Limnol. Oceanogr., 51(1), 2006, 247–256

A spatially explicit model of iron loading to lakes

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Abstract

Terrestrial and aquatic ecosystems are intimately linked by the export of elements from watersheds. Although export is influenced by land cover within watersheds, few models evaluate how the spatial configuration of land cover influences loading. In this study we examined spatial variation of land cover at a 10×10 m resolution by developing a mass balance, maximum likelihood model of lake iron (Fe) concentrations in 93 watersheds. The model estimated lake iron concentrations based on loading, within-lake processes and losses. Two models were developed. One considered loading from eight land cover types, whereas the second model included the distance of each grid cell to account for Fe losses along flow paths to the lake. In-lake production and losses were accounted for as a function of lake area, water color, and discharge. If we treated watersheds as homogeneous source areas, export was estimated as 450 mg Fe m^{-2} yr^{-1}; however, in spatial models export varied from negligible to 5,400 mg Fe m^{-2} yr^{-1} based on differential loadings from eight cover types. Accounting for losses of Fe based on distance from the lake did not improve the model. Although areal export of Fe was greater from wetlands, upland forests dominate the landscape and thus accounted for on average 75% of the total Fe load. Fe losses from lakes were primarily regulated by discharge; however, water color and lake depth were also important. Overall, the analysis revealed that lake Fe concentrations are related to land cover based on strong differential Fe loadings.

The chemical composition of a lake is influenced by several features of its watershed, including the area and spatial distribution of vegetation and land-use (Rasmussen et al. 1989; Gergel et al. 1999; Canham et al. 2004). Lake loading models have focused largely on determining the factors influencing the export of phosphorus, nitrogen, and dissolved organic carbon (DOC) because of their biological importance and impacts of human activity on the loading of these elements (Dillon and Molot 1997). There are also models to describe the inputs of toxic metals such as mercury and aluminum (Driscoll et al. 1995), but few models describe the loading and cycling of biologically important metals such as iron (Nürnberg and Dillon 1993).

Iron is an essential micronutrient to all organisms with the exception of *Lactobacillus.* Iron is a cofactor for hemoglobin and for many important enzymes including those required for respiration, photosynthesis, and nitrogen metabolism (Hewitt 1983). Although iron (Fe) is the fourth most abundant element in the earth's crust, Fe, in general, is not in a form that is readily available to organisms. In the presence of oxygen at biologically relevant pH, iron readily forms hydroxides and binds to other elements forming a variety of complexes. Indeed, the reactive nature of Fe often mediates the bioavailability, transformation, and mobilization of many elements, thus influencing the biogeochemical cycling of C, N, and P in both terrestrial and aquatic systems.

In terrestrial ecosystems, the Fe oxide layer in soil B-horizons plays an important role in regulating dissolved organic matter mobilization through the watershed (Moore et al. 1992). In highly calcareous soils, plants are often limited by the availability of Fe due to the formation of biologically inaccessible complexes (Morris et al. 1990). High concentrations of Fe in the humus layer can limit the availability of P to trees (Geisler et al. 2002). Recently, it has been suggested that through a series of dark oxidation and reduction reactions in the presence of DOC, Fe can transform NO_3 into dissolved organic nitrogen species, enhancing N storage in soils (Davidson et al. 2003).

In oxygenated aquatic environments with circum-neutral pH, Fe readily hydrolyzes and is deposited out of the water column (Stumm and Morgan 1996). Orthophosphate sorbs to these hydroxides and as a consequence is removed from the water column. Indeed the addition of Fe salts to eutrophied lakes has been used to precipitate and immobilize P to the sediment, thus reducing internal phosphorus loading (Smolders et al. 2001). However, in some cases when bottom waters of the hypolimnion become anaerobic, the Fe hydroxides become reduced and both Fe and P are released from lake sediments.

Lakes that are brown have elevated concentrations of humic and fulvic acids. The aliphatic and aromatic carboxyl and hydroxyl functional groups of this DOC can readily bind Fe, thereby keeping Fe in the dissolved state in surface waters (Pullin and Canabiss 2003; McKnight et al. 2003). These Fe-DOC complexes also bind P, keeping this limiting element in suspension (Shaw et al. 2000). However the bioavailability of the Fe-P complex is unclear (Maranger and Pullin 2003). Indeed it has been suggested that Fe chelated to DOC is not readily available and may limit primary production in some lakes (Jackson and Hecky 1980).

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Acknowledgments

We thank Heather Malcom, Denise Schmidt, Mark Maglienti, and Ben Conaway for excellent technical and field assistance, and comments from two anonymous reviewers greatly improved the manuscript. We also thank Edward McNeil for flying us in to some of the more remote lakes.

This research was supported by an EPA grant to M.L.P. and C.D.C. R.M. was supported by an NSERC of Canada postdoctoral fellowship. This is a contribution to the Institute of Ecosystem Studies.

Given that Fe is biologically relevant to organisms and also plays an active role in influencing the chemistry of other biologically important elements in natural waters it is important to identify the sources of Fe to lakes and how they influence lake Fe concentration. Most of the models of Fe dynamics in lakes focus primarily on within-lake processes (Nürmberg and Dillon 1993; Molot and Dillon 1997). Models that do report Fe export functions, in general, treat the watershed as a homogenous source area (Heikkenen 1990; Nürmberg and Dillon 1993; Dillon and Molot 1997) and do not account for variation in inputs to lakes from differences in vegetation, soil, or land use within watersheds. Given the reactive nature of Fe, losses may occur along the flow path from the source site to the lake, resulting in variable Fe loading from a given vegetation type depending on its position within the watershed.

In this study, we developed a spatially explicit Fe-loading model using a mass balance, inverse modeling approach to estimate dissolved Fe concentrations in lakes. Results are based on samples collected from 93 lakes in the Adirondack Park in New York State. Here we report estimates of Fe loading from both wetland and upland cover types in the watershed. We examine whether export from wetlands is higher than from upland cover types, given the links between Fe and colored DOC (Rasmussen et al. 1989; Maranger and Pullin 2003) and the higher rates of DOC export reported from wetlands (Rasmussen et al. 1989; Gergel et al. 1999; Canham et al. 2004). We also examine whether export rates differ among wetland types and as a function of hydrologic conditions within the wetlands, assuming conditions promoting reduced oxygen concentrations and low redox potential should favor Fe release. Finally, we examine whether there was reduced input of Fe to lakes from cover types located a greater distance from the lake, given the reactive nature of Fe in the soil.

Materials and methods

A spatially explicit, mass-balance analysis of lake iron concentrations—Our analyses are based on the principles of mass-balance, in which variation in a chemical constituent of a lake (e.g., Fe, DOC) 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. Following the approach used by Canham et al. (2004), the total amount of Fe_{t+1} in a lake at any given time can be described in terms of a difference equation:

$$\mathrm{Fe}_{t+1} = \mathrm{Fe}_t + \mathrm{inputs}_{t\to t+1} - \mathrm{sedimentation}_{t\to t+1} - \mathrm{discharge}_{t\to t+1} \qquad (1)$$

where Fe_t is the current amount (in grams), inputs and losses (sedimentation and discharge) are amounts scaled to a predefined interval (e.g., a year). Inputs to the lake are assumed to be independent of in-lake Fe concentration (g m^{-3}), while losses are assumed to be proportional to in-lake Fe concentration. This results in a predicted steady-state when Fe concentration reaches a level where losses balance inputs. Our analysis is designed to predict midsummer dissolved Fe concentrations in individual lakes.

Inputs—There are three major allochthonous inputs of Fe to lakes: (a) atmospheric deposition, (b) streams that carry Fe exported from upstream lakes and their associated watersheds, and (c) inflowing stream water and groundwater from wetlands and upland areas within the immediate watershed. In addition, there is in situ ''input'' as a result of resuspension or mobilization of Fe from sediments. For the purposes of our model, we assume that both in situ resuspension and atmospheric deposition of Fe directly to the lake are linearly proportional to lake surface area, so we combine these two sources into a single input term, net lake area based inputs (*ABI* in g Fe m^{-2} of lake surface area).

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, and stream flow within the watershed. In the simplest model, total annual input (g) of Fe to the lake is specified by:

$$\mathrm{inputs} = (\mathrm{ABI} \times \mathrm{surface\ area}) + \sum_{j=1}^{M} \lambda \times \mathrm{ULE}_j + \sum_{i=1}^{N} \mathrm{export}_c\, e^{-\alpha_c D_i} \qquad (2)$$

ULE is the export (in g) from $j = 1...M$ upstream lakes, and λ is the average proportion of this export that reaches the downstream lake. The parameter λ reflects processing that occurs within streams as water flows between lakes and for simplicity λ is assumed independent of stream length. *Export*$_c$ is the export (in g) of the *i*th grid cell (100 m^2) of cover 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 distance decay parameter α. Loss of Fe along the flow path is assumed to occur because of several processes, including (a) sedimentation and mineral complexing in soils and sediments along the flow path, and (b) loss to deep groundwater.

Equation 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 Fe from each source area that reaches the lake is potentially a 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 Fe moves.

Losses—Again, following the approach used by Canham et al. (2004), losses of Fe from the lake are conceptually separated into (a) lake discharge and (b) within-lake losses (primarily sedimentation). 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. Within-lake losses occur

Table 1. Summary statistics of physical and chemical characteristics of the 93 lakes and associated watershed used in this study.

	Mean	Minimum	Maximum	Median
Lake area (10^4 m^2)	19.74	0.32	188.49	7.63
Watershed area (10^4 m^2)	314.02	0.97	4779.41	122.69
Volume (10^6 m^3)	1.01	0.003	14.5	0.182
Flushing rate (yr^{-1})	18.6	0.31	535.3	4.7
Mean depth (m)	3.16	0.6	11.9	2.5
Color (440 nm, m^{-1})	3.79	0.23	17.2	3.22
Fe (mg L^{-1})	0.23	0.05	0.93	0.15
DOC (mg L^{-1})	5.7	1.42	14.26	5.08
ANC (mmol kg^{-1})	4.75	−4.05	44.75	0.9
pH	5.71	3.72	7.38	5.65
% Wetland	13.02	0	96.88	10.87
% Upland	86.98	3.12	100	89.13

primarily as sedimentation whereby Fe hydroxides formed in the surface waters rapidly settle to the lake bottom. Fe bound to particulate organic matter can also sediment from the surface. This process is slowed in the presence of colored DOC in which reactive moieties of these organic acids readily bind Fe, keeping it suspension. We also expected that losses would be slowed in deeper lakes, partially as a function of a slowed flushing rate (accounted for, see previous), but also due to a decrease in the surface area to volume ratio in deeper lakes. Fe would have relatively fewer surfaces to bind to in deeper lakes as compared to shallower ones. Thus, we tested a number of formulations for within-lake decay (k) as a linear or nonlinear function of both lake depth and color. The most parsimonious model was:

$$k = k' e^{a \times \mathrm{depth}^{b} \times \mathrm{color}} \tag{3}$$

Combining Eqs. 1–3, at steady state the Fe concentration (g m^{-3}) is:

$$\mathrm{Fe} = \left[(\mathrm{ABI} \times \text{surface area}) + \sum_{j=1}^{M} \lambda \times \mathrm{ULE}_j + \sum_{i=1}^{N} \mathrm{export}_c \, e^{-\alpha_c D_i} \right] \bigg/ [\mathrm{volume}(k + \text{flushing rate})] \tag{4}$$

Lake sampling and watershed data sources—The wetlands and forests for the major river drainage systems in the Adirondack 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 geographic information system (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. Detailed methods for wetland and watershed mapping (as well as other GIS data layers noted below) are presented in the original sources as cited here as well as in Canham et al. (2004).

We sampled 93 lakes within the Oswegatchie River and Black River drainage areas that had a wide range of DOC concentrations (Table 1). Accessing many of the lakes in this study was logistically quite difficult due to their remote location. Lakes could only be sampled once between June and September 2000; thus, the model reflects midsummer concentrations. Water was collected in the lakes' epilimnion at a depth of 1.5 m or at 0.5 m in the more shallow ponds and stored in acid-washed 1-liter bottles at 4°C until processed later in the day. Water was filtered through a Whatman GF/F glass fiber filter by using a hand pump and the filtrate was used for both color and dissolved Fe measurements. Samples were stored in acid-washed bottles at 4°C. Dissolved Fe was measured using a Perkin-Elmer P400 ICP-AES (Inductively Couples Plasma-Atomic Emission Spectrometer; detection limit, 10 μg Fe L^{-1} with a coefficient of variation [CV] of 3%). Color was measured spectrophotometrically at 350 nm and 440 nm (Cuthberg and del Giorgio 1992) and absorbance values at 440 nm expressed as m^{-1} were used for the analysis.

Wetlands—Wetlands within the four river drainages 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 six major groups: Emergent Marshes (EM), Forested Swamps (FS), ''Dry'' Deciduous Shrub Swamps (DDSS), ''Wet'' Deciduous Shrub Swamps (WDSS), ''Dry'' Evergreen Shrub Swamps (DESS), and ''Wet'' Evergreen Shrub Swamps (WESS) (Table 2). The demarcation between areas considered wet or dry was based on water regime modifiers described in Roy et al. (1997). Those wetlands considered ''wet'' were permanently or semipermanently flooded areas, whereas those we call ''dry'' still typically had saturated soils.

Uplands—The APA also mapped and classified upland vegetation in the four drainages using 30-m resolution LANDSAT 5 Thematic Mapper imagery (Roy et al. 1997; Primack et al. 2000). The classification delineated upland

Table 2. Cover type abbreviations and details on main land cover types.

Cover type	Abbreviation	Dominant Species	Saturation level
Upland forested	UF	Deciduous, mixed, and coniferous forests	N/A
Upland open	UO	Nonwoody vegetation	N/A
Emergent marsh	EM	Cattails (*Typha*) and sedges	N/A
Forested swamp	FS	Red maple (*Acer rubrum*), red spruce (*Picea rubens*), black spruce (*Picea mariana*), or balsam fir (*Abies balsamia*)	N/A
Dry deciduous shrub swamp	DDSS	Speckled alder (*Alnus incana* sp. *rugosa*) and willows (*Salix* ssp.)	Saturated
Wet deciduous shrub swamp	WDSS	Speckled alder (*Alnus incana* sp. *rugosa*) and willows (*Salix* ssp.)	Permanently or semipermanently flooded
Dry evergreen shrub swamp	DESS	Bogs dominated by ericaceous shrubs or stunted black spruce	Saturated
Wet evergreen shrub swamp	WESS	Bogs dominated by ericaceous shrubs or stunted black spruce	Permanently or semipermanently flooded

N/A = not applicable.

vegetation into four major forest 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). Previous studies revealed remarkably similar export of DOC from the different forest types (Canham et al. 2004). To keep the number of cover types manageable, we aggregated the upland vegetation into just two classes: forest and nonforest (''open'') vegetation.

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 Fe export. Roads can have significant impact on hydrologic flow paths, particularly for overland flows (Tague and Band 2001). However, 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), combined with our own scripts. Ten-meter resolution digital elevation map (DEM) data were downloaded from the Cornell University Geospatial Data Information Repository (CUGIR) (http://cugir.mannlib.cornell.edu/index.html). 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 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.

Flow path distances—Flow path lengths were calculated from each point (i.e., 100 m^2 grid cell) in each watershed to the lake shore 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 datasets—For the 93 watersheds we classified each 10 $\times$ 10 m grid cell into either a nonsource area (lakes, streams, and roads) or one of the eight 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 (as previously) to the lakeshore. Data from prior lake surveys provided volume, and flushing rate estimates (based on watershed runoff calculations that used long-term average precipitation values) (Kretser et al. 1989). Relative to long-term average precipitation values, the year 2000 was higher from June to September (approximately 20%) and may have resulted in a slight overestimate of the average Fe loading estimates of our model. To increase the speed of the iterative process used to estimate model parameters (see following), 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. 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 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 Fe concentration is the dependent variable, and the independent parameters are (1) lake volume and surface area, (2) lake flushing rate, and (3) the cover type and distance from lake for each of the grid cells in the immediate watershed. The basic model in Eq. 4 requires $2 \times n + 5$ parameters where n is the number of cover types, for a total of 21 parameters given 8 cover types. The parameters are analogous to regression coefficients. We solve for the parameter estimates that maximize the likelihood of the observed lake Fe 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 developed using Delphi (Borland International) for a PC running Windows (Microsoft Corp.).

Statistical analyses—We compared alternate models with different numbers of parameters using Akaike's Information Criterion (AIC), corrected for small sample sizes (Burnham and Anderson 2002). 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 under a likelihood ratio test. The fit of a model was evaluated using three metrics. Bias was evaluated by fitting a linear regression (without intercept) to the observed versus predicted Fe 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

Simple regression models—Traditional regression models provide a simple alternative to our spatially explicit, mass-balance approach. Total dissolved Fe concentration in these Adirondack lakes could be predicted from simple least squares regression as a function of both lake color (Fig. 1A; $r^2 = 0.64$, Fe $= 0.055 \times$ color $+ 0.022$, $n = 93$, $p < 0.0001$), and albeit with considerably less predictive power, as a function of lake DOC concentrations (Fig. 1B; $r^2 = 0.44$, Fe $= 0.053 \times$ DOC $- 0.07$, $n = 93$, $p < 0.0001$). These models are appealing in part because of their simplicity; however, they provide no information on sources of Fe or internal lake processes that regulate Fe concentrations. Percent wetland cover in the catchment is known to be an important contributor to color and DOC into lakes and was therefore considered a potentially important predictor of Fe concentration. We found no significant relationship between the two variables (Fig. 1C), suggesting that (a) there is a differential Fe export among different wetland types and/or (b) that other loading sources to the lake are significant contributors.

Likelihood estimation of model parameters—The likelihood analysis produced unbiased fits to the data (i.e., slope of the regression of observed versus predicted was $\cong$1) explaining between 61% and 69% of the variation in lake Fe concentration for the 93 lakes. Root mean square error for the best model (Model 7; Table 3) was 114.3 μg L^{-1} (Fig. 2).

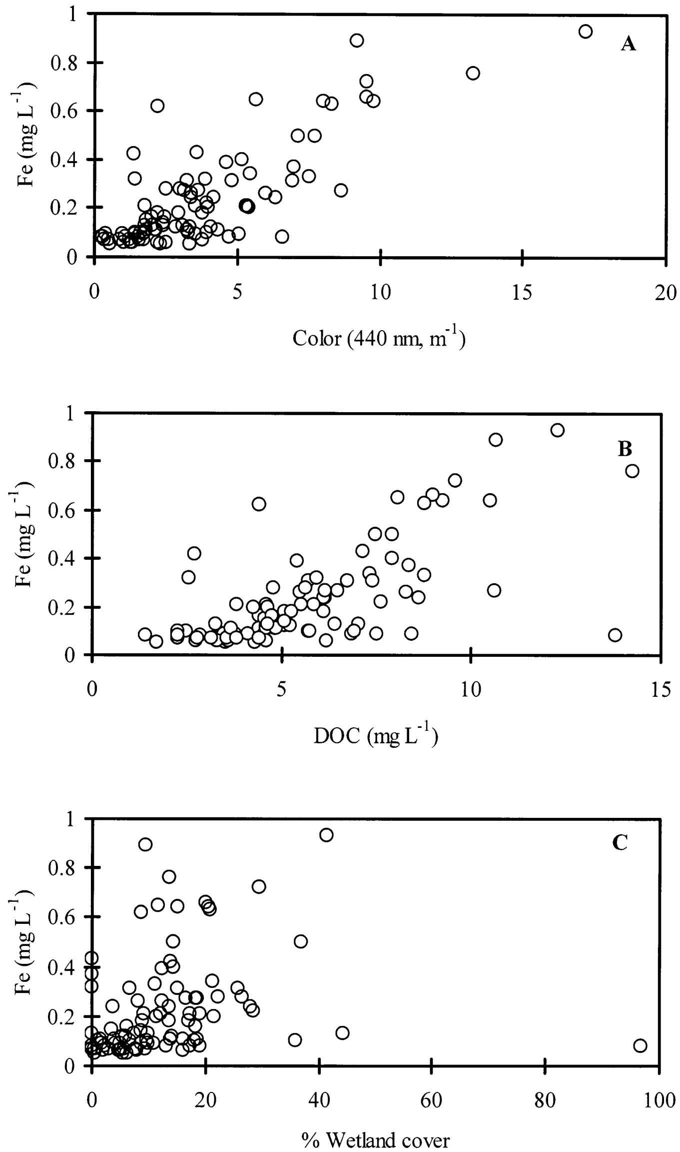

Fig. 1. The relationships between dissolved Fe concentration (mg L^{-1}) and color (absorbance at 440 nm in m^{-1}) (A), DOC concentration (mg L^{-1}) (B), and percent wetland cover in the watershed (C).

Importance of distance decay and Fe export by cover type—Our analyses estimate both the total annual export of Fe for the different watershed cover types (mg Fe m^{-2} yr^{-1}) and the proportion of the export that reaches the lake (i.e., loading) as a function of distance from the lake. Although our analysis allowed loading from the cover types to vary as a function of distance from the lake (α), we found that few cover types showed significant decline in loading as a function of distance (Fig. 3). Specifically, the upland forests (UF), emergent marshes (EM), dry deciduous shrub swamps (DDSS), and dry evergreen shrub swamps (DESS) showed no change in Fe loading as a function of distance from the lakeshore. In contrast, sharp declines with distance were observed for both the forested swamps (FS) and the wet deciduous shrub swamps (WDSS). Loading from both of these

Table 3. Comparison of alternate models of lake Fe concentration. The most parsimonious model (Model 7) has the lowest Akaike Information Criterion score corrected for small sample size (AIC_c). ΔAIC is the difference between the AIC_c of the best model (7) and alternate models. Model goodness of fit (R^2 of observed vs. predicted Fe) is also reported, as is the number of parameters in the model. For models with no distance decay, all of the covertype specific distance decay coefficients (α) were set = 0. For the area-based input term (ABI), the different models either estimated nonzero ABI for all lakes, for anoxic lakes only, or the only the subset of lakes with a mean depth greater than an estimated threshold. Number of lakes (observations) for all models is 93.

Model	No. of cover types	Distance decay	In-lake decay	ABI	No. of parameters	R^2	AIC_{corr}	Δ AIC
1	8	All	Color	All	20	0.62	793.49	38.19
2	8	All	Color×depth	All	21	0.68	779.21	23.91
3	8	Two cover types	Color×depth	All	15	0.68	759.10	3.80
4	8	None	Color×depth	All	13	0.67	758.58	3.28
5	8	None	Color×depth	Anoxic only	13	0.65	769.69	14.39
6	8	Two cover types	Color×depth	Threshold	15	0.69	756.10	0.80
7	8	None	Color×depth	Threshold	14	0.68	755.30	0.00
8	1	None	Color×depth	Threshold	7	0.61	758.27	2.97

cover types was reduced to practically nil 10 m from the shoreline. The decay term was more gradual from upland open vegetation (UO) and wet evergreen shrub swamps (WESS). Beyond 200 m from shore, both of these cover types had reached a stable loading.

Given the negligible distance decay for loading from most of the cover types, with the exception perhaps of upland UO and WESS, we tested both a mixed model with distance decay for only these two cover types (i.e., UO and WESS) and no distance decay for the other 6 (Model 3), and a completely nonspatial model with no distance decay (Model 4). Both Models 3 and 4 (Table 3) were a dramatic improvement over the completely spatial model (Model 2, $\Delta\ AIC_{c\ 2\text{–}3}$ = 20.1 and $\Delta\ AIC_{c\ 2\text{–}4}$ = 20.6). There was relatively little difference between models 3 and 4 ($\Delta\ AIC_c < 2$).

The Fe export coefficients differed widely among the cover types (Fig. 4). An alternate model that combined all of the watershed into a homogeneous cover type (Model 8) had less support and provided less information (Model 8, $\Delta\ AIC_{c\ 8\text{–}7}$ = 2.97), with an estimated overall watershed export of 454 mg Fe m^{-2} yr^{-1}. Highest loading came from DDSS, predominantly alder swamps, at an average rate of 5,430 mg Fe m^{-2} yr^{-1}. Soil water content strongly influenced the export, given WDSS exported Fe at a rate 7-fold lower (780 mg Fe m^{-2} yr^{-1}). Fe export was considerable from EM (4,070 mg Fe m^{-2} yr^{-1}) and WESS (e.g., bogs) (1,600 mg Fe m^{-2} yr^{-1}) and negligible from UO, FS, and DESS. Export per unit area from both upland cover types (UF and UO) was quite low (e.g., UF, 340 mg Fe m^{-2} yr^{-1}) relative to many of the wetland cover types. Although some of the wetlands on average export much more Fe per unit area than upland forests, the watersheds of these Adirondack lakes are predominantly forested. As a result, upland forests were the predominant sources of lake Fe. On average, wetland cover made up 13.1% of the watershed area but contributed 25% of the Fe loading to these lakes. UF made up the difference, accounting for 75% of the Fe load on average.

Upstream loading—Of the 93 lakes in our dataset, the majority were headwater lakes, with only 15 receiving upstream inputs of Fe. These upstream inputs represented only 5.4% (λ parameter, 95% support intervals = 3.4–7.4%) of

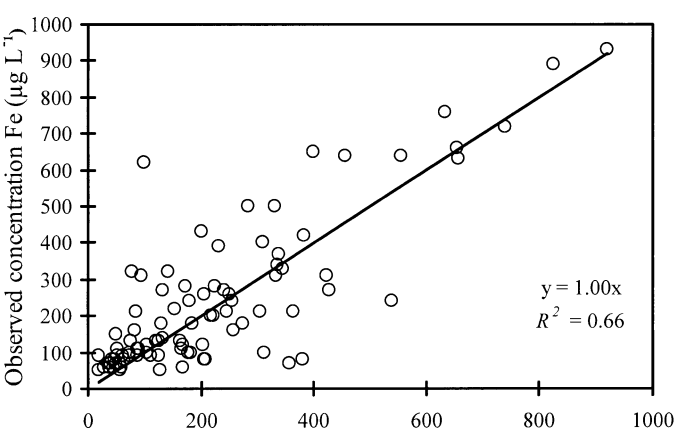

Fig. 2. Goodness of fit of the most parsimonious model of lake Fe concentration (Model 7; Table 3).

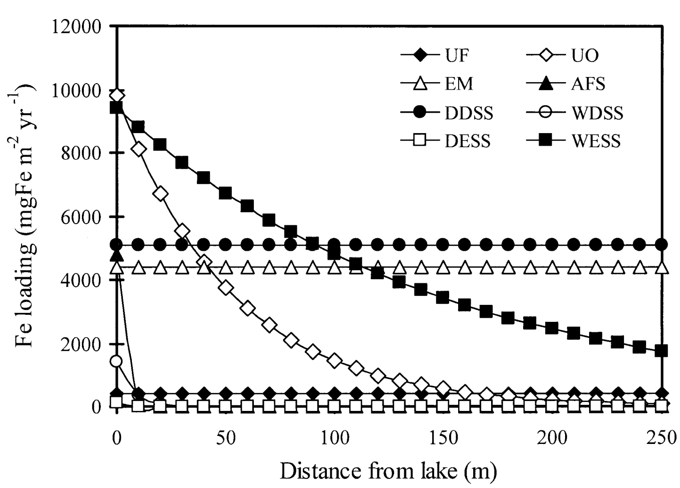

Fig. 3. Loading of Fe (mg Fe m^{-2} yr^{-1}) as a function of distance to the lake from the specific source area in the watershed as predicted in the spatially explicit model, Model 2 in Table 3. Cover type abbreviations are described in Table 2.

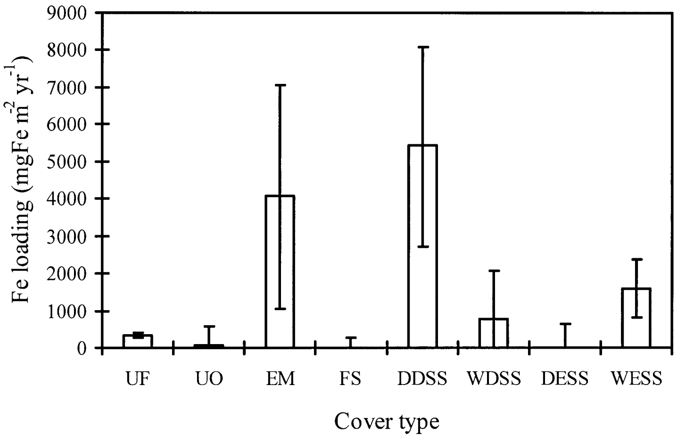

Fig. 4. Average predicted Fe loading (mg Fe m^{-2} yr^{-1}) from the different cover types based on the most parsimonious model, Model 7 in Table 3. Error bars are 2-unit support intervals as estimated by the model. Cover type abbreviations are described in Table 2.

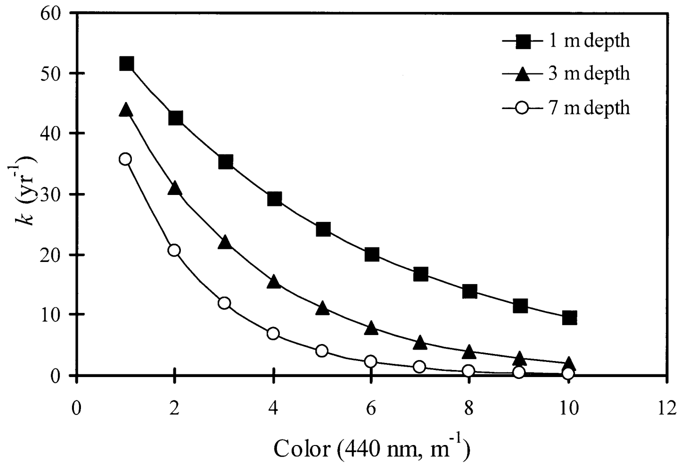

Fig. 5. The relationship between in lake loss rate (k, yr^{-1}) as a function of color and average lake depth.

the Fe exports estimated from upstream lakes, indicating that there is significant loss of Fe during downstream transport.

Area-based inputs—Area based inputs (ABI) are a function of both atmospheric deposition of Fe to the lake and the internal load from the resuspension of Fe bound in the sediment. We explored three different functional forms for ABI (Table 3): (1) where ABI was a function of lake surface area for all lakes (Models 1–4), (2) where ABI was a function of surface area in those lakes we measured as having anoxic hypolimnia (Model 5), and (3) in which the model estimated a minimum depth (threshold) below which ABI was negligible (Models 6–8). This third approach produced the most parsimonious model (Table 3), with an estimated critical depth threshold of 1.01 m (Model 7). Approximately 85% of the lakes in our dataset had an average depth that exceeded this threshold. The average ABI was extremely low compared with the export from most cover types and was estimated at 56 mg Fe m^{-2} yr^{-1} (42–66 mg Fe m^{-2} yr^{-1}).

In-lake losses—The in-lake decay coefficient (k) was first estimated as a function of a linear decline in lake color ($k = -3.7$ color $+ 30.3$) (Table 3, Model 1). However, examination of the residuals of this model suggested that settling rates from large, deep lakes were being overestimated. We therefore tested a function for k involving both color and depth in an exponential functional form as described by Eq. 3 (Materials and Methods). This improved the model, by both increasing predictive power (r^2) and decreasing AIC$_c$ (Table 3, Model 2 vs. Model 1). The best model parameter estimates were:

$$k = 62e^{-0.19\times \text{color}\times \text{depth}^{0.56}} \quad (5)$$

Indeed, in-lake decay (presumably in the form of settling) was slow in deep lakes relative to shallow ones with the same color (Fig. 5).

Discussion

Our results indicate highly variable loading of Fe to lakes from different cover types within watersheds. If we treated the watersheds in this study as homogeneous source areas for Fe, estimated Fe loading rates would be 454 mg Fe m^{-2} yr^{-1}. This estimate is very similar to the reported literature average of 481 mg Fe m^{-2} yr^{-1} with a range of 49–2,270 mg Fe m^{-2} yr^{-1} (Nürmberg and Dillon 1993). Our analyses indicate that export from different cover types within a watershed, however, can vary by over an order of magnitude from this average rate. The amount of Fe loaded per unit area was highest from DDSS, followed by EM, wet (permanently or semipermanently flooded) evergreen shrub swamps, WDSS and UF (Fig. 4). Negligible loading was estimated from upland open areas, forested swamps, or DESS.

The strong differential loading among wetland types was surprising given the reported strong link and suspected simultaneous loading of Fe and DOC to lakes (Rasmussen et al. 1989; Maranger and Pullin 2003). The estimated loading of DOC per unit area per year is remarkably similar among the different shrub wetlands types in these same Adirondack lakes (Canham et al. 2004), so a 50-fold difference in Fe loading among these different wetland types was unexpected. However, the large differences in loading are consistent with the lack of a relationship between percentage of wetland cover and total lake Fe concentration. Fe and DOC can be uncoupled in bogs located in the same region (Moore 1988). Hence the differential export of Fe suggests the variable importance of Fe in the biogeochemistry among different wetlands and their saturation conditions.

Wetlands typically have anaerobic soils (Schlesinger 1997) that should favor the release of Fe, given that ferrous Fe would be the predominant form. If we assume that all wetland sites were anaerobic, the observed higher loading from certain wetland types is likely a function of greater Fe concentration in the associated soil and/or a relatively lower redox potential (<-50 mV) when the microbial reduction of Fe oxyhydroxides would begin.

The observed high loading of Fe from alder swamps is interesting given the links between Fe and nitrogen metabolism. Alder swamps are important sites of nitrogen fixation and the nitrogenase proteins of the symbiotic *Frankia* spp. that carry out N-fixation are metaloenzymes that require Fe (Hewitt 1983). Hence these sites likely have relatively higher concentrations of biologically accessible Fe. Fe loading varied with soil saturation level within the two deciduous shrub swamp types (DDSS vs. WDSS). Nonflooded deciduous shrub swamps released seven times more Fe than their flooded counterparts. Experimental and process studies seem to support different possibilities in terms of Fe mobility in alder swamps where the biological conditions observed under flooding may favor (Kaelke and Dawson 2002) or impinge (Batzli and Dawson 1999) Fe release from the soil. The landscape level characterization of our model is not precise enough, however, to elucidate the mechanism that might cause the observed variation in Fe loading, but our results do suggest that Fe has greater mobility in nonflooded alder swamps.

Emergent marshes are also apparently a significant source (per unit area) of Fe to lakes, although they were not reported to be an important source of DOC to these lakes (Canham et al. 2004). The EM in this study largely consisted of cattail marshes (*Typha*) with a mix of grasses and sedges (Roy et al. 1996). Typically, EM are considered important sites of metal accumulation. Elevated concentrations of Fe have been observed on the top 5 cm of sediments of a predominantly *Typha* marsh (Ye et al. 2001). However *Typha* tend to increase sediment OM content, microbial respiration, and the redox potential of the sediment (Goulet and Pick 2001) resulting in conditions that would favor the release of Fe (Weiss et al. 2004). The diffusion of O_2 from cattail roots is also limited in some cases resulting in the reduction of a marsh's capacity to keep metal oxides bound longer term in sediment (Goulet and Pick 2001).

In contrast to deciduous shrub swamps, loading from flooded evergreen shrub swamps was quite high whereas loading from the nonflooded counterparts was negligible. Flooding tends to lower the redox potential of the anoxic peat in these bogs (Bellemakers and Maessen 1998) creating conditions that favor Fe release (Darke and Waldbridge 2000). Given the important roles that iron plays in both the abiotic and biotic cycling of N and P, this differential loading of iron among wetland types may in part explain why some wetlands act as sources of these macroelements and others act as sinks (Richardson 1985).

One of the objectives of this model was to determine whether Fe was lost in transport from the source to the lake. The most parsimonious model suggested that there was no important distance decay for Fe from any of the cover types. Hence the amount of Fe loading per unit area for a given cover type was the same whether the source area was adjacent to the lake or hundreds of meters away. A similar result was observed for DOC (Canham et al. 2004) suggesting that there is little adsorption along the flow path. Note, however, that our model does not take into account the trajectory of a source point (i.e., which cover types it flows through) to the lake, only the distance. Given the differential loading of Fe from the cover types, differential adsorption may be expected at least in surface water flow.

Although on average wetlands delivered more Fe than forests per unit area, total loading was primarily from forested systems. The same was observed for DOC in this region (Canham et al. 2004). On average, forests represented 87% of the watershed cover in our survey area and accounted for on average 75% of the Fe loading to the 93 lakes. According to our models, the location of a source area within the watershed had little effect on how much exported Fe was actually being delivered to the lake, with the exception perhaps of ''wet'' evergreen shrub swamps and upland open areas. We estimated that only 5.4% (3.4–7.4%) of upstream lake outputs made it to the lake downstream. However, only 13 of the lakes had inputs from upstream lakes, so we consider this model parameter estimate to be interesting but tentative. Only direct measurements of in stream dissolved Fe processing will confirm our model results.

Our analyses suggest that in-lake Fe loss was regulated by both lake color and depth. Lakes that are characteristically brown are considered highly colored systems. Color is not only representative of DOC concentration but also of the humic acid component of that DOC. These dissolved organic acids have a high affinity for binding Fe, keeping it in suspension in a dissolved state, thus preventing particulate formation and sedimentation (McKnight et al. 2003; Pullin and Canabiss 2003). Indeed it has been observed that iron loss from lakes, as measured by mass transfer coefficients is reduced in lakes with higher DOC (Molot and Dillon 2003). The observed higher rates of in lake loss in shallow lakes may also be a function of greater surface area for binding and subsequent removal of Fe from the water column. The surface to volume ratio would be greater in shallow systems relative to deep ones.

The combination of atmospheric inputs and sediment resuspension (ABI) represented relatively low fluxes in these lakes, accounting for only 56 mg Fe m^{-2} yr^{-1} (46–66 mg Fe m^{-2} yr^{-1}), as compared with the loading from the various sources in the catchment. This internal loading was low compared with the reported literature average 154 mg Fe m^{-2} yr^{-1} and range of 0–893 Fe m^{-2} yr^{-1} of Fe resuspension (Nürmberg and Dillon 1993). Lakes in this study were very shallow, in general, with high flushing rates and reduced Fe settling rates. Thus, they may not be not subject to the internal Fe load that would be observed in deeper systems with anoxic hypolimnia (Carignan and Lean 1991). Atmospheric deposition can be an important source of Fe to some lakes, accounting for as much as 20% of the external load (Nürnberg and Dillon 1993). However, our model suggests that only a small amount of Fe is entering these Adirondack lakes via precipitation.

Other models looking at the loading of P, N, and DOC have taken spatial configuration of the landscape into account. For example, Gergel et al. (1999) found that fringing wetlands (50 m) could explain the same amount of variability in lake DOC concentration as total percent wetland in the watershed for a series of lakes located in Wisconsin. This result suggested that the spatial location of the DOC source was important. However their study inferred loss along a flow path but did not test it. Canham et al. (2004), using the identical approach to our model, found no distance decay for DOC in the Adirondacks (New York) suggesting regional differences in the effects of watershed configuration. The variability in ecoregion surficial geology may explain, at least in part, why in some studies spatial location of source area is important and in others it is not. Using hierarchical and multivariate approaches, Hunsaker and Levine (1995) found that spatial configuration of the landscape was important in determining N and P loading in watersheds evaluated in Texas but not in watersheds evaluated in Illinois. The models used in their study are difficult to compare, however, because they are fundamentally very different. Spatial configuration and loading have also evaluated or highlighted the importance of buffer strips (Soranno et al. 1996; Weller et al. 1998). However our mass balance likelihood approach differs from most of the afore-mentioned models in that we consider not only differential source area and distance to lake, but internal processes and other external inputs (i.e., atmospheric).

The model framework developed here to estimate Fe concentrations should be easily applicable to other lake districts. Regional modifications in land cover type would obviously need to be incorporated. Surficial geology combined with land cover type would also be an interesting addition to the model as till thickness apparently plays an important role in Fe export (Dillon and Molot 1997; Momen and Zehr 1998). We did not include surficial geology in our model as reliable surficial geology data-layers were not available for our watersheds. Modifications of the original model framework may also be required in the evaluation of internal processes. For example lakes in regions with a greater range of pH may include pH as a negative linear or exponential function of within lake sedimentation of Fe. Other important modifiers of within lake losses could include more precise estimates of humic content, alkalinity, or lake S and Ca concentrations.

Land–water interactions are a focal concern in management of surface waters, especially in the context of protecting water quality in the face of extensive land-use change within watersheds. Therefore, the lake and its associated watershed should ideally be treated as an integrated system. Our spatially explicit inverse modeling approach allows estimation of the key terms that govern regional scale variation in lake chemistry. Maximum likelihood modeling is ideal in this context, because alternative models can be formulated, tested, and compared. The method has a number of advantages in comparison with multivariate analyses that are not spatially explicit and not based on mass-balance principles. In particular, our approach partitions loading from among specific source areas within the watershed, as a function of cover type and distance to the lake. 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. The method should also be generally applicable to analysis of watershed loading and in-lake processing of other important nutrients and elements such as P, N, and S that are of concern for both lake eutrophication and acidification in the Adirondack Park and in other regions in the world.

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Received: 29 November 2004
Accepted: 2 August 2005
Amended: 16 September 2005