GLOBAL BIOGEOCHEMICAL CYCLES, VOL. 14, NO. 1, PAGES 127-138, MARCH 2000

Soil C:N ratio as a predictor of annual riverine DOC flux at local and global scales

J. A. Aitkenhead and W. H. McDowell
Department of Natural Resources, University of New Hampshire, Durham

Abstract. Dissolved organic carbon (DOC) is important in a wide variety of chemical, physical, and biological processes in surface waters. We examined the relationship between DOC flux and soil C:N ratio on a biome basis. DOC fluxes for 164 rivers were subdivided into 15 biome types including tropical rain forest, coniferous forests, peatland, deciduous forests, mixed forests, and grasslands. A database of soil C:N ratios was constructed and subdivided into biome types. At a global scale, mean soil C:N ratio of a biome accounts for 99.2% of the variance in annual riverine DOC flux among biomes. The relationship between soil C:N ratio and DOC flux at the biome scale was used to predict annual riverine DOC flux at the watershed scale for three test watersheds not included in the original model. Predicted flux of each watershed was within 4.5% of the actual DOC flux. Using the C:N model, we estimated the total export of carbon from land to the oceans to be 3.6 x 10^{14} g yr^{-1}. This empirical model should be useful in predicting changes in DOC flux under changing climatic conditions.

1. Introduction

The flux of dissolved organic carbon (DOC) from terrestrial landscapes to surface runoff is a fundamental part of the global carbon cycle with wide-ranging consequences for aquatic chemistry and biology. DOC affects the complexation, solubility, and mobility of metals [*Perdue et al.*, 1976; *Driscoll et al.*, 1988; *Martell et al.*, 1988] as well as the adsorption of pesticides to soils [*Senesi*, 1992; *Worral et al.*, 1997]. Formation of trihalomethanes when drinking water is disinfected with chlorine, a worldwide threat to water supplies, is also linked to DOC concentrations [*Siddiqui et al.*, 1997]. Finally, DOC attenuates UV-B radiation and thus provides some protection to aquatic biota from exposure to harmful UV radiation [e.g., *Williamson and Zagarese*, 1994].

Because estimated DOC fluxes are 1-2 orders of magnitude smaller than the global transfer of carbon between vegetation and atmosphere (110 Pg C yr^{-1}) [*Schneider*, 1989; *Dixon and Turner*, 1991], small changes in the carbon balance of the biosphere could result in large changes in DOC export. DOC concentrations and flux are sensitive to changes in temperature and moisture conditions in soils [*Christ and David*, 1996; *Mulholland and Hill*, 1997] and increased atmospheric CO_2 [*Jones et al.*, 1998]. Any effort to model DOC flux under conditions of a changing global climate must be based on an understanding of the underlying mechanisms regulating that flux.

Soils are an important pool of organic carbon and play a major role in the global carbon cycle. Approximately 50% of surface soil carbon is fast cycling with a turnover time of between 10 and 100 years [*Harrison et al.*, 1995; *Trumbore et al.*, 1996]. The estimated soil organic carbon pool in the near surface soil horizon is 1500 Pg C [*Schlesinger*, 1977; *Post et al.*, 1982; *Eswaran et al.*, 1993]. Soils also contain 95 Pg N [*Post et al.*, 1985], 80% of which is in the surface horizons. Within the soil profile, sorption of DOC is common in podzolic soils and is often thought to be important in regulating DOC flux in particular watersheds [*McDowell and Wood*, 1984]. Although the podzolization process typically results in net retention of DOC, mature spodosols appear to be a net DOC source to tributaries of the Amazon [*McClain et al.*, 1997], and they may be a net source of DOC to rivers in other regions as well. Enhanced anthropogenic nitrogen input seems to accelerate this DOC release in well-developed spodosols [*Guggenberger and Zech*, 1993].

Controls on riverine DOC concentration and flux have been the focus of much research over the last 15 years [e.g., *McDowell and Wood*, 1984; *Eckhardt and Moore*, 1990; *Clair et al.*, 1994; *Hope et al.*, 1997a]. Most of the studies on riverine DOC dynamics have been small-scale and watershed-specific. Relatively few have examined the factors that might be responsible for differences in DOC flux between watersheds or biome types.

The objectives of this study were to investigate (1) the extent to which soil C:N ratio can be used to predict soil solution DOC concentration and riverine DOC flux at a range of watershed sizes and vegetation types and (2) to estimate the total dissolved organic carbon flux to the oceans.

2. Materials and Methods

2.1. DOC Export and Soil C:N Ratios

Mean annual riverine DOC flux for 164 rivers ranging in watershed size from 0.38 ha to 3.2 x 10^8 ha was obtained from the published literature (Table 1). We only included data for which sampling covered all hydrologic regimes and which we

Paper number 1999GB900083.
0886-6236/00/1999GB900083$12.00

Table 1. Descriptions of the 164 Watersheds used to Estimate Mean Annual Riverine DOC Export by Biome.

Biome/Watershed	DOC, kg ha^{-1} yr^{-1}	Area, ha	Data Source
Cool Grasslands			
Brazos River, Texas*	2.11	1.14×10^{7}	*Malcolm and Durum* [1976]
Missouri River*	1.58	1.08×10^{8}	*Malcolm and Durum* [1976]
Mississippi River*	5.34	3.22×10^{8}	*Malcolm and Durum* [1976]
Colorado River, Texas	1.00	1.07×10^{7}	*Mulholland and Watts* [1982]
Trinity River, Texas	6.50	4.45×10^{6}	*Mulholland and Watts* [1982]
Salinas River, California	5.50	1.04×10^{6}	*Mulholland and Watts* [1982]
San Joaquin River, California	5.00	3.5×10^{6}	*Mulholland and Watts* [1982]
Rio Grande, Texas	1.00	4.56×10^{7}	*Mulholland and Watts* [1982]
Colorado River, California	1.00	6.39×10^{7}	*Mulholland and Watts* [1982]
Guadalupe River, Texas	9.50	1.35×10^{6}	*Mulholland and Watts* [1982]
S. Kings Creek, Kansas	3.97	1.06×10^{3}	*W. Dodds* (unpub data, 1997)
Tropical Savanna			
Gambia River, West Africa	2.66	4.20×10^{6}	*Lesack et al.* [1984]
Apure River, Venezuela	21.35	1.67×10^{7}	*Saunders and Lewis* [1988]
Paraguay River, Brazil	8.69	3.60×10^{7}	*Hamilton et al.* [1997]
Taiga			
MacKenzie River, NW. Territories	12.00	1.66×10^{8}	*Mulholland and Watts* [1982]
Back River, NW. Territories	4.50	9.80×10^{6}	*Mulholland and Watts* [1983]
Thelon River, NW. Territories	6.50	1.54×10^{7}	*Mulholland and Watts* [1984]
Coppermine River, NW. Territories	5.50	2.03×10^{6}	*Mulholland and Watts* [1985]
Kazan River, NW. Territories	8.50	7.23×10^{6}	*Mulholland and Watts* [1986]
Quoich River, NW. Territories	5.00	2.87×10^{6}	*Mulholland and Watts* [1987]
Siberian Steppe			
River Volga, Russia	12.90	1.4×10^{8}	*Skopintsev* [1979]
Warm Deciduous			
Watershed 18, Coweeta, South Carolina	15.35	13	*Tate and Meyer* [1983]
Watershed 13, Coweeta, South Carolina	12.85	16	*Tate and Meyer* [1983]
Warm Mixed Forests			
Fourmile Branch, South Carolina	17.14	1.26×10^{3}	*Dosskey and Bertsch* [1994]
Cool Deciduous			
Bear Brook, New Hampshire	17.80	100	*Fisher and Likens,*[1973]
Augusta Creek, Michigan	27.70	3.64×10^{3}	*Moeller et al.* [1979]
Augusta Creek, Michigan	18.70	6.27×10^{3}	*Moeller et al.* 1979]
Smith Creek, Michigan	22.10	78	*Moeller et al.* 1979]
Hubbard Brook, (W6) New Hampshire	8.51	13	*Hobbie and Likens* [1973]
Bear Brook, New Hampshire	20.80	100	*McDowell and Likens* [1988]
Warm Conifer			
Eel River, California	39.00	8.06×10^{5}	*Mulholland and Watts* [1982]
Russian River, California	26.00	3.46×10^{5}	*Mulholland and Watts* [1982]
Klamath River, California	18.50	3.13×10^{6}	*Mulholland and Watts* [1982]
St. Johns River, Florida	27.50	2.26×10^{6}	*Mulholland and Watts* [1982]
Peace River, Florida	37.50	3.56×10^{5}	*Mulholland and Watts* [1982]
Suwannee River, Florida	42.50	2.5×10^{6}	*Mulholland and Watts* [1982]
Apalachicola River, Florida	37.50	4.56×10^{6}	*Mulholland and Watts* [1982]
Choctawatchee River, Florida	52.50	1.13×10^{6}	*Mulholland and Watts* [1982]
Escambia River, Florida	45.50	9.88×10^{5}	*Mulholland and Watts* [1982]
Alabama River, Alabama	37.00	5.57×10^{6}	*Mulholland and Watts* [1982]

Table 1. (continued)

Biome/Watershed	DOC, kg ha^{-1} yr^{-1}	Area, ha	Data Source
Pascagoula River, Mississippi	47.50	1.73×10^6	*Mulholland and Watts* [1982]
Pearl River, Louisiana	31.50	1.72×10^6	*Mulholland and Watts* [1982]
Satilla River, Georgia	45.50	7.23×10^5	*Mulholland and Watts* [1982]
Watershed 1, Carteret County, North Carolina	27.82	no data	*Amatya et al.* [1998]
Cool Conifer			
Kelly River, Nova Scotia, Canada	35.90	6.3×10^3	*Clair et al.* [1994]
Wallace River, Nova Scotia, Canada	30.70	2.98×10^4	*Clair et al.* [1994]
Salmon River, Nova Scotia, Canada	50.60	1.99×10^4	*Clair et al.* [1994]
NE Margaree River, Nova Scotia, Canada	29.90	3.68×10^4	*Clair et al.* [1994]
Clam Harbour, Nova Scotia, Canada	71.50	4.5×10^3	*Clair et al.* [1994]
St. Mary's River, Nova Scotia, Canada	41.90	1.35×10^5	*Clair et al.* [1994]
Rocky River, Newfoundland	77.20	2.85×10^4	*Clair et al.* [1994]
Eagle River, Labrador	37.20	1.09×10^6	*Clair et al.* [1994]
Churchill River, Labrador	23.90	9.25×10^6	*Clair et al.* [1994]
Birkness, Norway	58.80	41	*Lydersen and Henriksen*[1994]
Langtjern, Norway	57.50	480	*Lydersen and Henriksen*[1994]
Katajaluoma - SW Finland	66.00	1.1×10^3	*Kortelainen et al.* [1997]
Tollinja - SW Finland	43.00	340	*Kortelainen et al.* [1997]
Kesselinpuro - SE Finland	74.00	2.1×10^3	*Kortelainen et al.* [1997]
Teecressuonoja - S Finland	37.00	69	*Kortelainen et al.* [1997]
Paunulanpuro - S Finland	48.00	140	*Kortelainen et al.* [1997]
Heinajoki - S Finland	58.00	950	*Kortelainen et al.* [1997]
Kellojoki - NE Finland	71.00	190	*Kortelainen et al.* [1997]
Myllypuro - NE Finland	59.00	1.1×10^3	*Kortelainen et al.* [1997]
Vaarajoki - NE Finland	37.00	1.9×10^3	*Kortelainen et al.* [1997]
Vaha-Askanjoki – N Finland	40.00	1.6×10^3	*Kortelainen et al.* [1997]
Kuusivaaranpuro - Arctic	35.00	2.8×10^3	*Kortelainen et al.* [1997]
Myllyoja – Arctic	26.00	2.9×10^3	*Kortelainen et al.* [1997]
Kobuk River, Alaska	16.00	2.47×10^6	*Mulholland and Watts* [1982]
Yukon River, Alaska	15.50	8.31×10^7	*Mulholland and Watts* [1982]
Susitna River, Alaska	29.50	5.02×10^6	*Mulholland and Watts* [1982]
Copper River, Alaska	41.50	5.34×10^6	*Mulholland and Watts* [1982]
Stikine River, Alaska	21.50	5.10×10^6	*Mulholland and Watts* [1982]
Kuskokwim River, Alaska	16.00	8.05×10^6	*Mulholland and Watts* [1982]
McKenzie River, Oregon	18.60	1.02×10^5	*Moeller et al.* [1979]
Heath/Moorland			
Ochil Hills, Scotland, UK	84.00	51	*Grieve* [1984]
Pipers Hole, Newfoundland	53.60	2.64×10^4	*Clair et al.* [1994]
Indian River, Newfoundland	32.60	9.74×10^4	*Clair et al.* [1994]
Isle aux Morts, Newfoundland	110.60	2.05×10^4	*Clair et al.* [1994]
Torrent River, Newfoundland	64.30	6.24×10^4	*Clair et al.* [1994]
Baddoch Burn, Scotland, UK	21.40	2.3×10^3	*Hope et al.* [1997b]
Kaatvatn, Norway	20.20	2.56×10^3	*Lydersen and Henriksen*[1994]
Glen Dye, Scotland, UK	67.60	4.1×10^3	*Reid* [1979]
Afon Cyff, Wales, UK	54.00	4	*Reynolds* [1986]
Mixed Northern Forests			
LaHave River, Nova Scotia, Canada	60.00	1.25×10^5	*Clair et al.* [1994]
Liscomb River, Nova Scotia, Canada	123.50	3.89×10^4	*Clair et al.* [1994]
Medway River, Nova Scotia, Canada	67.60	1.39×10^5	*Clair et al.* [1994]
Meteghan River, Nova Scotia, Canada	67.80	1.67×10^4	*Clair et al.* [1994]
Tusket River, Nova Scotia, Canada	97.40	1.07×10^5	*Clair et al.* [1994]
Roseway River, Nova Scotia, Canada	123.00	4.95×10^4	*Clair et al.* [1994]
Mersey River, Nova Scotia, Canada	77.30	2.7×10^4	*Clair et al.* [1994]

Table 1. (continued)

Biome/Watershed	DOC, kg ha^{-1} yr^{-1}	Area, ha	Data Source
Lepreau River, New Brunswick	48.50	2.39×10^4	*Clair et al.* [1994]
Point Wolfe River, New Brunswick	27.70	1.3×10^4	*Clair et al.* [1994]
Salmon River, New Brunswick	34.20	1.05×10^5	*Clair et al.* [1994]
North Branch, Oromocto, New Brunswick	54.70	5.70×10^4	*Clair et al.* [1994]
Storgama, Norway	38.00	60	*Lydersen and Henriksen*[1994]
BC1 Blue Chalk Dorset LTR, Ontario, Canada	9.90	20	*Dillon and Molot* [1997]
CB1 Chubb, Dorset LTR, Ontario, Canada	22.90	60	*Dillon and Molot* [1997]
CB2 Chubb, Dorset LTR, Ontario, Canada	60.20	126	*Dillon and Molot* [1997]
CN1 Crosson Dorset LTR, Ontario, Canada	43.60	456	*Dillon and Molot* [1997]
DE10 Dickie, Dorset LTR, Ontario, Canada	65.70	79	*Dillon and Molot* [1997]
DE11 Dickie, Dorset LTR, Ontario, Canada	85.50	76	*Dillon and Molot* [1997]
DE5 Dickie Dorset LTR, Ontario, Canada	73.10	30	*Dillon and Molot* [1997]
DE6 Dickie Dorset LTR, Ontario, Canada	90.80	22	*Dillon and Molot* [1997]
DE8 Dickie Dorset LTR, Ontario, Canada	68.10	67	*Dillon and Molot* [1997]
HP3 Harp, Dorset LTR, Ontario, Canada	45.60	26	*Dillon and Molot* [1997]
HP3A Harp, Dorset LTR, Ontario, Canada	19.30	20	*Dillon and Molot* [1997]
HP4 Harp, Dorset LTR, Ontario, Canada	29.90	120	*Dillon and Molot* [1997]
HP5 Harp, Dorset LTR, Ontario, Canada	55.80	191	*Dillon and Molot* [1997]
HP6 Harp, Dorset LTR, Ontario, Canada	32.80	10	*Dillon and Molot* [1997]
HP6A Harp, Dorset LTR, Ontario, Canada	32.70	15	*Dillon and Molot* [1997]
PC1 Plastic, Dorset LTR, Ontario Canada	48.60	23	*Dillon and Molot* [1997]
RC1 Red Chalk,Dorset LTR, Ontario, Canada	19.00	134	*Dillon and Molot* [1997]
RC2 Red Chalk, Dorset LTR, Ontario, Canada	62.20	27	*Dillon and Molot* [1997]
RC3 Red Chalk, Dorset LTR, Ontario, Canada	41.70	71	*Dillon and Molot* [1997]
RC4 Red Chalk, Dorset LTR, Ontario, Canada	34.70	46	*Dillon and Molot* [1997]
Merrimack River, Massachusetts	49.00	1.2×10^6	*Mulholland and Watts* [1982]
Saco River, Maine	54.50	3.36×10^5	*Mulholland and Watts* [1982]
Androscoggin River, Maine	55.00	8.83×10^5	*Mulholland and Watts* [1982]
Kennebec River, Maine	44.50	7.04×10^5	*Mulholland and Watts* [1982]
Penobscot River, Maine	54.50	1.73×10^6	*Mulholland and Watts* [1982]
Hubbard Brook (W7), New Hampshire	24.90	76	Campbell et al. (in press)
Hubbard Brook (W8), New Hampshire	44.65	59	Campbell et al. (in press)
Hubbard Brook (W9), New Hampshire	101.70	68	Campbell et al. (in press)
Cone Pond, New Hampshire	42.45	33	Campbell et al. (in press)
Sleepers River, Vermont	14.35	39	Campbell et al. (in press)
Lye Brook (W4), Vermont	25.00	163	Campbell et al. (in press)
Lye Brook (W6), Vermont	29.10	106	Campbell et al. (in press)
Lye Brook (W8), Vermont	65.40	130	Campbell et al. (in press)
Tropical Forests			
Orinoco River, Venezuela	52.41	1×10^8	*Lewis and Saunders* [1989]
W3 Mendalong, Sabah, Malaysia	35.20	18	*Grip et al.* [1994]
W6 Mendalong, Sabah, Malaysia	138.80	5	*Grip et al.* [1994]
Q. Sonadora, Puerto Rico	74.33	262	*McDowell and Asbury* [1994]
Q. Toronja, Puerto Rico	32.97	16	*McDowell and Asbury* [1994]
Rio Icacos, Puerto Rico	93.97	326	*McDowell and Asbury* [1994]
Lanyang His, Taiwan	41.00	8.2×10^4	*Kao and Lui* [1997]
Rio Sauce, Guatemala*	30.00	3×10^4	*Brinson* [1976]
Rio Polochic, Guatemala*	46.00	5.25×10^5	*Brinson* [1976]
R. Beni, Bolivia	57.00	2.82×10^5	*Guyot and Wasson* [1994]
Vargem Grande, Brazil	48.00	no data	*Richey et al.* [1990]
Rio Içá, Brazil	56.00	no data	*Richey et al.* [1990]
Rio Jutaí, Brazil	87.00	no data	*Richey et al.* [1990]
Rio Juruá, Brazil	32.00	no data	*Richey et al.* [1990]
Rio Japurá, Brazil	51.00	no data	*Richey et al.* [1990]
Rio Purús, Brazil	48.00	no data	*Richey et al.* [1990]

Table 1. (continued)

Biome/Watershed	DOC, kg ha^{-1} yr^{-1}	Area, ha	Data Source
Rio Negro, Brazil	120.00	no data	*Richey et al.* [1990]
Caura River, Venezuela	96.80	4.75×10^6	*Lewis et al.* [1987]
Boreal/Peat			
Pahkaoja, S Finland	63.00	2.1×10^3	*Kortelainen et al.* [1997]
Huhtisuonoja, S Finland	42.00	500	*Kortelainen et al.* [1997]
Heinastonluoma, S Finland	86.00	1.6×10^3	*Kortelainen et al.* [1997]
Sydanmaanoja, SW Finland	74.00	380	*Kortelainen et al.* [1997]
Joutenpuro, NE Finland	66.00	350	*Kortelainen et al.* [1997]
Kirsioja, N Finland	59.00	2.3×10^3	*Kortelainen et al.* [1997]
Kotioja, N Finland	59.00	1.8×10^3	*Kortelainen et al.* [1997]
Ylijoki, N Finland	53.00	5.6×10^3	*Kortelainen et al.* [1997]
River Kiiminkijoki, Finland	69.40	3.6×10^5	*Heikkenen* [1989]
Peatlands			
Allt Darrarie, Scotland UK	101.70	1.3×10^3	*Hope et al.* [1997b]
Vertailualue, S Finland	88.00	250	*Kortelainen et al.* [1997]
Krunioja, N Finland	63.00	1×10^3	*Kortelainen et al.* [1997]
River Thurso, Scotland	87.60	4.13×10^4	*Hope et al.* [1997a]
River Halladale, Scotland	103.40	2.05×10^4	*Hope et al.* [1997a]
River Dionard, Scotland	70.00	7.3×10^3	*Hope et al.* [1997a]
Thoreau's Bog, Massachusetts	84.00	0.38	*McKnight et al.* [1985]
Swamp Forests			
Swamp Forest Louisiana	104.00	7.7×10^4	*Day et al.* [1977]
Sopchoppy River, Florida*	94.26	7.5×10^4	*Malcolm and Durum* [1976]

*Estimated from authors' data.

could confidently assign to a biome type. Each river was classified according to the dominant biome type of its watershed using the major world ecosystem complexes [*Olson and Watts*, 1982] described by *Zinke et al.* [1986]. Fifteen biome types were identified. The average annual riverine DOC flux for each of the biome types was then calculated.

A database of soil C:N ratio was constructed using soil organic carbon and total nitrogen data from the Carbon Dioxide Inventory Center database [*Zinke et al.*, 1986] and data reported in the published literature [e.g., *Glentworth*, 1954; *Heslop and Brown*, 1969; *Laing*, 1976; *Huntington et al.*, 1988; *McDowell et al.*, 1992; *Johnson and Lindberg*, 1992; *David and Lawrence*, 1996; *Huang and Schoenau*, 1997; *McClain et al.*, 1997]. Only soil profiles that had been sampled to 1m in depth or to bedrock were included in the database. This would ensure that hydrological flow through the mineral soil during base flow and the organic horizon during storm flow would be accounted for, and that the mean annual riverine export would reflect the annual hydrology. The soil C:N database was subdivided into biome types, and the mean soil C:N ratio was calculated for each biome. The C:N database holds soil C:N data for over 2000 soil profiles divided into Olson Ecosystem complexes [*Olson and Watts*, 1982].

Mean annual DOC flux and mean soil C:N ratio for each biome were used in regression analysis to derive a global empirical model. To validate this model, a technique known as the "leave one out" cross validation method [*Efron and Tibshirani*, 1993] was used. One observation of mean biome DOC flux and soil C:N was left out. The regression model being tested was refitted and used to compute the predicted value of the DOC flux for the missing biome. This procedure was repeated for each biome in turn. The average difference between the observed and predicted annual DOC flux was then calculated.

Our ultimate goal was to predict annual riverine DOC flux at the local and regional scale as well as at the biome scale. We used the biome relationship to predict annual DOC flux in a number of watersheds which have extensive data on soil C:N. To test the model at the watershed scale, annual riverine DOC flux was predicted for three watersheds not included in the construction of the model. *Johnson and Lindberg* [1992] reported a soil C:N ratio for a 13-year-old white pine watershed at the Coweeta Hydrologic Laboratory, South Carolina. The C:N ratio was inserted into the model equation to predict DOC flux. The predicted flux was compared to data reported by *Tate and Meyer* [1983]. Mean watershed soil C:N was calculated for a moorland site with some commercial conifer plantation at Glenbuchat in northeast

Scotland using data from *Heslop and Brown* [1969] and used to predict DOC flux. The predicted DOC flux was compared to the observed flux reported for the same site by *Creasey* [1984]. Finally, the C:N model equation was used to predict DOC flux for an undisturbed native evergreen forest watershed (M6) in Maimai, South Island, New Zealand. *McKie* [1978] characterized the soil C and N content for a similar, adjacent watershed (M5). Watershed mean soil C:N was calculated and used in the C:N model equation. The flux predicted for M5 was compared to that reported by *Moore* [1989] for the adjacent M6 watershed.

2.2. Soil Solution DOC Concentrations and Soil C:N Ratios

A wide range of data is available to assess the relationship between DOC in soil solution in the field and soil C:N ratio. Mean DOC concentrations from the organic horizons of nine coniferous forests were obtained from the published literature; in each case, soil solution was obtained using a zero tension lysimeter. Forests were single coniferous species or mixed conifers at sites located in Europe and the Unites States. To quantify the relationship between soil solution DOC concentration and soil C:N ratio, we used either total soil carbon and nitrogen content, C:N ratio reported along with DOC concentrations, or a recently published soil C:N ratio for the site. Regression analysis was used to quantify the relationship between soil solution DOC concentration and soil C:N ratio.

2.3. Estimate of Annual Dissolved Organic Carbon Flux From Terrestrial Ecosystems to the Ocean

We made two approximations of global DOC export to the oceans that would provide appropriate comparisons with previously published values. For the first estimate, we used the climatic zones described by *Meybeck* [1981]. These were tundra, taiga, temperate, tropical, and semiarid/desert, with areas of 7.55, 15.85, 22.0, 37.3, and 17.2 x 10^8 ha, respectively. For each climatic zone we calculated soil C:N ratios using the soil C:N database previously described in section 2.1. We calculated the mean annual DOC flux for each of *Meybeck*'s [1981] climatic zones using a mean soil C:N ratio for each zone and inserting it into the model equation. This gave us a value of kg ha^{-1} yr^{-1} for each climatic zone, which we then multiplied by the land area and summed to estimate total global carbon flux from terrestrial ecosystems to the oceans. For the second estimate, we used the ecosystems and land use areas described by *Schlesinger and Melack* [1981]. These were tropical forest, temperate forest, boreal forest, woodland and shrubland, tropical grassland, temperate grassland, tundra, semidesert, cultivated, and swamp with areas of 24.5, 12, 12, 8.5, 15, 9, 8, 8, 14 and 2 x 10^8 ha, respectively. We assigned a C:N ratio from the soil C:N database to each ecosystem and inserted it into the model equation to calculate annual areal values of DOC flux. These values were then multiplied by the land area of each ecosystem type and summed to estimate total global carbon export.

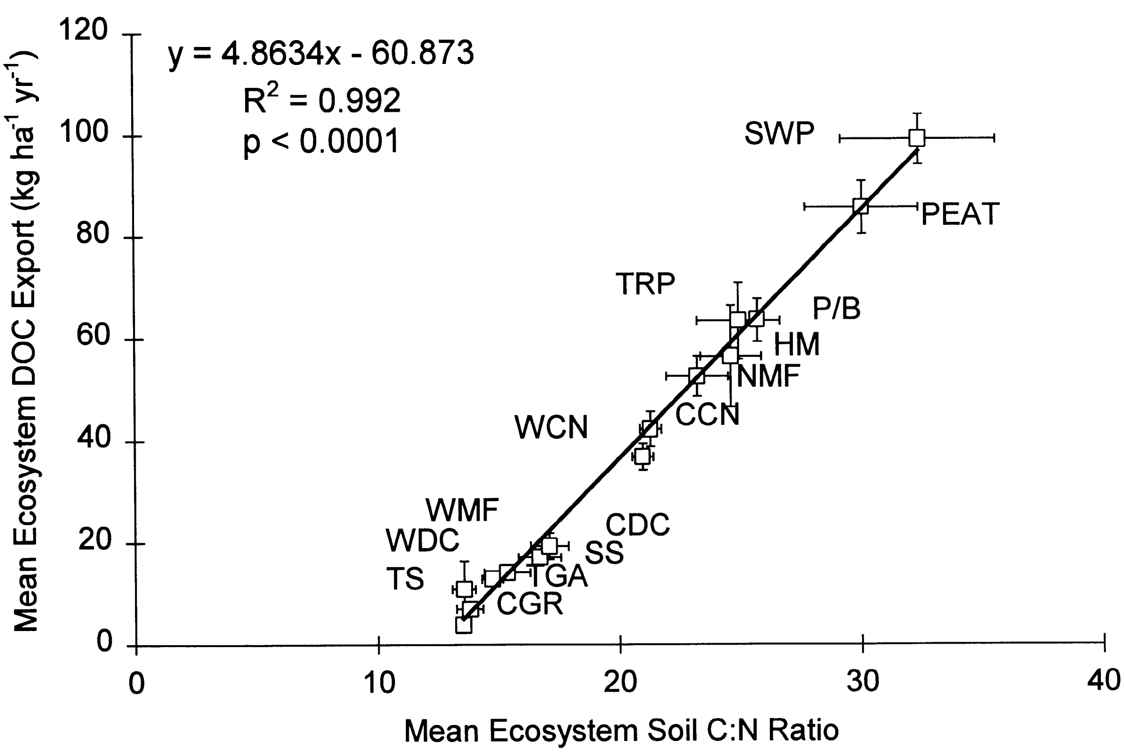

Figure 1. The relationship between mean (± SE) annual riverine DOC flux and mean (± SE) soil C:N for the 15 biome types used in the model construction. (CGR, cool grasslands; TS, tropical savanna; TGA, taiga; SS, Siberian steppe; WDC, warm deciduous forests; WMF, warm mixed forests; CDC, cool deciduous forests; WCN, warm conifer forests; CCN, cool conifer forests; NMF, northern mixed forests; HM, heath moorland; TRP, tropical forests; P/B, peat/boreal mix; PEAT, peatland; SWP, swamp forests). The regression is based upon the average soil C:N and average DOC export for each of the 15 biomes.

Table 2. Observed and Predicted Annual Riverine DOC Flux Using the "Leave One Out Cross Validation" Method for Each Biome

Biome	Soil C:N	Observed DOC Flux, kg ha^{-1} yr^{-1}	Predicted DOC Flux, kg ha^{-1} yr^{-1}	Percent Difference Between Observed and Predicted DOC Flux
Cool Grasslands	13.53	3.86	5.13	+32.9
Tropical Savannah	13.56	10.90	3.98	-63.5
Taiga	13.79	7.00	6.05	-13.6
Siberian Steppe	14.74	12.90	10.50	-18.6
Warm Deciduous Forests	15.34	14.10	13.68	-3.0
Warm Mixed Woodlands	16.69	17.14	20.62	+20.3
Cool Deciduous Forests	17.10	19.27	22.58	+17.2
Warm Conifer Forests	20.97	36.84	41.42	+12.4
Cool Conifer Forests	21.03	42.26	42.75	-1.2
Northern Mixed Forests	23.24	52.60	52.11	-0.9
Heath/Moorlands	24.64	56.50	59.23	+4.8
Tropical Forests	24.96	63.36	60.19	-5.0
Boreal/Peat mix	25.73	63.49	64.36	+1.4
Peatlands	30.05	85.67	85.15	-0.6
Swamp Forests	32.40	99.13	95.50	-3.7

3. Results

3.1. Mean Soil C:N Ratios and Mean Annual Riverine DOC Flux by Biome

The range of annual riverine DOC flux was large within some biomes (Figure 1). For example, tropical forests had the largest range of DOC flux, from 30 to 139 kg ha^{-1} yr^{-1}. The lowest reported annual riverine DOC flux was 1 kg ha^{-1} yr^{-1} from the Colorado and Rio Grande Rivers in Texas and the Colorado River in California draining watersheds of predominantly grasslands and agriculture. The highest, 138.8 kg ha^{-1} yr^{-1}, was from watershed 6 on the Mendalong in Malaysia draining a tropical forest (Table 1). The range of soil C:N ratios within each biome was also fairly large in some cases (Figure 1). For example, soil C:N ratios in tropical forests ranged between 11.5 and 53.05 (n = 44) and swamp forests from 14 to 61 (n = 12). In some biomes the range was much smaller; soil C:N ratios in cool grasslands ranged between 7.5 and 20.8 (n = 127) and taiga between 5.5 and 25.8 (n = 61).

There was a very strong relationship between mean soil C:N ratio and mean annual riverine DOC flux for biomes of the world ($R^2 = 0.992$; $p < 0.0001$). The model successfully predicted annual DOC flux for all the biomes during model validation (Table 2) and model testing at the smaller, watershed scale (Table 3). The predicted annual riverine DOC flux for each biome using the take one out cross validation approach was within 63.5% of the actual value with the greatest error in prediction occurring at the lower end of watershed soil C:N ratios (Table 2). Testing the predictive ability of the C:N model at the smaller, watershed scale, where soil C:N for individual watersheds was available, proved to be very successful (Table 3). In each case, predicted DOC flux was within 4.5% of the observed riverine DOC flux. The average percent difference between predicted and observed values was -3.7% for the validation and -3.6% for the test watersheds.

3.2. C:N Ratios and DOC Concentrations in Organic Horizons Sampled by Lysimeters

A strong relationship was observed between soil solution DOC concentration and soil C:N across the nine coniferous sites (Figure 2). Soil C:N ratios ranged from 11 to 55. Soil solution DOC concentrations ranged from 23.9 in a Douglas fir forest in the Beaujolais Mountains of France to 105.0 mg L^{-1} in a red spruce forest in Howland, Maine. Ninety-four percent of the variance in soil solution DOC concentration was explained by soil C:N ratios ($p < 0.001$).

Table 3. Observed and Predicted Annual Riverine DOC Flux (kg ha^{-1} yr^{-1}) for the Three Test Watersheds

Biome Type	Observed DOC Flux	Predicted DOC Flux	Percent Difference	Country	Watershed Soil C:N Ratio	Source of Soil Data	Source of DOC Flux Data
Warm Conifer	14.3	13.8	-3.2	USA	15.4	*Johnson and Lindberg* [1992]	*Tate and Meyer* [1983]
Heath/Moorland	24.9	24.1	-3.3	UK	17.5	*Heslop and Brown* [1969]	*Creasey* [1984]
Native Evergreen	89.0	85.0	-4.5	NZ	30.0	*McKie* [1978]	*Moore* [1989]

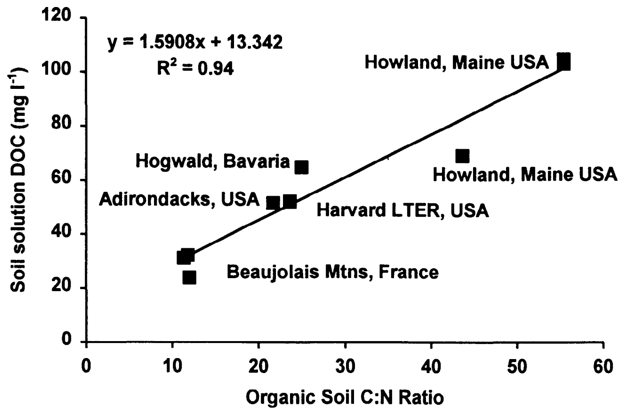

Figure 2. The relationship between DOC concentration in soil solution collected with zero tension lysimeters and soil C:N. Data from *Kreutzer* [1995], *McDowell et al.* [1998], *Marques and Ranger* [1997], *Christ and David* [1994], *David and Driscoll* [1984], *Dai et al.* [1996], and *Fernandez et al.* [1995].

3.3. Estimate of Global Annual Riverine DOC flux

Our first approximation of flux of riverine DOC to the oceans is 3.61 x 10^{14}g yr^{-1} (Table 4). The highest flux was from tropical climatic zones (2.26 x 10^{14}g yr^{-1}), which represent 37.3% of the total land area described by *Meybeck* [1981]. The lowest flux, from the taiga climatic zone, was 0.10 x 10^{14}g yr^{-1}. This climatic area covers 15.9% of the total land area (Table 4) considered in our analysis. Our second estimate of riverine DOC export, using ecosystem complexes described by *Schlesinger and Melack* [1981], was 3.63 x 10^{14}g yr^{-1}. The highest flux was from tropical forests (1.48 10^{14}g yr^{-1}) which represents 21.7% of the land area described by *Schlesinger and Melack* [1981]. The lowest flux in our second estimate was from desert and scrub ecosystems (0.05 x 10^{14}g yr^{-1}) representing 7% of the total land area (Table 4).

4. Discussion

Detailed studies in small watersheds have shown that the rates of DOC production in organic soils, the rates of DOC adsorption in mineral soils, and the flow path of water through different soil horizons to the stream, can all influence streamwater DOC concentration and flux [e.g., *McDowell and Wood,* 1984; *Cronan and Aiken*, 1985; *Guggenberger and Zech*, 1993]. At a larger scale, riverine export of carbon has been modeled using physiographical attributes of a watershed such as river discharge, precipitation, basin size, and slope [*Rasmussen, et al.*, 1989; *Eckhardt and Moore*, 1990; *Esser and Kohlmeier*, 1991; *Clair et al.*, 1994]. The amount of variance explained by these models is 40-50%, much lower than the variance explained by our C:N model of DOC flux. *Clair et al.* [1994], building on the work of *Rasmussen et al.* [1989] and *Eckhardt and Moore* [1990], hypothesized that basin topography was important in controlling total organic carbon (TOC) flux. They reasoned that the flatter the basin, the more likely the occurrence of wetlands and thus the greater amount of TOC produced and exported. Using multiple regression analysis with basin area, slope, and precipitation as the independent variables, they were able to explain 54% of the variance in riverine TOC export among 26 watersheds in Canada. More recently, *Clair and Ehrman* [1996] utilized a neural network approach to model TOC flux from 15 river basins in Canada. They used basin area and slope as the major network variables to predict regional TOC export. Basin area does not appear to be a major controller of DOC flux in the data set used to generate our C:N model. Watershed areas for the cool conifer biome alone range from 41 to 9.25 x 10^6 ha, suggesting that basin area, slope and precipitation are parameters indirectly related to the true dependent variable.

None of the current empirical models describing annual riverine DOC flux address adsorption and desorption of DOC in the mineral soil. One of the most perplexing observations from our analysis is that despite the fact that most DOC is retained in mineral soil in various biomes [e.g., *McDowell*

Table 4. Comparison of Dissolved Organic Carbon Flux From Terrestrial Ecosystems to the Oceans Estimated by *Meybeck* [1981], *Schlesinger and Melack* [1981] and our Global C:N Model

Biome	This Study Flux ($kg ha^{-1} yr^{-1}$)	*Meybeck* [1981] Area ($x10^8$ ha)	*Meybeck* [1981] Flux ($kg ha^{-1} yr^{-1}$)	*Meybeck* [1981] Export ($x10^{14}$ g)	This Study Export ($x 10^{14}$ g)	*Schlesinger and Melack* [1981] Area ($x10^8$ ha)	*Schlesinger and Melack* [1981] Flux ($kg ha^{-1} yr^{-1}$)	*Schlesinger and Melack* [1981] Export ($x10^{14}$ g)	This Study Export ($x 10^{14}$ g)
Taiga	6.2	15.90	24.9	0.40	0.10	-	-	-	-
Tundra	26.4	7.55	6.0	0.04	0.20	8.0	10.0	0.08	0.21
Temperate	42.7	22.00	42.3	0.93	0.94	12.0	40.0	0.48	0.51
Wet Tropical	60.5	37.30	64.6	2.41	2.26	24.5	50.0	1.23	1.48
Semi arid/Desert	6.7	17.20	2.7	0.05	0.11	8.0	5.0	0.04	0.05
Boreal	64.3	-	-	-	-	12.0	50.0	0.60	0.77
Wood and Shrub	26.7	-	-	-	-	8.5	40.0	0.34	0.23
Tropical Grass	5.1	-	-	-	-	15.0	10.0	0.15	0.08
Temperate Grass	4.9	-	-	-	-	9.0	10.0	0.09	0.04
Cultivated	5.3	-	-	-	-	14.0	50.0	0.70	0.07
Swamp/Marsh	96.7	-	-	-	-	2.0	200.0	0.40	0.19
Total	-	99.95	-	3.83	3.61	113.0	-	4.11	3.63
Rest of Earth	-	29.05	-	-	1.20	16.0	-	-	0.55

and Wood, 1984; *Kennedy et al.*, 1996; *McDowell*, 1998] we still observe a strong relationship between annual riverine DOC flux and watershed soil C:N. This could be due to the fact that mean soil C:N was calculated for a solum depth of 1m and would thus take into account the chemistry of both the organic and mineral soil horizons. Or it could be due to an as yet unknown interaction between soil C:N and the retention of DOC in the mineral horizons, such as an effect of C:N ratio upon the DOC retention capacity of the soil.

It is not easy to speculate upon the mechanisms responsible for the relationship between DOC flux and soil C:N and indeed which of the two is the independent variable. This is due to the complex interactions between vegetation, microbes, and climate that drive terrestrial C and N dynamics [*Reich et al.*, 1997]. Perhaps the quality or bioavailability of DOC entering the forest floor dictates the rate of decomposition of soil organic matter and hence both DOC production and soil C:N ratio. It is also possible that soil C:N simply reflects the amount of refractory soil organic matter in the soil profile, and that this is determined by vegetation type. Biomes with a higher soil C:N ratio typically contain vegetation with a greater proportion of refractory carbon [*Finzi et al.*, 1998]. This refractory carbon might enhance the net microbial production of DOC (due to lower microbial uptake) and thus provide a larger DOC pool available for fluvial export. Finally, C:N ratio may reflect the cumulative impact of climate and age of soil carbon on the availability of DOC for export. Soil C:N may be a proxy for the climatic variables temperature and precipitation, each of which controls both the production and flux of DOC via biotic and hydrologic pathways.

Empirical models that predict riverine DOC flux using catchment variables such as carbon content or basin area and slope appear to rely on a simple, abiotic leaching rather than a biotic production of DOC. Using an empirical model which we term the carbon model, *Hope et al.* [1997a] found that 91% of the variance in British riverine DOC flux is explained by mean soil carbon content of the watershed. There are several problems inherent in the widespread use of soil carbon content as a predictor of DOC flux. Globally, regional data on the standing stock of soil carbon are far from complete. Carbon pools are more difficult to measure than soil C:N or other soil attributes because differences in bulk density with depth and difficulties in accounting for the volume of rocks in a soil profile make a quantitative estimate of standing stocks problematic. Estimated carbon content also may vary dramatically within a watershed depending upon the grid scale used. For example, the British database [*Howard et al.*, 1995; *Milne and Brown*, 1997] uses the dominant soil series for every 1 x 1 km grid. This is likely to cause problems at the smaller watershed scale [*Aitkenhead et al., 1999*]. If a grid square contains 52% humic iron spodosol and 48% histosol, then the carbon density of the humic iron spodosol is used to characterize that grid square. Humic iron spodosols have a carbon density of 38.6 kt C km^{-2}, whereas histosols have a carbon density of 173.2 kt C km^{-2} [*Milne and Brown*, 1997]. Carbon storage and subsequently annual riverine DOC flux in a watershed of < 1 km^2 could therefore be underestimated by 67 kt C km^{-2} and 23.7 kg ha^{-1} yr^{-1} (87%), respectively. It is probable that soil C:N ratios will show less heterogeneity within a grid square resulting in less likelihood of any large underprediction or overprediction of riverine DOC flux. For example, the mean soil C:N ratio is 30.0 for peatland (histosols) and 24.6 for moorland humic iron spodosols. Thus a change in classification between these two soil types for a grid square would only change DOC flux by 22%, compared to the 87% potential error in DOC flux using soil carbon content.

Changes in carbon storage are notoriously difficult to quantify over a short time interval. For example, after clear cutting watershed 5 at Hubbard Brook Experimental Forest, *Johnson et al.* [1995] found that the mean carbon content of the whole solum did not show a significant change in the 8 years after logging, although significant losses did occur in the Oa horizon, and the solution chemistry changed dramatically. Change in soil C:N may occur more readily, but data are limited. *Zarin et al.* [1999] found soil C:N varied from 6.4 to 10.8 in tidal flood plains of the Amazon over 1.5 years. Data in *Heslop and Brown* [1969] suggest that soil C:N ratio increased from 9.8 to 17.0 over a 6-year period during which grassland was converted to a larch forest plantation.

Previous work has shown that DOC flux is related to a number of physical, chemical, and biological variables. Other authors have shown that high runoff leads to high DOC flux [e.g., *Mulholland and Watts*, 1982; *Eckhardt and Moore*, 1990; *McDowell and Asbury*, 1994]. A high percentage of wetlands in a watershed can also lead to high DOC flux [e.g., *Mulholland and Kuenzler*, 1979], and coniferous forests tend to have higher DOC flux than deciduous forests [see *Hope et al.*, 1994]. We do not suggest that these relationships are invalid but rather that watershed soil C:N is an effective integrator that incorporates the effects of all the other important variables and is thus the best predictor of DOC flux. The relationship between soil solution DOC concentration and soil C:N ratio (Figure 2) suggests that riverine DOC flux may be much more intimately linked to biotically driven soil organic matter dynamics than previously suspected.

4.1. Model Validations

The linear relationship found between annual riverine DOC flux and soil C:N is an improvement on other empirical models in the amount of variance in DOC flux explained [*Clair et al.*, 1994; *Clair and Ehrman*; 1996; *Hope et al.*, 1997a]. In a predictive capacity, neither the basin and slope nor the carbon content model appear to have been tested using data that were not incorporated in the model construction. To validate their model, *Hope et al.* [1997a] used the "leave one out cross validation" method [*Efron and Tibshirani,* 1993] to predict flux for each watershed in the model. The model overestimated and underestimated DOC flux by as much as 75 and 46%, respectively, for their individual watersheds using this cross validation technique. *Clair and Ehrman* [1996] consistently underpredicted DOC flux with their neural network model by an average 8%. The C:N model presented here was fairly successful in its prediction of annual DOC flux using the "leave one out cross validation" technique, the greater errors occurring at low soil C:N. Prediction of DOC flux from test watersheds was very successful. While our model underpredicted annual DOC flux in each test watershed, the predicted DOC fluxes were within 4.5% of the observed fluxes.

4.2. Comparison of Estimated Global DOC Flux

Our first approximation of global dissolved organic carbon flux to the oceans of 3.61×10^{14} g yr^{-1} was similar to the value of 3.83×10^{14} g yr^{-1} estimated by *Meybeck* [1981]. Our second approximation of 3.63×10^{14} g yr^{-1} was lower than the global carbon flux estimate of 4.1×10^{14} g yr^{-1} reported by *Schlesinger and Melack* [1981]. *Meybeck* [1981] based his estimate on flux data from 100 rivers subdivided into five climatic zones covering a global land area of 1×10^{10} ha. *Schlesinger and Melack* [1981] report two approximations of DOC export. The first was from a regression of total organic carbon load as a function of annual discharge using 12 major world rivers. The second was based on flux data from 58 rivers subdivided into 10 ecosystems covering a global land area of 1.13×10^{10} ha. Other global organic carbon flux estimates in the published literature range from 0.4 to 10×10^{14} g yr^{-1} [*Garrels and MacKenzie*, 1971; *Skopintsev*, 1971; *Garrels et al.*, 1975; *Duce and Duursma*, 1977; *Richey et al.*, 1981; *Mulholland and Watts*, 1982]. Most of these estimates are based on average DOC concentration multiplied by annual discharge.

While the total global exports are similar, closer inspection of the annual DOC flux per hectare for some of the climatic or ecosystem zones indicates large differences among the different papers describing global DOC flux (Table 4). For example, *Meybeck* [1981] assigned per hectare fluxes that were similar to our own with the exception of taiga and tundra. His average flux for taiga was 24.9 kg ha^{-1} yr^{-1} based on 57 rivers with exports ranging from 10 to 40 kg ha^{-1} yr^{-1} while our flux for taiga was only 6.2 kg ha^{-1} yr^{-1} based on a mean soil C:N ratio of 13.79 (n = 61). Our taiga biome contains six rivers with exports ranging from 5 to 12 kg ha^{-1} yr^{-1} (Table 1). *Schlesinger and Melack* [1981] assigned a unit flux of 50 kg ha^{-1} yr^{-1} for cultivated, tropical, and boreal watersheds. While we feel that the flux values they assigned for tropical and boreal ecosystems are realistic, the value assigned for cultivated ecosystems seems exceptionally high.

Our estimates of global carbon flux from terrestrial ecosystems to the oceans only include carbon losses from the 5 climatic zones considered by *Meybeck* [1981] and the 10 ecosystems considered by *Schlesinger and Melack* [1981]. They represent 78% [*Meybeck*, 1981] and 88% [*Schlesinger and Melack*, 1981] of the total land area of the Earth, excluding ice. If we expand our estimate to all the land surfaces of the Earth, our value of global DOC flux is increased by 1.2×10^{14} and 0.55×10^{14} g, respectively (Table 4). This relates to an underestimation of temperate biomes by *Meybeck* [1981] and an underestimation of boreal, temperate and tropical biomes by *Schlesinger & Melack* [1981].

4.3. Limitations and Implications

Our results to date suggest that annual riverine DOC flux from biomes is predictable using biome soil characteristics and that this same relationship can be used to predict DOC flux for individual watersheds. We do not know to what extent the relationship holds true within a biome or to what extent it is capable of dealing with the impacts of agricultural conversion, deforestation, forest wildfires, increased nitrogen deposition, and enhanced atmospheric CO_2 on DOC flux. Research on the timescale involved for measurable changes in soil C:N ratio under land use change and other anthropogenic influences would enhance the C:N model's predictive ability. We also believe that the linear regression presented here is the midsection of a second-order polynomial function. Our model actually predicts DOC values less than zero at C:N ratios < 12.46. Further field samples of DOC flux will be needed to establish the shape of this relationship for environments such as agriculture, croplands, and dry tropical forests with lower soil C:N.

Our ultimate goal is to quantify the sensitivity of DOC flux to changes in global climate and biogeochemistry. This will be possible to the extent that climate change can be linked to changes in soil organic matter dynamics. For example, *Houghton et al.* [1998] suggest that global warming will decrease soil C:N, which they attribute to loss of carbon through CO_2 evolution with no equivalent loss of mineralized nitrogen. Changing N deposition could also result in decreased C:N ratio in soils. *Aber* [1992] proposes that increased plant uptake of nitrogen, with increased N deposition, will result in higher N concentrations in foliage, the outcome of which will be plant litter with a lower C:N ratio and hence a lower C:N ratio in the forest floor. If such reductions in soil C:N do occur, our model predicts a decline in DOC flux. For example, a decrease of one C:N unit could decrease annual riverine DOC flux by 4.9 kg ha^{-1} yr^{-1} (Figure 1). Decreases in soil C:N could lead to significant declines in the DOC flux from those watersheds with lower initial mean soil C:N such as grasslands, savanna, taiga, and deciduous forests.

Acknowledgments. We thank Rick Jackson for providing additional references for the Maimai watershed, Walter Dodds for contributing DOC flux data for the Konza LTER grassland site, Jukka Laine and Hannu Pajuren for several peat C:N ratios in Finland, and Suki Kao and Tom Clair for additional watershed information. Larry Mayer and an anonymous reviewer provided useful comments on the manuscript. Linda Scogin provided assistance in manuscript preparation. Scientific contribution #2013 from the New Hampshire Agricultural Experiment Station.

References

Aber, J. D., Nitrogen cycling and nitrogen saturation in temperate forest ecosystems, *Trends Ecol. Evolut.*, *7*, 220-223, 1992.

Aitkenhead, J. A., D. Hope, and M. F. Billett, The relationship between dissolved organic carbon in streamwater and soil organic carbon pools at different spatial scales, *Hydrol. Processes*, *13*, 1289-1302, 1999.

Amatya, D. M., J. W. Gilliam, R. W. Skaggs, M. E. Lebo, and R. G. Campbell, Effects of controlled drainage on forest water quality, *J. Environ. Qual.*, *27*, 923-935, 1998.

Brinson, M. M., Organic matter losses from four watersheds in the humid tropics, *Limnol. Oceanogr.*, *21*, 572-582, 1976.

Campbell, J. L., J. W. Hornbeck, W. H. McDowell, D. C. Buso, and J. B. Shanley, Dissolved organic nitrogen budgets for upland, forested ecosystems in New England, *Biogeochemistry*, In press.

Christ, M. J., and M. B. David, Fractionation of dissolved organic carbon in soil water: Effects of extraction and storage methods, *Commun. Soil Sci. Plant Anal.*, *25*, 3305-3319, 1994.

Christ, M. J., and M. B. David, Temperature and moisture effects on the production of dissolved organic carbon in a spodosol, *Soil Biol. Biochem.*, *28*, 1191-1199, 1996.

Clair, T. A., and J. M. Ehrman, Variations in discharge and dissolved organic carbon and nitrogen export from terrestrial basins with changes in climate: A neural network approach, *Limnol. Oceanogr.*, *41*, 926-927, 1996.

Clair, T. A., T. L. Pollock, and J. M. Erhman, Exports of carbon and nitrogen from river basins in Canada's Atlantic provinces, *Global Biogeochem. Cycles, 8,* 441-450, 1994.

Creasey, J., The Geochemistry of a Small Upland Catchment in Northeast Scotland, Ph.D. dissertation, Univ. of Aberdeen, Aberdeen, U. K., 1984.

Cronan, C. S., and G. R. Aiken, Chemistry and transport of soluble humic substances in forested watersheds of the Adirondack Park, New York, *Geochim. Cosmochim. Acta., 45,* 1697-1705, 1985.

Dai, K.'O.H., M. B. David, and G. F. Vance, Characterization of solid and dissolved carbon in a spruce fir spodosol, *Biogeochemistry, 35,* 339-365, 1996.

David, M. B., and C. T. Driscoll, Aluminum speciation and equilibria in soil solutions of a haplorthod in the Adirondack mountains (New York USA), *Geoderma, 33,* 297-318, 1984.

David, M. B., and G. B. Lawrence, Soil and soil solution chemistry under red spruce stands across northeastern United States, *Soil Sci., 161,* 314-328, 1996.

Day, J. W., T. J. Butler, and W. H. Conner, Productivity and nutrient export studies in a cypress swamp and lake system in Louisiana, in *Estuarine Processes, vol. 2,* edited by M. Wiley, pp. 255-269, Academic, San Diego, Calif., 1977.

Dillon, P. J., and L. A. Molot, Effect of landscape form on export of dissolved organic carbon, iron and phosphorus from forested stream catchments, *Water Resour. Res., 33,* 2591-2600, 1997.

Dixon, R. K., and D. P. Turner, The global carbon cycle and climate change: Responses and feedbacks from below ground systems, *Environ. Pollut., 73,* 245-262, 1991.

Dosskey, M. G., and P. M. Bertsch, Forest sources and pathways of organic matter transport to a blackwater stream: A hydrologic approach, *Biogeochemistry, 24,* 1-19, 1994.

Driscoll, C. T., R. D. Fuller, and D. M. Simone, Longitudinal variations in trace metal concentrations in a northern forested ecosystem, *J. Environ. Qual., 17,* 101-107, 1988.

Duce, R. A., and E. K. Dursma, Inputs of organic matter to the ocean, *Mar. Chem., 5,* 319-339, 1977.

Eckhardt, B., and T. R. Moore, Controls on dissolved organic carbon concentrations in streams, southern Quebec, *Can. J. Fish Aquat. Sci., 47,* 1537-1544, 1990.

Efron, B., and R. J. Tibshirani, *An Introduction to the Bootstrap,* Chapman and Hall, New York, 1993.

Esser, G., and G. H. Kohlmeier, Modeling terrestrial sources of nitrogen, phosphorous, sulfur and organic carbon to rivers, in *Biogeochemistry of Major World Rivers,* edited by E. T. Degens et al., pp. 297-322, John Wiley, New York, 1991.

Eswaran, H., E. Van den Berg, and P. Reich, Organic carbon in soils of the world, *Soil Sci. Soc. Am. J., 57,* 192-194, 1993.

Fernandez, I. J., G. B. Lawrence, and Y. Son, Soil solution chemistry in a low elevation spruce fir ecosystem, Howland, Maine, *Water Air Soil Pollut., 84,* 129-145, 1995.

Finzi, A. C., N. Van Breeman, and C. D. Canham, Canopy tree-soil interactions within temperate forests: Species effects on soil carbon and nitrogen, *Ecol. App., 8,* 440-446, 1998.

Fisher, S. G., and G. E. Likens, Energy flow in Bear Brook, New Hampshire: An integrative approach to stream ecosystem metabolism, *Ecol. Monogr.,43,* 421-439, 1973.

Garrels, R. M., and F. T. MacKenzie, *Evolution of Sedimentary Rocks,* W. W. Norton, New York, 1971.

Garrels, R. M., F. T. MacKenzie, and C. Hunt, *Chemical Cycles and the Global Environment,* William Kaufman, Los Altos, Calif., 1975.

Glentworth, R., *The Soils of the County Around Banff, Huntly & Turriff,* Her Majesty's Stationery Office, Dep. of Agric. for Scotland, Edinburgh, U.K., 1954.

Grieve, I. C., Concentrations and annual loading of dissolved organic matter in a small moorland stream, *Freshwater Biol., 14,* 533-537, 1984.

Grip, H., A. Malmer, and F. K. Wong, Converting tropical rain forest to forest plantation in Sabah, Malaysia, Part 1, Dynamics and net losses of nutrients in control catchment streams, *Hydrol. Proc., 8,* 179-194, 1994.

Guggenberger, G., and W. Zech, Dissolved organic carbon control in acid forest soils of the Fichtelgebirge (Germany) as revealed by distribution patterns and structural composition analysis, *Geoderma, 59,* 109-129, 1993.

Guyot, J. L., and J. G. Wason, Regional pattern of riverine DOC in the Amazon drainage basin of Bolivia, *Limnol. Oceanogr., 39,* 452-458, 1994.

Hamilton, S. K., S. Sippel, D. F. Calheiros, and J. F. Melack, An anoxic event and other biogeochemical effects of the Pantanal wetland on the Paraguay river, *Limnol. Oceanogr., 42,* 257-272, 1997.

Harrison, K. G., W. M. Post, and D. D. Richter, Soil carbon turnover in a recovering temperate forest, *Global Biogeochem. Cycles, 9,* 449-454, 1995.

Heikkinen, K., Organic carbon transport in an undisturbed boreal humic river in northern Finland, *Arch. Hydrobiol., 117,* 1-19, 1989.

Heslop, R. E. F., and C. J. Brown, *The Soils of Candacraig and Glenbuchat,* The Macaulay Inst. for Soil Res., Craigiebuckler, Aberdeen, U.K., 1969.

Hobbie, J. E., and G. E. Likens, Output of phosphorous, dissolved organic carbon and fine particulate carbon from Hubbard Brook watersheds, *Limnol. Oceanogr., 18,* 734-742, 1973.

Hope, D., M. F. Billett, and M. S. Cresser, A review of the export of carbon in river water: Fluxes and processes, *Environ. Pollut., 84,* 301-324, 1994.

Hope, D., M. F. Billett, R. Milne, and T. A. W. Brown, Exports of organic carbon in British rivers, *Hydrol. Proc., 11,* 325-344, 1997a.

Hope, D., M. F. Billett, and M. S. Cresser. The export of organic carbon in two river systems in N E Scotland, *J. Hydrol. 193,* 61-82, 1997b.

Houghton, R. A., E. A. Davidson, and G. M. Woodwell, Missing sinks, feedbacks, and understanding the role of terrestrial ecosystems in the global carbon balance, *Global Biogeochem. Cycles, 12,* 25-34, 1998.

Howard, P. J. A., P. J. Loveland, R. I. Bradley, F. T. Dry, D. M. Howard, and D. C. Howard, Carbon content of soil and its geographical distribution in Great Britain, *Soil Use Manage., 11,* 9-15, 1995.

Huang, W. Z., and J. J. Schoenau, Forms, amounts and distribution of carbon, nitrogen and phosphorus and sulfur in a boreal aspen forest soil, *Can. J. Soil Sci.,76,* 373-385, 1997.

Huntington, T. G., D. F. Ryan, and S. P. Hamburg, Estimating soil nitrogen and carbon pools in a northern hardwood forest ecosystem, *Soil Sci. Soc. Am. J., 52,* 1162-1167, 1988.

Johnson, C. E., C. T. Driscoll, T. J. Fahey, T. G. Siccama, and J. W. Hughes, Carbon dynamics following clear-cutting of a northern hardwood forest in *Carbon Forms and Functions in Forest Soils,* edited by W. W. McFee and J. M. Kelly, pp. 463-488, Soil Sci. Soc. of Am., Madison, Wisc., 1995.

Johnson, D. W., and S. E. Lindberg. *Atmospheric Deposition and Forest Nutrient Cycling: A Synthesis of the Integrated Forest Study,* Springer-Verlag, New York, 1992.

Jones, T. H., et al., Impacts of rising atmospheric carbon dioxide on model terrestrial ecosystems, *Science, 280,* 441-443, 1998.

Kao, S. J., and K. K. Lui, Fluxes of dissolved and non-fossil particulate organic carbon from an Oceania small river (Lanyang Hsi) in Taiwan, *Biogeochemistry, 39,* 255-269, 1997.

Kennedy, J., M. F. Billett, D. Duthie, A. R. Fraser, and A. F. Harrison, Organic matter retention in an upland humic podzol: The effects of pH and solute type, *Eur. J. Soil Sci., 47,* 615-625, 1996.

Kortelainen, P., S. Saukkonen, and T. Mattson, Leaching of nitrogen from forested catchments in Finland, *Global Biogeochem. Cycles, 11,* 627-638, 1997.

Kreutzer, K., Effects of forest liming on soil processes, *Plant Soil., 168-169,* 447-470, 1995.

Laing, D., *The Soils of the Country Around Perth, Arbroath and Dundee,* Her Majesty's Stationery Office, Dep. for Agric. and Fish., Edinburgh, U.K., 1976.

Lesack, L. F. W., R. E. Hecky, and J. M. Melack, Transport of carbon, nitrogen, phosphorous and major solutes in the Gambia River, West Africa, *Limnol. Oceanogr. 29,* 816-830, 1984.

Lewis, W. M., Jr., and J. F. Saunders III, Concentration and transport of dissolved and suspended substances in the Orinoco River, *Biogeochemistry, 7,* 203-240, 1989.

Lewis, W. M., Jr., S. K. Hamilton, S. L. Jones, and D. D. Runnels, Major element chemistry, weathering and element yields for the

Caura River drainage, Venezuela, *Biogeochemistry, 4,* 151-181, 1987.

Lydersen, E., and A. Henriksen, Total organic carbon in streamwater from four long-term monitored catchments in Norway, *Environ. Int., 20,* 713-729, 1994.

Malcolm, R. L., and W. H. Durum, Organic carbon and nitrogen concentrations and annual organic carbon load of six selected rivers of the United States, U. S. Geol. Surv. Water Supply Pap., *1817-F,* F1-F21, 1976.

Marques, R., and J. Ranger, Nutrient dynamics in a chronosequence of Douglas fir (*Pseudotsuga menziesii* (Mirb) Franco) stands in the Beaujolais Mounts (France), 1, Qualitative approach, *For. Ecol. Manage., 91,* 255-277, 1997.

Martell, A. E., R. J. Motekaitis, and R. M. Smith, Structure stability relationships of metal complexes and metal speciation in environmental aqueous solutions, *Environ. Toxicol. Chem., 7,* 417-434, 1988.

McClain, M. E., J. E. Richey, J. A. Brandes, and T. P. Pimentel, Dissolved organic matter and terestrial-lotic linkages in the central Amazon basin of Brazil, *Global Biogeochem. Cycles, 11,* 295-311, 1997.

McDowell, W. H., Internal nutrient fluxes in a Puerto Rican rain forest, *J. Trop. Ecol., 14,* 521-536, 1998.

McDowell, W. H., and C. E. Asbury, Export of carbon, nitrogen and major ions from three tropical montane watersheds, *Limnol. Oceanogr., 39,* 111-125, 1994.

McDowell, W. H., and G. E. Likens, Origin, composition and flux of dissolved organic carbon in the Hubbard Brook valley, *Ecol. Monogr., 58,* 177-195, 1988.

McDowell, W. H., and T. Wood, Podzolization: Soil processes control dissolved organic carbon concentrations in stream water, *Soil Sci., 137,* 23-32, 1984.

McDowell, W. H., W. B. Bowden, and C. E. Asbury, Riparian nitrogen dynamics in two geomorphologically distinct tropical rain forest watersheds: Subsurface solute patterns, *Biogeochemistry, 18,* 53-75, 1992.

McDowell, W. H., W. S. Currie, J. D. Aber, and Y. Yano, Effects of chronic nitrogen amendment on production of dissolved organic carbon and nitrogen in forest soils, *Water Air Soil Pollut.*, 105, 175-182, 1998.

McKie, D. A., A Study of soil variability within the Blackball Hill Soils, Reefton, New Zealand, M. S. dissertation, Lincoln College, Univ. of Canterbury, Christchurch, New Zealand, 1978.

McKnight, D., E. A. Thurman, and R. L. Wershaw, Biogeochemistry of aquatic humic substances in Thoreau's bog, Concord, Massachusetts, *Ecology, 66,* 1339-1352, 1985.

Meybeck, M., River transport of organic carbon to the ocean, in *Flux of organic carbon by rivers to the ocean, NTIS Rep. CONF-8009140 UC-11,* U. S. Dep. of Energy, Washington D. C., 1981.

Milne, R., and T. A. Brown, Carbon pools in the vegetation and soils of Great Britain, *J. Environ. Manage., 49,* 413-433, 1997.

Moeller, J. R., G. W. Minshall, K. W. Cummins, R. C. Petersen, C. E. Cushing, J. R. Sedell, R. A. Larson, and R. L. Vannote, Transport of dissolved organic carbon in streams of differing physiographic characteristics, *Org. Geochem., 1,* 139-150, 1979.

Moore, T. R., Dynamics of dissolved organic carbon in forested catchments, Westland, New Zealand, 1, Maimai, *Water Resour. Res., 25,* 1321-1330, 1989.

Mulholland, P. J., and W. W. Hill, Seasonal patterns in streamwater nutrient and dissolved organic carbon concentrations: Separating catchment flow path and in-stream effects, *Water Resour. Res., 33,* 1297-1306, 1997.

Mulholland, P. J., and E. J. Keunzler, Organic carbon export from upland and forested wetland watersheds, *Limnol. Oceanogr., 24,* 906-926, 1979.

Mulholland, P. J., and J. A. Watts, Transport of organic carbon to the oceans by rivers of North America: A synthesis of existing data, *Tellus, 34,* 176-186, 1982.

Olson, J. S., and J. A. Watts, Major world ecosystem complexes in *Carbon Dioxide Review,* edited by W. C. Clark, Oxford Univ. Press, Oxford, New York, 1982.

Perdue, E. M., K. C. Beck, and J. Helmut-Reuter, Organic complexes of iron and aluminum in natural waters, *Nature, 260,* 418-420, 1976.

Post, W. M., W. R. Emanuel, P. J. Zinke, and A. G. Stagenberger, Soil carbon pools and world life zones, *Nature, 298,* 156-159, 1982.

Post, W. M., J. Pastor, P. J. Zinke, and A. G. Stagenberger, Global patterns of soil nitrogen, *Nature, 317,* 613-616, 1985.

Rasmussen, J. B., L. Godbout, and M. Schallenberg, The humic content of lake water and its relationship to watershed and lake morphometry, *Limnol. Oceanogr., 34,* 1336-1343, 1989.

Reich, P. B., D. F. Grigal, J. D. Aber and S. T. Gower, Nitrogen mineralization and productivity in 50 hardwood and conifer stands on diverse soils, *Ecology, 78,* 335-347, 1997.

Reid, J. M., Geochemical balances in Glen Dye, an upland catchment in Grampian region, Ph.D. dissertation, Univ. of Aberdeen, Aberdeen, U. K., 1979.

Reynolds, B., A comparison of element outputs in solution, suspended sediments and bedload for a small upland catchment, *Earth Surf. Processes Landforms, 11,* 217-221, 1986.

Richey, J. E., Fluxes of organic matter in rivers relative to the global carbon cycle, in *Flux of organic carbon by rivers to the ocean, NTIS Rep. CONF-8009140 UC-11,* U.S. Dep. of Energy, Washington D. C., 1981.

Richey, J. E., J. I. Hedges, A. H. Devol, P. D. Quay, V. Reynolds, L. Martinelli, and B. R. Forsberg, Biogeochemistry of carbon in the Amazon River, *Limnol. Oceanogr. 35,* 352-371, 1990.

Saunders, J. F. III, and W. M. Lewis Jr., Transport of phosphorous, nitrogen and carbon by the Apure River, Venezuela, *Biogeochemistry 5,* 323-342, 1988.

Schiff, S.L., R. Aravena, S. E.Trumbore, M. J. Hinton, R. Elegood, and P. J. Dillon, Export of DOC from forested catchments on the precambrian shield of central Ontario: Clues From ^{13}C and ^{14}C, *Biogeochemistry, 36,* 67-88, 1997.

Schlesinger, W. H., Carbon balance in terrestrial detritus, *Ann. Rev. Ecol. Syst., 8,* 51-81, 1977.

Schlesinger, W. H., and J. M. Melack, Transport of organic carbon in the world's rivers, *Tellus, 33,* 172-187, 1981.

Schneider, S. H., The changing climate, *Sci. Am., 261,* 70-79, 1989.

Senesi, N., Binding mechanisms of pesticides to soil humic substances, *Sci. Total Environ., 123/124,* 63-76, 1992.

Siddiqui, M. S., G. L. Amy, and B. D. Murphy, Ozone enhanced removal of natural organic matter from drinking water sources, *Water Research, 31,* 3098-3106, 1997.

Skopintsev, B. A., Recent advances in the study of organic matter in the oceans, *Oceanology, 11,* 775-789, 1971.

Skopintsev, B. A., Organic matter, in *The River Volga and Its Life,* edited by Mordukhai-Boltovskoi, Dr. W. Junk, Norwell, Mass., 1979.

Tate, C. M., and J. L. Meyer, The influence of hydrologic conditions and successional state on dissolved organic carbon export from forested watersheds, *Ecology, 64,* 25-32, 1983.

Trumbore, S. E., O. A. Chadwick, and R. Amundson, Rapid exchange between soil carbon and atmospheric carbon dioxide driven by temperature change, *Science, 272,* 393-396, 1996.

Williamson, C. E., and H. E. Zagarese, The impact of UV-B radiation on pelagic freshwater ecosystems, *Ergeb. Limnol., 43,* 9-11, 1994.

Worrall, F., A. Parker, J. E. Rae, and A. C. Johnson, A study of the sorption kinetics of isoproturon on soil and subsoil, the role of dissolved organic carbon, *Chemosphere, 34,* 87-97, 1997.

Zarin, D. J., A. L. Duchesne, and M. Hiraoka, Shifting cultivation on the tidal floodplains of Amazonia: Impacts on soil nutrient status. *Agrofor. Syst., 41,* 307-311, 1999.

Zinke, P. J., A. G. Stangenberg, W. M. Post, W. R. Emanuel, and J. S. Olson . Worldwide organic soil carbon and nitrogen data, *Report NDP-018,* Carbon Dioxide Info. Cent., Oak Ridge Nat. Lab., Oak Ridge, Tenn., 1986.

J. A. Aitkenhead and W. H. McDowell, Department of Natural Resources, 215 James Hall, University of New Hampshire, Durham, NH 03824, USA. (jaa@christa.unh.edu; bill.mcdowell@unh.edu).

12

(Received October 29, 1998; revised March 15, 1999; accepted April 29, 1999.)