) from the nonspatial model in which loading was independent of distance from the source area to the lake. Error bars are 95% support intervals on the mean loading. See the legend for Fig. 3 for description of the cover-type codes.

47.7% for the spatial model), but used 12 fewer parameters, and was not significantly worse than the spatial model that allowed distance decay in loading (Table 4). Because the analysis of the headwater lakes showed that distance decay could be adequately described by setting $\beta_c = 1$ and allowing α_c to vary, the basic model for the ''all lakes'' analysis used only 29 parameters (Table 4). The 95% support intervals for the estimated DOC export from the 12 cover types varied substantially (Fig. 4). In general, the estimated exports were more precise for the upland cover types than for the wetland types, and more precise for the cover types that showed no distance decay in the spatial models (Fig. 4).

Upland vs. wetland sources of DOC.—Variation in lake DOC concentration is often correlated with the area of wetlands in the watershed (Engstrom 1987, Kortelainen 1993, Watras et al. 1995). The correlation is weak but highly significant for the headwater lakes in our data set (r = 0.41, P < 0.001, n = 355). Our results confirm that wetlands are a rich source of DOC on a per-unit-area basis, and that much of the variation around the regional mean DOC concentration can be attributed to the relative area of wetlands in individual watersheds. Wetlands, however, occupy on average only 12.3% of the surface area of the 355 headwater watersheds. Because of their high rates of export per unit area, wetlands contributed a disproportionately larger percentage of total watershed loading (mean = 30.4%, SD = 22.1%). Nonetheless, our results indicate that for most of the watersheds in our sample, the majority of the DOC entering lakes originates in upland forests, not wetlands. The lakes with the highest percentage of DOC loading from wetlands were generally shallow lakes with low ANC (correlation between percent wetland loading and lake depth = −0.256, P < 0.001; correlation with ANC = −0.183, P = 0.009), but were not necessarily embedded in small watersheds (correlation between percentage of loading from wetlands and watershed area = −0.128, P = 0.290).

Effects of interannual variability in hydrology.—Our analysis indicates that total loading to headwater lakes in 1986 was 25.7% greater than in 1984, while 1985 was not significantly different than 1984, and 1987 was only slightly higher than 1984 (Table 5). Examination of both total annual and summer precipitation data from six stations within the study region confirms that the summer of 1986 had heavier than normal precipitation (Table 5). For the four-year period, the pattern of interannual variation in rainfall mirrored the estimated interannual variation in DOC loading, although the magnitude of variation in summer rainfall was greater than the magnitude of variation in estimated DOC loading. This is a rudimentary analysis, but it highlights the importance of incorporating temporal variability in runoff into our analyses.

The role of in-lake processes and lake discharge.—We estimate that net autochthonous production of DOC within the 355 headwater lakes (including atmospheric deposition) was extremely low (0.27 kg $C·ha^{-1}·yr^{-1}$), compared to ~40 kg $C·ha^{-1}·yr^{-1}$ for intact forests, and 200 kg $C·ha^{-1}·yr^{-1}$ for the most common wetland types. The estimated in situ production for the total sample of 428 lakes was higher but still extremely low (0.67 kg $C·ha^{-1}·yr^{-1}$). There were broad likelihood support intervals on both estimates (i.e., 95% support interval = 0–18.16 kg $C·ha^{-1}·yr^{-1}$ for the sample of 428 lakes). The low average rates of within-lake DOC production reflect the generally oligotrophic condition of lakes in this region. The broad support intervals may reflect significant between-lake variation in autochthonous DOC production due to variation in nitrogen and phosphorus loading, which is not accounted for by our model.

The estimated in-lake decay coefficient (k) for the headwater lakes was 0.82 yr^{-1} (95% support interval = 0.69–1.00), and was similar for the entire sample of 428 lakes (0.92 yr^{-1}, 95% support interval = 0.75–1.12). Examination of alternate models for the headwater lakes that allowed k to vary as a function of lake and watershed attributes revealed a significant (P =

TABLE 5. Interannual variation in estimated total within-watershed loading to headwater lakes, relative to the baseline year in 1984.

Year	Estimated loading (%)	Annual rainfall (%)	Summer rainfall (%)
1984	100	100	100
1985	98.9 (92.5–108.8)	100.1	76.7
1986	125.7 (118.8–135.8)	116.8	142.8
1987	108.4 (101.3–118.1)	112.4	122.5

Notes: Support intervals (95%) on the estimated loading for 1985–1987 are indicated in parentheses. Also shown is the percentage variation in total annual and summer (June–August) precipitation, relative to rainfall in 1984 (1171.4 mm annual, 313.2 mm summer), taken from U.S. Weather Service data for six stations within the study region.

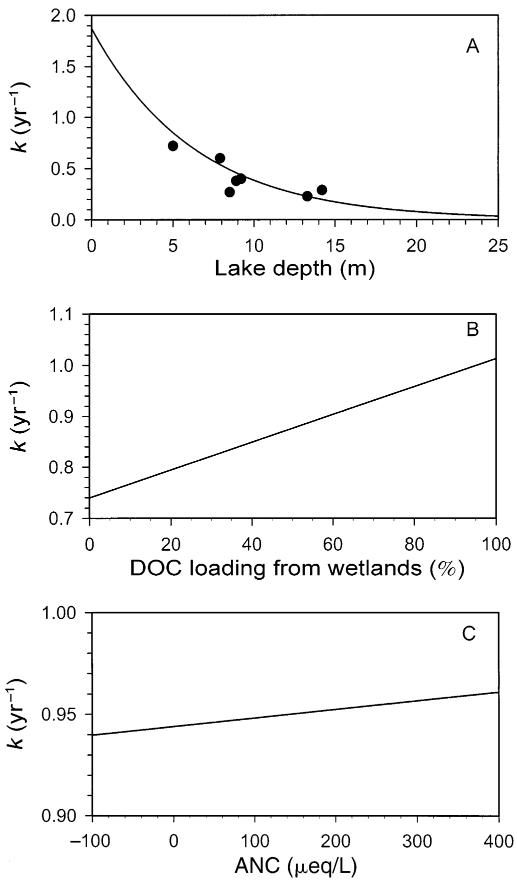

FIG. 5. Estimated relationships between the in-lake loss coefficient (k) and (A) mean lake depth (m), (B) the percentage of estimated DOC loading to the lake that originated from wetlands, and (C) acid neutralizing capacity (ANC) of the lake. The relationships were estimated from alternate models (summarized in Table 4) for the 355 headwater lakes. Also shown in panel A are direct measurements of k from seven lakes in a separate study in the Dorset region of Ontario by Dillon and Molot (1997).

0.023) decline in k with increasing mean lake depth (labeled ''basic model + depth'' in Table 4, see Fig. 5). There was also a slight and marginally significant ($P = 0.077$) increase in k as the percent of loading from wetlands increased (Table 4 and Fig. 5). We tested for the latter effect because of the hypothesis that the much larger loading of DOC per unit area from wetlands could be interpreted to suggest that the DOC exported from wetlands was qualitatively different than the DOC exported from forests, and that it may represent a more labile form of organic carbon. Our analysis supports this hypothesis, although the magnitude of the increase in k was relatively small. Based on recent research on photobleaching in lakes (Reche et al. 1999), we also tested for an effect of acid neutralizing capacity (ANC) on k. The effect was marginally significant ($P = 0.067$), but very small in magnitude (Fig. 5).

Many of the headwater lakes have large watersheds relative to lake volume, and have correspondingly high flushing rates (median = 4.34 yr^{-1} for the 355 headwater lakes). Given these relatively high flushing rates, examination of Eq. 4 suggests that losses due to lake discharge have a much larger effect on lake DOC concentrations than the in-lake decay coefficient.

Export of DOC from headwater to downstream lakes.—Our analyses estimate that half to three quarters of the predicted DOC discharge from headwater lakes reaches the next downstream lake (mean = 64.4%, 95% support intervals = 50.9–76.0%). Model runs in which we arbitrarily assumed that 100% of headwater lake DOC discharge reached the next downstream lake gave a poorer fit to the data, and resulted in biased models in which DOC in downstream lakes was consistently overestimated (data not presented). Our results suggest relatively high rates of DOC degradation or strong sinks for DOC in Adirondack streams and rivers.

Alternate models based on limiting inputs to areas near lakes.—Gergel et al. (1999) recently presented a model of DOC in which loading was limited to specified distances from the lakeshore. We tested a set of alternate models in which we limited our analyses to only watershed areas within 250 and 500 m of the lakeshore, rather than the entire watershed. Both of the models had a much lower likelihood than a model based on loading from the entire watershed (250 m, log likelihood = −972.2; 500 m, log likelihood = −942.4; vs. log likelihood = −818.7 for loading from the entire watershed). Moreover, the predicted exports of DOC from the more restricted source areas became unrealistically high to account for observed lake DOC concentrations. The poor fit of models based on near-shore areas alone reinforces our conclusion that there is very little distance decay of DOC export from source areas throughout the watershed.

Alternate models based on ground- vs. stream-flow paths.—We also tested alternate models in which the effective flow-path distance to the lake from any grid cell within the watershed was (1) calculated as the distance to the nearest open water (stream or lakeshore) rather than all the way to the lakeshore (i.e., combining both groundwater and stream flow paths); labeled ''basic model: ground distance'' in Table 4), or (2) calculated as the total length of surface water along the flow path before reaching the lake (i.e., flow-path length = 0 for paths that do not reach the lake via stream input (''basic model: stream distance'' in Table 4). The ground distance model was tested on the assumption that residence time for DOC in the stream before reaching the lake might be short enough that no significant decay would occur. The stream distance model was motivated by the countervailing logic that, given the known high rates of decomposition of terrestrial DOC once it reaches surface waters (Cole 1999), there may have been significant distance-dependent loss of DOC that reached lakes via a long

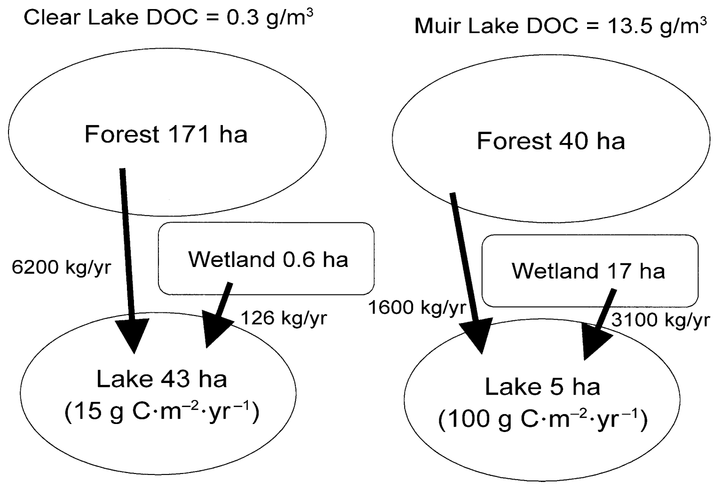

FIG. 6. Schematic diagram of the loading of DOC from forests vs. wetlands from a representative low-DOC lake (Clear Lake, DOC concentration = 0.3 g/m^3, total loading = 15 g C$\cdot$yr$^{-1}\cdot$m^{-2} of lake surface area) and a representative high-DOC lake (Muir Lake, DOC concentration = 13.5 g/m^3, total loading = 100 g C$\cdot$m$^{-2}\cdot$yr^{-1} of lake surface area).

stream flow path. We also tested a version of the model in which separate exponential decay coefficients for each cover type were estimated for the ground vs. surface-water flow-path lengths (data not presented). Given the results described above, in which there was relatively little distance decay in loading from source areas anywhere within the watershed, it was not surprising that none of these alternate models had significantly higher likelihoods than the basic model, which did not distinguish between ground and surface water flow paths.

DISCUSSION

Our analyses required a large sample of extensive and detailed watershed spatial data. Where such data are available, our spatially explicit inverse modeling approach allows estimation of the key terms that govern regional-scale variation in lake DOC concentrations. The method has a number of advantages in comparison with multivariate analyses that are not spatially explicit and not based on mass-balance principles. For example, our approach partitions loading among specific source areas within the watershed, as a function of cover type and distance to the lake. Because the model is based on mass-balance principles, the estimates of loading are in units (i.e., kg C$\cdot$ha$^{-1}\cdot$yr^{-1}) that can be directly related to carbon fluxes within both the watershed and the lake. The method should also be generally applicable to analysis of watershed loading and in-lake processing of other nutrients and elements such as P, N, and S, which are parameters of concern to both lake eutrophication and acidification in the Adirondack Park.

Loading from uplands vs. wetlands

Multivariate analyses have consistently identified the percent of the watershed in wetlands as a predictor of variation in lake DOC (e.g., Gergel et al. 1999). The same pattern is present in our data, but the relationship is weak (R^2 = 16.8% for the relationship between percent cover of wetlands and lake DOC, for the 355 headwater lakes). The correlation between wetland area and lake DOC has led to the perspective that wetlands are the predominant source of allochthonous DOC in lakes (e.g., Gergel et al. 1999). Our analyses, based on a mass-balance model, allow us to calculate the total loading from wetlands vs. upland areas of the watershed. Our results indicate that uplands are the source areas for $\sim$70%, on average, of total watershed loading of DOC to the 355 headwater lakes. The area of wetlands varies widely among individual watersheds within our data set, with some watersheds almost entirely composed of wetlands (Table 3). Thus, the relative proportion of loading from wetlands varies widely as well. Nonetheless, our results clearly suggest that upland forests are important sources of lake DOC in this region. This point can be illustrated by examining estimates of export and loading for representative low and high DOC lakes (Fig. 6). Clear Lake has a watershed dominated by forest with an estimated annual export of 6100 kg C and a small additional contribution from wetlands. These inputs result in an areal loading rate (per unit of lake surface area) of 15 g C$\cdot$m$^{-2}\cdot$yr^{-1}. Muir Lake, in contrast, has a high average areal loading rate (100 g C$\cdot$m$^{-2}\cdot$yr^{-1}) because of extensive wetland areas within the watershed. Wetlands dominate inputs to Muir Lake, but a third of the annual load still comes from uplands (Fig. 6).

Variation in DOC loading as a function of cover type and distance

Our estimates of DOC export from different cover types are consistent with studies that calculate total watershed export of DOC (Dillon and Molot 1997, Aitkenhead and McDowell 2000). Those studies typically estimate whole watershed losses that are intermediate between our estimates for upland forests and our estimates for wetlands, and presumably reflect the weighted average loading from different cover types within the watershed. Our results also confirm the general expectation that wetlands export far more DOC, on a unit area basis, than upland ecosystems (Aitkenhead and McDowell 2000). The only exception suggested by our analyses is in the case of disturbed upland areas (''open vegetation'' cover type) immediately adjacent to the lakeshore (i.e., within 30 m, Fig. 3), for which we estimate export of 200–300 kg C·ha^{-1}·yr^{-1}. Nonetheless, our estimated export rates from the different cover types contained some surprises. For example, the three main forest types are remarkably similar, with relatively tight 95% support intervals (Fig. 4). We had expected that the conifer forests might be a larger net exporter of DOC, because of generally slower rates of litter decomposition and higher levels of soil organic matter (D'Arcy and Carignan 1997). Soil solution concentrations of DOC in B horizons of coniferous forest plots in the Adirondacks were almost twice as high as in hardwood and mixed forest plots (9.9 mg C/L for conifer plots, vs. 5.5 and 6.8 mg C/L for hardwood and mixed-forest plots; Cronon and Aiken 1985). Our results suggest that these differences disappear by the time the soil solution mixes into groundwater. The four main wetland types also had remarkably similar average export of DOC (Fig. 4). The support intervals on the estimates were much larger than for the upland forests, suggesting that classifying wetland cover types based on vegetation structure hides considerable variability in decomposition processes and DOC loading. This may be due to unaccounted-for variation in hydrologic regimes, particularly the frequency and duration of inundation.

Even more surprising was the lack of decline in DOC loading as a function of distance from the lake for the major forest and wetland cover types (Fig. 3). Schiff et al. (1997), using isotope methods, attributed the DOC export from forested catchments to a combination of relatively old carbon from uplands transported to streams by groundwater, and younger C transported from wetlands by shallow or surface flow. There is growing evidence that a significant fraction of the DOC in rivers is ancient carbon (>1000 yr old, by radiocarbon dating) that has been washed in from upland area (Raymond and Bauer 2001). While some of this is presumably due to surface erosion of highly recalcitrant organic compounds from upland soils due to agriculture and logging, it suggests very low rates of decomposition of DOC once it reaches groundwater (Gron et al. 1992). Surface soils clearly have a very high capacity to adsorb DOC (McDowell and Wood 1984, McDowell and Likens 1988), but our results suggest that there is relatively little further adsorption of DOC while in transit to the lake via groundwater.

The lack of distance decay of inputs from wetlands may be caused by a different set of factors. Most of the wetlands either fringe lakes or are distributed along stream channels feeding into lakes. Thus, while the area-weighted mean flow-path distance for the wetland cover types was not generally shorter than for upland

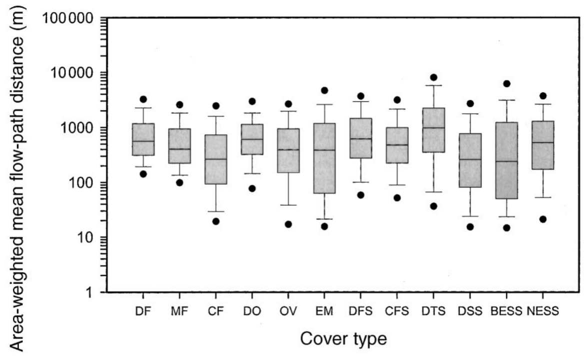

FIG. 7. Box plot of area-weighted mean flow-path distance from the 12 different cover types to the 355 headwater lakes. Boxes show the median and 25th and 75th percentile. Error bars display the 10th and 90th percentiles, and the circles mark the fifth and 95th percentiles. See the legend for Fig. 3 for a description of the cover-type codes.

forests (Fig. 7), stream water represented a much greater percentage of the flow-path length for the wetlands (data not shown). The relatively high rates of decay once DOC reaches the lake reflect the importance of sunlight in the degradation process (Moran and Zepp 1997). This degradation takes place in streams as well as in the lake, but the transit time for DOC in streams is rapid and there is less time for solar-driven decay, particularly in small streams where forest canopy cover limits light penetration.

Atmospheric inputs vs. exports from forests and wetlands

For the entire sample of 428 watersheds, we estimate an average net export of 37–51 kg C·ha^{-1}·yr^{-1} from the three main forest types (Fig. 4). We do not have separate estimates of atmospheric deposition of DOC in the Adirondacks, but studies in other regions of northeastern North America have measured precipitation inputs ranging from 8.4 kg C·ha^{-1}·yr^{-1} in central Ontario (Dillon and Molot 1997) and 13.9 kg C·ha^{-1}·yr^{-1} at Hubbard Brook in New Hampshire (Likens et al. 1983) to 31.8 kg C·ha^{-1}·yr^{-1} in northwestern Ontario (Schindler et al. 1997), where inputs varied threefold over a 20-yr measurement period. Thus, export from the upland forests is not much greater than the inputs from atmospheric deposition. The estimated annual flux of DOC via stream water from the Bear Brook watershed in New Hampshire was only ~50% higher than the estimated flux into the watershed via precipitation (McDowell and Likens 1988), although it should be noted that the estimated flux from this watershed was low (20.8 kg C·ha^{-1}·yr^{-1}) relative to our estimates and estimates of average watershed-scale fluxes in many other studies (Aitkenhead and McDowell 2000). For wetlands, our estimated annual export rates (~200 kg C·ha^{-1}·yr^{-1}) are clearly much higher than inputs via precipitation, indicating that the bulk of the DOC export is derived from in situ production.

DOC exports as a component of terrestrial carbon cycling

Net ecosystem production (NEP) presumably varies widely across the forests and wetlands of the 428 watersheds considered here. Recent estimates of NEP for northeastern forests based on both budgeting methods and eddy flux towers are $\sim$2000 kg $C\cdot ha^{-1}\cdot yr^{-1}$ (Barford et al. 2001), compared to our estimated net DOC exports of $<$50 kg $C\cdot ha^{-1}\cdot yr^{-1}$ from upland forests in the Adirondacks. Given that some fraction of the net export from forests could represent atmospheric deposition to the forests, net DOC export appears to represent only several percent of NEP in the upland forests. There are fewer measurements of wetland NEP in the region, but the estimates of net primary production are typically comparable to or lower than for upland forests (Brinson et al. 1981). Given the much higher estimated net export of DOC from Adirondack wetlands ($\sim$200 kg $C\cdot ha^{-1}\cdot yr^{-1}$), the export as a fraction of NEP is probably an order of magnitude higher than in the forests (10–20% in wetlands vs. 1–2% in forests).

In-lake processing

The estimated net in situ production of DOC per unit of lake surface area was very low relative to uplands and wetlands in the watershed ($<$1 kg $C\cdot ha^{-1}\cdot yr^{-1}$ for lakes vs. $\sim$40 kg $C\cdot ha^{-1}\cdot yr^{-1}$ for forests and $\sim$200 kg $C\cdot ha^{-1}\cdot yr^{-1}$ for wetlands). The estimated DOC production per unit of lake area is even significantly lower than regional estimates of DOC deposition in rainfall (8–31 kg $C\cdot ha^{-1}\cdot yr^{-1}$; Likens et al. 1983, Dillon and Molot 1997, Schindler et al. 1997). The predicted low rates of net autochthonous DOC production may be a function of two factors: (1) high rates of production and consumption of labile DOC produced within the lake but not explicitly considered in the model, and (2) the generally oligotrophic condition of many of the lakes. Many of the lakes are in protected wilderness areas, and have little human development within the watershed. The lakes typically have low total phosphorus (median = 13 mg/m^3 total P for 434 lakes in the Oswegatchie and Black River basins; Kretser et al. 1989), although some lakes have much higher phosphorus levels (maximum = 233 mg/m^3). The large support intervals on our estimates of in-lake DOC production may reflect the variation in lake primary productivity implied by this variation in phosphorus concentration.

The watersheds in our analysis are relatively small (median size 76 ha), but the median lake area is still only 9.9% of the total watershed area. Even in the watersheds with the highest ratio of lake area to watershed area (47.6% of watershed area), estimated in situ production of DOC would be less than 2% of the allochthonous inputs from the watershed, and in most lakes would be much less than 1% of total watershed loading.

The estimated decay time ($1/k$) for DOC of slightly over 1 year is in sharp contrast to the dramatically lower decay rates of DOC while buried in the soil (Qualls 2000). Once terrestrial DOC reaches surface water it is exposed to light, resulting in direct photo-oxidation as well as photolytic changes that promote microbial degradation (Moran and Zepp 1997). We tested for variation in the in-lake losses (k) in relation to lake depth, alkalinity, and the fraction of allochthonous loading that originated in wetlands, and found at least marginal statistical support for all three (Table 4). Of the three factors, mean lake depth had the greatest effect on DOC loss, with loss coefficients declining as lake depth increased (Fig. 5). The pattern of k with depth was similar to directly measured in-lake losses for a set of lakes in Ontario (Dillon and Molot 1997) (Fig. 5A). Again, exposure to light presumably provides the mechanism for this relationship, with DOC in deeper lakes receiving less exposure than DOC in shallow lakes.

Interannual variability in loading and lake DOC concentration

Our analyses indicate that total annual watershed loading of DOC across the four years of measurement (1984–1987) was correlated with total annual rainfall (Table 5). DOC loading during the wettest year of measurement (1986, with 47% more rainfall than during 1984) was roughly 25% higher than during 1984. These results are consistent with the long-term studies of Schindler et al. (1997) at the Experimental Lakes Area in Ontario, where individual lakes had two- to fourfold variation in total DOC inputs over a 20-yr period, and the variation in inputs was correlated with precipitation and stream flow. In our data set, the magnitude of variation in rainfall was much larger than the magnitude of variation in DOC. High rainfall years can have countervailing effects on lake DOC concentrations, with high stream flow flushing large amounts of DOC out of upland areas (Boyer et al. 1997), while at the same time contributing to higher lake flushing rates (and hence greater discharge from the lake). These considerations suggest that our model predictions could be substantially improved by better spatially distributed estimates of annual variation in runoff from the 428 watersheds.

Land–water interactions and management implications

Land–water interactions are a focal concern in management of surface waters, especially in the context of protecting water quality in the face of eutrophication and acidification. Much of our understanding of the effects of land–water interactions on surface-water quality have come from intensive case studies of individual watersheds. Our analysis provides an alternative to this traditional approach, and treats the lake and its associated watershed as an integrated system. It ignores the specific processes that govern the production and transport of DOC from forests and wetlands to lakes, and instead uses mass-balance principles to focus on the net export and loading of DOC to lakes, at the watershed scale. Maximum-likelihood modeling is ideal in this context, because alternative models can be formulated, tested, and compared.

One of the strengths of our approach is its ability to be applied to large numbers of watersheds, at a regional scale. This allows the potential to investigate cumulative impacts of alteration in the spatial distribution and types of land cover within a watershed, either hypothetically in anticipation of change or as actual changes occur. For example, it has been demonstrated that forest harvesting with 10–20 m buffer strips can result in significant increases in DOC loading relative to reference lakes (Lamontagne et al. 2000). Our study suggests that buffer strips will need to be much wider than this to insulate lakes in the Adirondacks from increased DOC loading due to logging.

Availability of spatially distributed data sets of the type required for our approach is growing rapidly, and resource agencies increasingly rely on geographic information systems (GIS) to manage those data sets. Our approach can be readily incorporated within a GIS framework, and can increase the quantitative and scientific basis of management policies. It allows examination of scenarios such as loss of wetlands, alterations in forest management, or increases in conserved areas, as a function of the unique configuration of individual watersheds.

Acknowledgments

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