

# **Carbon Sequestration, Transport, and Emission From Inland Aquatic Ecosystems in the Eastern United States**

By Sarah Stackpoole, David Butman, David Clow, Cory McDonald, Edward Stets, and Robert Striegl

Chapter 5 of

## **Baseline and Projected Future Carbon Storage and Greenhouse-Gas Fluxes in Ecosystems of the Eastern United States**

Edited by Zhiliang Zhu and Bradley C. Reed

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# Chapter 5. Carbon Sequestration, Transport, and Emission From Inland Aquatic Ecosystems in the Eastern United States

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## 5.1. Highlights

- The total surface area of inland waters in the Eastern United States was 93,000 km<sup>2</sup>, which represented about 3.1 percent of the total land surface area of the region.
- Riverine ecosystems of the Eastern United States were carbon sources, exporting dissolved inorganic carbon and total organic carbon to coastal areas at a rate of 6.4 gC/m<sup>2</sup>/yr and emitting 14 gC/m<sup>2</sup>/yr as CO<sub>2</sub> to the atmosphere.
- Lacustrine systems of the Eastern United States were sources and sinks of carbon with 3.3 gC/m<sup>2</sup>/yr emitted as CO<sub>2</sub> to the atmosphere and 3.1 gC/m<sup>2</sup>/yr of carbon sequestered in sediments.
- There was considerable variability in the estimated carbon fluxes of inland waters among the seven ecoregions in the Eastern United States. This was likely due to the differences in the size and abundance of water bodies, topography, climate, and land cover associated with each ecoregion.

## 5.2. Introduction

Section 712 of the EISA specifically required an assessment of carbon fluxes related to freshwater aquatic ecosystems. This chapter focuses on freshwater ecosystems, including streams, rivers, perennial ponds, lakes, and impoundments, which collectively are categorized as inland waters. Carbon sequestration rates in coastal estuaries, which are transition zones between rivers and oceans, are presented in chapter 6, and carbon fluxes from wetland systems are addressed in chapter 7. Carbon fluxes associated with aquatic ecosystems (this chapter) were assessed separately from those of terrestrial ecosystems (chap. 7) in this report because of limited empirical aquatic data and a lack of a large-scale, spatially explicit carbon model that integrates terrestrial and aquatic fluxes.

Inland waters are active sites for transport, transformation, and storage of carbon between terrestrial landscapes and oceans

(Cole and others, 2007; Striegl and others, 2007; Tranvik and others, 2009). On a global scale, inland waters cover only about 1 percent of the land surface (Battin and others, 2009), but carbon emissions from inland waters to the atmosphere are comparable in magnitude with terrestrial NEP values (Tranvik and others, 2009). So although inland aquatic systems represent less than 3 percent of the total land surface of the United States (Zhu and others, 2010), they may play a significant role in the regional carbon budget in the Eastern United States.

The objective of this chapter is to provide baseline estimates of carbon sequestration, carbon transport, and gaseous carbon emissions from inland waters for the seven ecoregions of the Eastern United States. In addition to national maps depicting the spatial extent of water bodies, datasets of water chemistry, flow, and sedimentation rates, spanning from 1920 through 2011, were used to calculate the following fluxes: (1) lateral transport of DIC and total organic carbon (TOC) in riverine systems, (2) gaseous carbon emissions in the form of CO<sub>2</sub> from riverine systems, (3) gaseous carbon emissions in the form of CO<sub>2</sub> from lacustrine systems, and (4) carbon burial rates in sediments of lacustrine systems. All ecoregion boundaries used in this chapter are consistent with those presented in chapter 1 (U.S. Environmental Protection Agency, 2013a).

Differences in physiography, land cover, and climate associated with each ecoregion are expected to have an effect on carbon storage, transport, and loss to the atmosphere. Flux values presented in this chapter were normalized to total land surface area to produce yield estimates. These baseline estimates of carbon yields were then used in two integrated analyses to compare (1) relative magnitudes of yield values of inland waters among ecoregions and (2) yields of inland waters to terrestrial carbon storage.

## 5.3. Methods and Data

### 5.3.1. Lateral Carbon Transport in Riverine Systems

Lateral carbon fluxes in riverine systems account for carbon derived from terrestrial ecosystems, groundwater, and in-stream production (photosynthesis) minus the losses from sedimentation and CO<sub>2</sub> flux to the atmosphere. Water-quality

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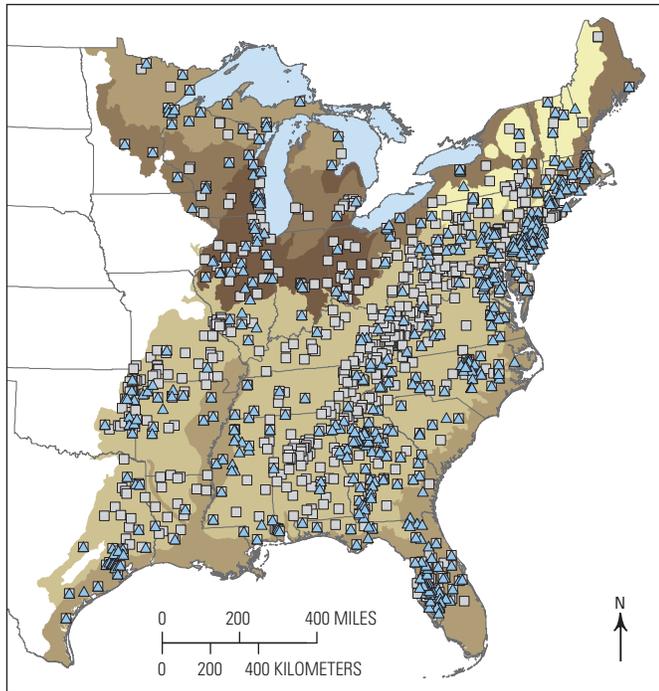
data for estimating lateral fluxes were obtained from the National Water Information Service (NWIS; U.S. Geological Survey, undated). In this chapter, lateral fluxes are represented by calculations derived from two different datasets, the Coastal Export Dataset and the Ecoregion Dataset.

Flux values calculated using the Coastal Export Dataset were categorized by the receiving body of water. For the Eastern United States, this included the Atlantic Ocean, Great Lakes, Gulf of Mexico, and Rainy River. The dataset represents the most downstream streamgages on rivers draining to the coast that had continuous stream discharge data. Therefore, areas heavily influenced by tides were not included, nor were the small coastal watersheds outside of the coastal boundary. Some of the watersheds that drain to coastal areas crossed political boundaries into Canada, but in most instances the area outside the United States border was small and no correction was made. However, since 56 percent of the Great Lakes total drainage area was in Canada, only watersheds

inside the United States border were used to calculate carbon flux to the Great Lakes. Ultimately, the Coastal Export Dataset included DIC estimates from 122 NWIS sites and TOC estimates from 109 NWIS sites (fig. 5–1). These sites covered approximately 2.5 Mkm<sup>2</sup> or 75 percent of the total drainage area for the regions of these receiving waters.

The Ecoregion Dataset included only drainage basins contained entirely within a single ecoregion of the Eastern United States. These estimates were useful to illustrate ecoregional variability in carbon fluxes across the entire Eastern United States. There was some overlap with the Coastal Export Dataset for streamgages located upstream from coastal areas that had watersheds entirely within ecoregional boundaries. The Ecoregion Dataset included DIC estimates from 1,001 NWIS sites and TOC estimates from 511 NWIS sites (fig. 5–1A). The flux estimates associated with this dataset were derived from small drainage basins, ranging in size from 3.4 to 59,000 km<sup>2</sup>. About 33 percent of the total

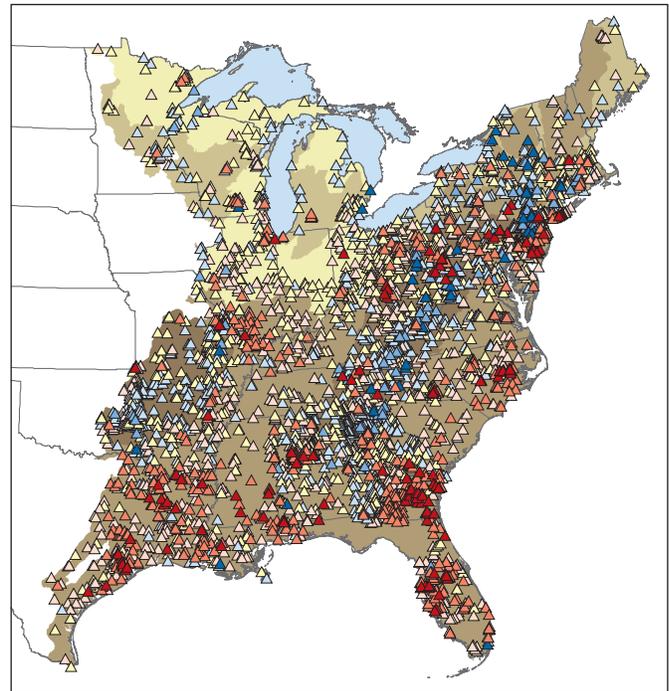
A. Riverine within-ecoregion carbon fluxes



**EXPLANATION**

<b>Carbon yield, in grams of carbon per square meter per year</b>	<b>Carbon sampling site</b>
0 to 5.2	▲ Total organic carbon
>5.2 to 8	◻ Dissolved inorganic carbon
>8 to 10	
>10 to 13	
>13	

B. Riverine carbon dioxide emissions

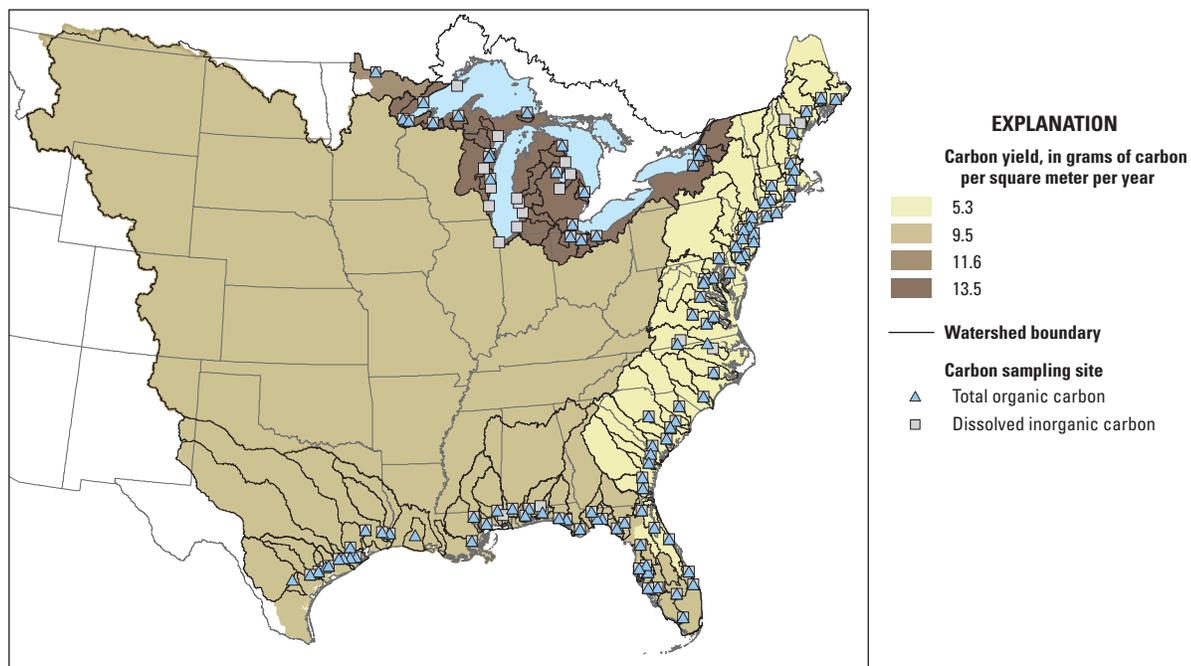


**EXPLANATION**

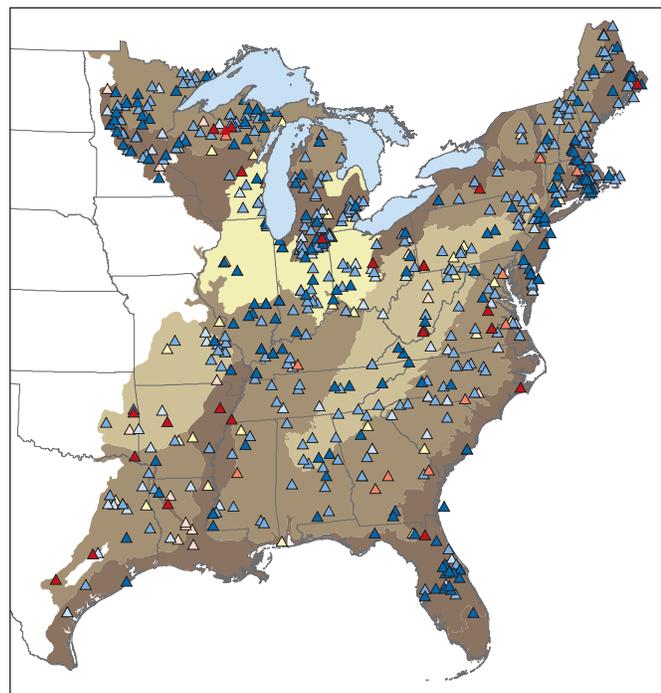
<b>Carbon yield, in grams of carbon per square meter per year</b>	<b>Partial pressure of carbon dioxide, in microatmospheres</b>
0 to 5	▲ 0 to 750
>5 to 10	▲ >750 to 1,000
>10 to 14.1	▲ >1,000 to 2,000
>14.1 to 26.2	▲ >2,000 to 3,000
	△ >3,000 to 6,000
	△ >6,000 to 12,000
	△ >12,000 to 30,000

**Figure 5–1.** Maps showing the estimated relative magnitude of carbon yields. *A*, Within-ecoregion lateral carbon transport by riverine systems. *B*, Carbon dioxide (CO<sub>2</sub>) emissions from riverine systems. *C*, Lateral carbon export to coasts by riverine systems. *D*, CO<sub>2</sub> emissions from lacustrine systems. *E*, Carbon burial rates in lacustrine systems. The maps show locations of calibrated sample data. Panels *B* and *D* also indicate the estimated relative magnitude of the partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) concentrations at the sampling locations.

C. Riverine lateral carbon fluxes to coastal waters



D. Lacustrine carbon dioxide emissions



**EXPLANATION**

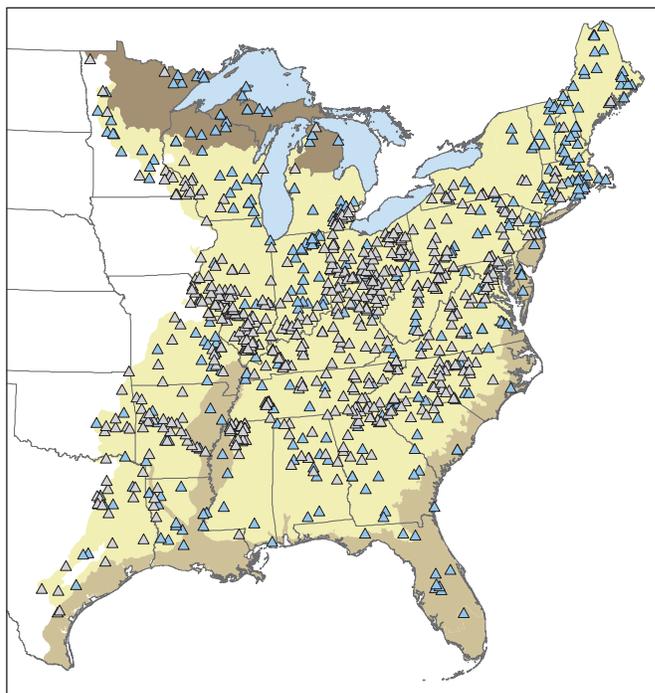
Carbon yield, in grams of carbon per square meter per year

- 0 to 1.1
- 1.2 to 2
- 2.1 to 4
- 4.1 to 5

Partial pressure of carbon dioxide, in microatmospheres

- ▲ <400
- ▲ >400 to 750
- ▲ >750 to 1,000
- ▲ >1,000 to 1,500
- ▲ >1,500 to 2,000
- ▲ >2,000 to 2,500
- ▲ >2,500

E. Lacustrine carbon burial



**EXPLANATION**

Carbon yield, in grams of carbon per square meter per year

- 0 to -4
- 4.1 to -8
- 8.1 to -12

Dataset and modeling method for sedimentation estimate

- ▲ Sedimentation rate location
- ▲ Sediment carbon location

Figure 5-1.—Continued

ecoregional area of the Eastern United States was accounted for by the drainage areas associated with these sites.

For all lateral carbon flux estimates, the DIC concentration was estimated from pH, temperature, and either filtered or unfiltered alkalinity. The estimated TOC concentration was taken directly from water-quality data or was calculated as the sum of dissolved and particulate organic carbon (Stets and Striegl, 2012). Carbon fluxes were estimated from water-quality and daily streamflow data using the USGS Load Estimator Model (LOADEST; Runkel and others, 2004). LOADEST is a multiple-regression adjusted maximum likelihood estimation model that uses measured DIC or TOC concentration values to calibrate a regression between constituent load, streamflow, seasonality, and time. The LOADEST model uses Akaike Information Criterion to select the best combination of coefficients at each streamgage station from the full model, which is based on the following equation:

$$\ln LOAD = a_0 + a_1 \ln Q + a_2 \ln Q^2 + a_3 \sin(2\pi dtime) + a_4 \cos(2\pi dtime) + a_5 dtime + a_6 dtime^2 + \varepsilon, \quad (5-1)$$

where

$\ln LOAD$	is the natural log of the constituent load,
$Q$	is the discharge,
$dtime$	is time in decimal years,
$a_0, a_1, \dots, a_6$	are regression coefficients, and
$\varepsilon$	is an independent and normally distributed error.

The model calibration required at least 12 paired water-quality and daily streamflow values. The input data were log-transformed to avoid bias and centered to avoid multicollinearity.

For the Coastal Export Dataset, daily carbon fluxes were converted to annual fluxes and then summed across the contributing area. Carbon export ( $Total E_C$ ) was estimated by extrapolating to the drainage area not captured by sites included in the dataset (Stets and Striegl, 2012) by using the following equation:

$$Total E_C = E_{C(IN)} \times (A_{TOT} / A_{IN}), \quad (5-2)$$

where

$E_{C(IN)}$	is the carbon export estimated from sites included in the database,
$A_{TOT}$	is the total exorheic drainage area (draining to coastal areas), and
$A_{IN}$	is the total drainage for which lateral flux estimates could be made.

This extrapolation assumed an equivalent areal carbon flux from the remaining (unmeasured) drainage area. The 5th and 95th confidence intervals were calculated from associated standard errors. Coastal carbon yields were calculated by dividing total carbon fluxes by associated drainage area. Ungaged area from the Coastal Export Dataset ranged from 0 percent at the Rainy River to 35 percent at the Atlantic Ocean, with an average of 15 percent ungaged area for the entire Eastern United States.

Large river basins in the Coastal Export Dataset included source areas that lay within ecoregions that were considered in the Central (Zhu and others, 2011) or Western (Zhu and Reed, 2012) United States assessment reports, which complicated flux estimates based on ecoregional boundaries due to potential double counting. For the assessment of the Eastern United States, total coastal export to the receiving waters was considered a part of the assessment if the coastal outlet was within the assessment boundaries of the Eastern United States; some additional explanation was provided to establish the significance of carbon and water entering the Eastern United States from ecoregions outside of this assessment area. For example, the Mississippi-Atchafalaya River Basin was the largest in the United States (total basin area of 3.18 Mkm<sup>2</sup>) and had its coastal outlet in the Eastern United States. However, only 40 percent of the total drainage area of the Mississippi-Atchafalaya River Basin is within the assessment area of the Eastern United States; 54 percent of the basin is in ecoregions that were considered in the report for the Central United States (Temperate Prairies, West-Central Semiarid Prairies, and South-Central Semiarid Prairies ecoregions), and 6 percent is within ecoregions considered in the report for the Western United States (Western Cordillera, Cold Deserts, and Warm Deserts ecosystems). The majority of the area outside the study area was encompassed by the Missouri River, Arkansas River, and Red River Basins. Total carbon yields from these rivers were 1.3 gC/m<sup>2</sup>/yr and 2.4 gC/m<sup>2</sup>/yr for the Arkansas and Missouri Rivers, respectively (Stackpoole and Stets, unpub. data, June 25, 2013). Ecoregions in the Eastern United States had much higher runoff and terrestrial primary production than ecoregions in the Central and Western United States and therefore had higher carbon yields as well. For example, total carbon yields for the Ohio River, which was entirely within the Eastern United States assessment area, had a total carbon yield of 10.2 gC/m<sup>2</sup>/yr (Sarah M. Stackpoole and Edward G. Stets, U.S. Geological Survey, unpub. data, June 25, 2013).

Rivers draining to the Gulf of Mexico west of the Mississippi River Basin also crossed regional boundaries. The headwaters of many of these rivers were in the South-Central Prairies and Southern Texas Plain ecoregions, but the outlets to the Gulf of Mexico were in the Mississippi Alluvial and Southeast USA Coastal Plains ecoregion. Carbon yields in the South-Central Prairies and Southern Texas Plain ecoregions were smaller than those in the Mississippi Alluvial and Southeast USA Coastal Plains ecoregion, suggesting that the absolute magnitude of carbon flux from the Southeast USA Coastal Plain ecoregion was small and had a minor effect on the total carbon export estimates for the Eastern United States.

Individual site fluxes from the Ecoregion Dataset were summed by ecoregion ( $E_{C(IN)}$ ), and the ecoregional carbon flux estimate ( $Total E_C$ ) was calculated using equation 5-2, where  $A_{TOT}$  represented the total ecoregional area and  $A_{IN}$  represented the sum of the drainage areas associated with sites included in the dataset. This correction also assumed an equivalent areal carbon flux from the remaining (unmeasured) drainage area.

To calculate 5th and 95th confidence intervals for the mean ecoregional fluxes, a bootstrap with replacement method was run for 1,000 iterations. Total carbon fluxes represent the sum of DIC and TOC fluxes. The total carbon yields for an ecoregion were calculated by dividing annual fluxes by area of the ecoregion.

### 5.3.2. CO<sub>2</sub> Flux From Riverine Systems

Three values were required to measure the gas fluxes from aquatic systems: (1) the concentration of dissolved CO<sub>2</sub>, (2) the gas transfer velocity, and (3) the surface area of the water body. The vertical flux of CO<sub>2</sub> from riverine systems in the Eastern United States was modeled according to established methods (Butman and Raymond, 2011) and as outlined in the following equation:

$$CO_2 \text{ flux} = (CO_2\text{-water} - CO_2\text{-air}) \times kCO_2 \times SA, \quad (5-3)$$

where

- $CO_2 \text{ flux}$  is the total net emission of CO<sub>2</sub> from riverine systems of the Eastern United States,
- $CO_2\text{-water}$  is the riverine CO<sub>2</sub> concentration,
- $CO_2\text{-air}$  is the CO<sub>2</sub> concentration in the atmosphere,
- $kCO_2$  is the gas transfer velocity of CO<sub>2</sub> across the air-water interface, and
- $SA$  is the riverine surface area.

The total flux was estimated by summing all of the mean annual fluxes for a stream order (Strahler, 1952) within an ecoregion.

The dissolved CO<sub>2</sub> concentrations [ $CO_2\text{-water}$ ] were estimated from stream and river alkalinity data available through NWIS using the Mathworks, Inc. CO2SYS program (van Heuven and others, 2009). CO2SYS used temperature, pH, and alkalinity to estimate the dissolved CO<sub>2</sub> concentrations by incorporating disassociation constants for carbonic acid (H<sub>2</sub>CO<sub>3</sub>) into its calculations. Disassociation constants are mathematical constants that describe the tendency of a large molecule, such as H<sub>2</sub>CO<sub>3</sub>, to disassociate into smaller molecules, such as bicarbonate (HCO<sub>3</sub><sup>-</sup>), carbonate (CO<sub>3</sub><sup>2-</sup>), and CO<sub>2</sub> in an aqueous environment. The disassociation constants used in the CO2SYS equations for this assessment were from Millero (1979).

Water-chemistry data were compiled from the late 1920s through 2011, and only daily measurements of pH paired with temperature and alkalinity measurements were used to estimate dissolved CO<sub>2</sub>. For the seven ecoregions in the Eastern United States, 4,040 USGS streamgages had an adequate chemistry record, and their data were used for the CO<sub>2</sub> flux estimate (fig. 5–1). At least 12 sampling dates were required for inclusion in this analysis. A total of 232,751 daily chemical measurements were identified. The concentration of CO<sub>2</sub> in the atmosphere ( $CO_2\text{-air}$ ) was assumed to be constant at 390 parts per million (ppm) in equation 5–3 for all the ecoregions in the Eastern United States.

The gas transfer velocity ( $kCO_2$ ) was modeled based on a meta-analysis of measurements of gas exchange and the gas

transfer velocity made by direct tracer injections across small to mid-sized river systems in the United States (Melching and Flores, 1999; Raymond and others, 2012). The variation in gas transfer velocities within riverine systems was a function of turbulence at the air-water interface (Zappa and others, 2007). Physical parameters of stream slope and water velocity were used to predict gas transfer velocity, according to the following equation:

$$k_{600} = S \times V \times 2,841.6 + 2.03, \quad (5-4)$$

where

- $k_{600}$  is the gas transfer velocity of CO<sub>2</sub> normalized to the Schmidt number (a dimensionless ratio that approximates the relationship between the viscosity and gas diffusivity across a boundary layer) for CO<sub>2</sub> at standard temperature (20 °C) and standard atmospheric pressure (Wanninkhof, 1992; Raymond and others, 2012),

$S$  is the average slope of a stream reach, and

$V$  is the average velocity of water

A total of 563 independent gas tracer injection measurements were included in the development of this model.

Average slope was derived from the NHDPlus (Horizon Systems Corporation, 2005) dataset for each stream order within each ecoregion of the Eastern United States. Velocity estimates were calculated from hydraulic geometry coefficients derived for each of the ecoregions in the Eastern United States using the NWIS database of measured slope and velocity at 4,900 streamgages from 1940 through 2011. A total of 630,182 discharge measurements were used to derive hydraulic geometry coefficients specific to each ecoregion. Hydraulic geometry of stream reaches showed remarkable consistency within and across watersheds to approximate channel width, velocity, and depth from measured discharge (Leopold and Maddock, 1953; Park, 1977). All scaling relationships derived by the calculation of hydraulic geometry exponents were statistically significant ( $p$ -value less than 0.001). However, velocity measurements had coefficient of determination ( $R^2$ ) values ranging from 0.23 to 0.56, whereas width measurements had  $R^2$  values ranging from 0.86 to 0.95. Modeled average annual discharge from the NHDPlus data was used to estimate average channel width and velocity by utilizing the ecoregion specific hydraulic geometry coefficients. Average slope and velocity were then calculated by stream order to estimate the gas transfer velocity of CO<sub>2</sub> based on equation 5–4.

Stream surface area was calculated based on the same hydraulic geometry coefficients discussed in the previous paragraph. Average discharge was utilized to then calculate an average width for each stream order within an ecoregion. The total stream length was then calculated for each stream order within an ecoregion. Stream and river surface area was then calculated as the product of the average width and total length of streams by stream order.

Error propagation and uncertainty analyses were performed for each component of equation 5–3. To estimate

error, a bootstrapping technique as outlined in Efron and Tibshirani (1993) and Butman and Raymond (2011) was utilized. Bootstrap with replacement ( $\alpha=0.05$ ) was run for 1,000 iterations to calculate 5th and 95th confidence intervals for the concentrations of the partial pressure of CO<sub>2</sub> ( $p\text{CO}_2$ ) for each stream order within an ecoregion. Similarly, bootstrap with replacement was utilized to estimate confidence intervals associated with the hydraulic geometry coefficients derived from the measurements of stream width and velocity, which were subsequently used to estimate the stream surface area and gas transfer velocity. Overall bias associated with estimates of  $p\text{CO}_2$  remained low and had a negligible effect on the error associated with the use of the mean value for each stream order. Similarly, the effect of bootstrapping the hydraulic geometry parameters produced minimal bias.

A Monte-Carlo simulation was performed for each stream order estimate of the total carbon flux from riverine surfaces (equation 5–3). The 5th and 95th confidence intervals derived from the bootstrapping discussed above were used to set the boundary conditions of the Monte Carlo simulation for each parameter of equation 5–3. One thousand replications of the total flux calculation were performed. This approach is considered conservative because it allowed for the same probability of all combinations of each parameter in the total flux equation to be selected for each stream order and may have overestimated the error associated with the riverine evasion flux.

All estimates for the total carbon flux within an ecoregion were presented with the 5th and 95th confidence intervals derived from the Monte Carlo simulation. In general, this conservative approach biased the range of estimate high due to a slight skew in the distribution of  $p\text{CO}_2$  concentration within a stream order and ecoregion. It should be noted that the mean concentration by stream order was chosen rather than the median values because incorporating mean values approximated a broader spatial representation of  $p\text{CO}_2$  concentrations in the Eastern United States. All estimates derived from the Monte Carlo simulation were adjusted to account for monthly temperatures below freezing under the assumption that stream and river flux did not occur when monthly temperatures averaged less than 0 °C. This adjustment reduced the flux for the Mixed Wood Shield ecoregion by 40 percent, the Atlantic Highlands ecoregion by 32 percent, the Mixed Wood Plains ecoregion by 30 percent, the Central USA Plains ecoregion by 24 percent, the Ozark, Ouachita-Appalachian Forests ecoregion by 6 percent, and the Southeastern USA Plains ecoregion by 1 percent; the adjustment had no effect on the Mississippi Alluvial and Southeast USA Coastal Plains ecoregion.

### 5.3.3. CO<sub>2</sub> Flux From Lacustrine Systems

Water-chemistry data used to estimate lacustrine CO<sub>2</sub> emissions were obtained from the 2007 national lakes assessment (NLA) of the EPA (U.S. Environmental Protection Agency, 2009). The NLA used a probability-based survey design to select lakes and reservoirs that met the following criteria: (1) greater than 4 hectares (ha) in area, with a

minimum of 0.1 ha of open water; (2) at least 1 m deep; and (3) not classified or described as treatment or disposal ponds or as brackish-water or ephemeral bodies (U.S. Environmental Protection Agency, 2009). Following outlier removal (McDonald and others, 2013), data from 549 lakes were used in the following calculations (fig. 5–1D); 45 of these lakes were sampled twice.

Sampling took place during summer 2007; 50 percent of the samples were obtained between July 12 and August 23, and nearly all (99 percent) were obtained between June 1 and September 30. The data were classified according to the seven ecoregions in the Eastern United States. The number of lakes ranged from 37 to 143 per ecoregion. Various biological, physical, and chemical indicators were measured during the NLA (U.S. Environmental Protection Agency, 2009), and only a subset of water-chemistry and physical data was used in this assessment and included acid-neutralizing capacity (ANC, assumed to be equal to alkalinity), pH, temperature, and dissolved organic carbon (DOC).

The estimated CO<sub>2</sub> flux from lacustrine systems was calculated using the general equation 5–3. The estimated dissolved CO<sub>2</sub> (CO<sub>2</sub>-water) was computed using the equilibrium geochemical model PHREEQC version 2 (Parkhurst and Appelo, 1999). This model is similar to CO2SYS in that parameters such as water temperature, pH, and alkalinity were used to estimate CO<sub>2</sub> concentrations.

The gas transfer velocity for lacustrine systems is largely a function of wind speed (Cole and Caraco, 1998). The estimated mean wind speeds in summer (June to September) were determined for each ecoregion from surface meteorology and solar energy data of the National Aeronautics and Space Administration (NASA; 2012). The surface area of lakes and reservoirs was tabulated for each ecoregion, as in McDonald and others (2012).

Many of the parameters involved in these calculations violated normality assumptions; therefore, nonparametric 5th and 95th confidence intervals were determined on 1 million ordinary bootstrap replicates. The confidence intervals for the estimated fluxes were determined by propagation of uncertainty, except for the total values (for example, the sum of the regional estimates). In those cases, the confidence intervals were assumed to be additive (uncertainty was not propagated) because potential errors in the regional estimates are likely to be systematic.

### 5.3.4. Carbon Burial in Lacustrine Systems

Carbon burial in lacustrine systems includes carbon buried in the sediments of lakes and reservoirs; it is a function of sedimentation rates, sediment carbon concentrations, and the areal extent of lacustrine systems. Carbon burial in lacustrine systems of the Eastern United States was modeled according to the following equation:

$$C_{\text{burial}} = \text{SedRt} \times C_{\text{conc}} \times \text{SA}_{\text{WB}} \quad (5-5)$$

where

$C_{\text{burial}}$	is the carbon burial rate,
$\text{SedRt}$	is the sedimentation rate,
$C_{\text{conc}}$	is the concentration of carbon in sediments, and
$\text{SA}_{\text{WB}}$	is the surface area of the water body.

Data on sedimentation rates and carbon concentrations in sediments were sparse, necessitating an empirical approach that relied on existing data to build geostatistical models, which were then used to estimate carbon burial rates in unsampled lakes and reservoirs. The input data included (1) sedimentation rates derived from a national database (for reservoirs) and peer-reviewed literature (for lakes) and (2) carbon concentrations obtained from measurements on sediment samples collected as part of the 2007 NLA (U.S. Environmental Protection Agency, 2009, §10.3.3).

The areal extents of lacustrine systems were derived from the high-resolution (1:24,000) USGS National Hydrography Dataset (NHD; U.S. Geological Survey, 2012c). Sedimentation rates in lakes and carbon concentrations in lake sediments usually are different from those in reservoirs (Mulholland and Elwood, 1982; Dean and Gorham, 1998); thus, the water bodies were separated into lake and reservoir classes. Water bodies were classified as reservoirs if they met any of the following criteria: (1) the water body was tagged as a reservoir in the NHD, (2) the water-body name included the word “reservoir” in it, or (3) the water body was included in the National Inventory of Dams database (U.S. Army Corps of Engineers, 2012). Water bodies that were not classified as reservoirs were assumed to be lakes. A comparison with ground-based observations on the 697 lakes that were sampled for carbon in sediments during the 2007 NLA indicated that this classification scheme was correct 80 percent of the time; however, misclassification rates might have been higher for small water bodies (area less than or equal to 4 ha), such as farm ponds, which were not sampled during the NLA.

The best available national dataset of reservoir sedimentation rates was the Reservoir Sedimentation Database (RESSED), which included sedimentation-rate data on more than 1,800 georeferenced reservoirs in the United States (fig. 5–1E; Mixon and others, 2008; Ackerman and others, 2009). The sedimentation rates in the RESSED database were derived from repeat bathymetric surveys with the purpose of estimating losses in reservoir storage. On the basis of the hypothesis that sedimentation rates were related to land use, topography, soils, and vegetation characteristics in the area surrounding the reservoirs, a geographic information system (GIS) analysis was performed to quantify these characteristics for each hydrologic unit (represented by a 12-digit hydrologic unit code (HUC); U.S. Department of Agriculture, Natural Resources Conservation Service, 2012) adjacent to each reservoir. The sedimentation rates in the RESSED database strongly correlated with the net contributing area ( $R^2$  equal to 0.94). However, the values for the net contributing area were not available for most reservoirs in the United States; therefore, a reservoir’s surface

area, which should scale with the net contributing area, was used as a surrogate for the net contributing area.

The RESSED dataset was split evenly into calibration and validation datasets, and a stepwise multiple-linear-regression (MLR) analysis was performed on the calibration data, where the sedimentation rate was the dependent variable, and the land use and basin characteristics were independent, explanatory variables. The independent variable that explained the most variance in the sedimentation rate entered the model first. The variances explained by the remaining explanatory variables were recalculated, and the variable that explained the next greatest amount of variance entered the model next. This iterative process was repeated until no additional variables showed statistically significant correlations to sedimentation rates, using a  $p$ -value less than or equal to 0.1. The multicollinearity among explanatory variables was evaluated using the variance inflation factor (calculated as  $1/(1-R^2)$ ; Hair and others, 2005), which had a threshold for exclusion of 0.2. The resulting MLR equation was used to estimate the sedimentation rates for all the reservoirs in the NHD. The standard error of the equation was used to calculate uncertainty at 95-percent confidence for the predicted sedimentation rates for sites in the validation dataset.

A national dataset of lake sedimentation rates does not exist; therefore, sedimentation rates in lakes were estimated from data in peer-reviewed literature. Lake sedimentation rates have been calculated for more than 80 lakes around the world using lead-210 and cesium-137 isotope dating techniques on sediment cores; in most studies, multiple cores were collected from each lake. A review of peer-reviewed literature identified data for sites in Africa, Antarctica, Asia, Europe, New Zealand, and North America. The data were compiled and a statistical analysis was performed to characterize a probability density function of lake sedimentation rates. A sedimentation rate was assigned to each lake from the probability density function using random sampling with replacement. This procedure was repeated 100 times, drawing a new value from the statistical distribution each time in order to obtain 100 possible sedimentation rate values for each lake. Each of these values was used to calculate a carbon burial rate using equation 5–5, providing a range of carbon burial estimates for each lake. Uncertainty at the 95-percent confidence level was calculated as  $2 \times F$ -pseudosigma, where  $F$ -pseudosigma is a nonparametric equivalent to the standard deviation.

Carbon concentrations were measured on sediment samples collected from 697 bodies of water during the 2007 NLA (fig. 5–1E; U.S. Environmental Protection Agency, 2009). The data were split into calibration and validation datasets, and a stepwise MLR analysis was performed using the same methods and explanatory variables as in the reservoir sedimentation-rate analysis. The resulting equation was used to estimate carbon concentrations in lake and reservoir sediments in unsampled water bodies across the Eastern United States. Uncertainty and model performance were evaluated in the same way as the reservoir sedimentation-rate analysis.

### 5.3.5. Exclusion of the Great Lakes From the Analysis

In this study, the surface area, CO<sub>2</sub> emissions, and carbon burial in sediments were not considered for the Laurentian Great Lakes, although their combined surface area is about equal to 160 percent of all other inland lakes in the contiguous United States combined (McDonald and others, 2012). Even using the most current modeling techniques, large uncertainty is still associated with carbon fluxes on these large water bodies (Bennington and others, 2012). CO<sub>2</sub> emission estimates for the entire system remain very poorly constrained, currently ranging from less than 1 to more than 30 TgC/yr (McKinley and others, 2011). There is also the additional difficulty of dividing gas emissions and carbon burial for four of the Great Lakes between the borders of Canada and the United States.

### 5.3.6. Limitations and Uncertainties

The within-ecoregion lateral flux results presented in this chapter were based on empirical data, but there were two main limitations of the associated methods used to calculate these fluxes. The lateral flux values determined from the Ecoregion Dataset (table 5–1) represented only small watersheds with drainage areas between 3 and 59,000 km<sup>2</sup>, because watershed boundaries had to be entirely within ecoregional boundaries to be included in this analysis. Lateral fluxes represent carbon concentrations multiplied by flow, and because flow from smaller watersheds is generally lower than flow from large ones, the fluxes from this dataset may be biased toward the low end of the range of lateral fluxes. Additionally, watersheds included in the Ecoregion Dataset ranged from 18 to 40 percent of the total ecoregional area, and an equivalent areal carbon flux from the remaining (unmeasured) drainage area was a major assumption in the

calculated flux. Additionally, large river basins included in the Coastal Export Dataset included source areas that lay within ecoregions that were considered in the Central (Zhu and others, 2011) or Western (Zhu and Reed, 2012) United States assessment reports, which complicated flux estimates based on ecoregional boundaries.

In this assessment, the estimated CO<sub>2</sub> flux rates from riverine systems dominated the estimated aquatic carbon fluxes. Validation data to support fluxes of this magnitude do not currently exist; however, recent research measuring oxygen transfer rates suggests that gas transfer velocities in the upper reaches of the Colorado River can range from 9 meters per day (m/d) in the large main channels up to 338 m/d in rapids (Hall and others, 2012). It is important to note that the model to estimate gas transfer velocity of CO<sub>2</sub> outlined in Raymond and others (2012) and used for this assessment was developed from a dataset that did not include any measurements from steep-slope or high-altitude locations, and as such, the application of this model in highly diverse riverine landscapes must be done with appropriate caution.

The contribution of organic acids to the calculation of total alkalinity potentially could have caused an over-estimation of the dissolved *p*CO<sub>2</sub> concentrations (Tishchenko and others, 2006; Hunt and others, 2011). In typical naturally occurring fresh water, the only major contributors to noncarbonate alkalinity are organic acids, primarily humic and fulvic acids (Lozovik, 2005). The concentration of free organic ions was estimated for the lakes included in the 2007 NLA (U.S. Environmental Protection Agency, 2009) using the empirical relations of Oliver and others (1983). The estimated organic anion concentration for each lake or reservoir was subtracted from the measured alkalinity before performing an analysis of *p*CO<sub>2</sub>; however, an appropriate correction algorithm has not been developed for the dataset that was used for the flux calculation in riverine systems because of the limited locations of paired DOC and alkalinity

**Table 5-1.** Estimated within-ecoregion carbon fluxes and yields from riverine systems in the Eastern United States.

[Sites represent U.S. Geological Survey streamgages in endorheic and exorheic basins for which data were available to calculate estimated dissolved inorganic carbon (DIC) and total organic carbon (TOC) fluxes, respectively. Values presented in parentheses represent errors associated with total flux and total yield (fluxes normalized to watershed areas) at the bootstrapped 5th and 95th confidence intervals. Total carbon fluxes and mean yields were calculated by summing the estimated DIC and TOC. gC/m<sup>2</sup>/yr, grams of carbon per square meter per year; TgC/yr, teragrams of carbon per year]

Ecoregion	Number of sites		Estimated total flux, in TgC/yr	Estimated total yield, in gC/m <sup>2</sup> /yr	Estimated flux as DIC, in percent of total flux
	DIC yields	TOC yields			
Mixed Wood Shield	25	18	1.3 (0.6, 2.1)	6.4 (2.9, 10.0)	55.7
Atlantic Highlands	61	21	0.2 (0.1, 0.4)	1.2 (0.6, 6.6)	75.1
Mixed Wood Plains	73	50	2.1 (1.0, 3.1)	5.5 (2.5, 8.3)	80.3
Central USA Plains	77	38	2.3 (1.6, 3.1)	9.8 (6.6, 12.9)	82.9
Southeastern USA Plains	321	203	5.6 (3.7, 7.4)	5.6 (3.8, 7.4)	48.9
Ozark, Ouachita-Appalachian Forests	338	78	5.5 (3.2, 7.8)	10.7 (6.3, 15.1)	86.1
Mississippi Alluvial and Southeast USA Coastal Plains <sup>1</sup>	106	103	3.0 (1.5, 4.4)	6.6 (3.3, 9.9)	43.2
<b>Eastern United States (total)</b>	<b>1,001</b>	<b>511</b>	<b>19.4 (15.2, 23.6)</b>	<b>6.5 (5.1, 8.0)</b>	<b>57.1</b>

<sup>1</sup>Includes the Everglades and Texas-Louisiana Coastal Plain level II ecoregions for the analysis of this assessment.

measurements within the NWIS database. Because the current methodology for estimating alkalinity in riverine systems does not account for organic acids, some of the existing estimates of riverine fluxes may be high. Uncertainties in the estimates may be reduced by accounting for noncarbonate alkalinity (organic acids) when deriving  $p\text{CO}_2$  concentration from total alkalinity measurements.

The stream and river surface-area estimates for each ecoregion ranged from 0.3 to 0.9 percent of the total area and are consistent with other published values (Aufdenkampe and others, 2011; Downing and others, 2012); however, the accuracy of stream and river surface area estimates may improve by using remote-sensing techniques to further constrain the hydraulic geometry parameters that are appropriate at the ecoregion scale (Striegl and others, 2012). Specifically, there is a need to constrain the surface areas of first-order stream systems (headwaters areas) that may be poorly characterized within the NHDPlus dataset and that may exhibit strong seasonal variation in water flow. Regional efforts to physically map first-order stream surface areas in combination with scaling laws would reduce uncertainties.

The locations of USGS streamgages, which were used to calculate the hydraulic geometry coefficients, introduced a bias because the streamgages were placed in a location that was best suited for accurate discharge measurements (Leopold and Maddock, 1953; Park, 1977). Therefore these streamgage locations most likely do not represent the entire range of variability in the relationships among stream depth, width, and velocity that exists along the flow paths of rivers in the Eastern United States. The results from the Monte Carlo simulation suggested levels of uncertainty approaching 52 percent for the Mixed Wood Shield ecoregion and between 32 and 40 percent for each of the six other ecoregions. In addition, the current application of bootstrapping and simulation was considered very conservative; however, as suggested above, without extensive efforts in field validation for both the gas transfer velocity and dissolved  $\text{CO}_2$  concentration in small stream environments, the model estimates reported in this assessment represent the most comprehensive to date.

Using the available data, it was not possible to accurately model the impact of seasonality on estimated mean  $\text{CO}_2$  flux from lacustrine systems. In dimictic lakes (lakes that experience ice cover and mix completely in the spring and fall),  $\text{CO}_2$

concentrations build up under ice cover and in the hypolimnion (bottom waters) during stratification as a result of heterotrophic respiration and are degassed rapidly during mixing (Michmerhuizen and others, 1996; Riera and others, 1999). Because the available data for the assessment were collected from surface waters only during the summer, this aspect of the seasonal  $p\text{CO}_2$  dynamics was not included in the estimates.

There were numerous sources of uncertainty in the carbon burial estimates. The datasets used to calibrate the regression models of sedimentation rates in reservoirs and carbon concentrations in sediments were derived from national databases; however, they represented less than 0.2 percent of the total number of water bodies in the conterminous United States. A national database of sedimentation rates in lakes does not exist, necessitating a statistical probability approach to estimating lake sedimentation rates, which probably misses substantial regional variability. Carbon concentrations in water body sediments were derived from surface sediment samples collected at single points within each water body and may not represent average carbon concentrations in the surface sediments. Important constants used in the carbon burial calculations include sediment bulk density and porosity; these parameters were assigned values based on information in the literature (Dean and Gorham, 1998), but the values may vary widely among lacustrine systems. Combining all these sources of uncertainty yields a conservative error estimate of approximately  $\pm 50$  percent in carbon burial rates. It may be possible to reduce the uncertainty in these estimates in the future, as additional data on sedimentation rates and sediment carbon concentrations become available.

## 5.4. Results

### 5.4.1. Lateral Carbon Transport in Riverine Systems

The total carbon export from exorheic basins, calculated using the Coastal Export Dataset, was estimated to be 36.5 TgC/yr (with lower and upper confidence intervals of 28.1 TgC/yr and 44.8 TgC/yr, respectively; table 5–2), with 74 percent of the export occurring as DIC. The Mississippi

**Table 5–2.** Estimated coastal carbon exports and yields from riverine systems in the Eastern United States.

[Sites represent U.S. Geological Survey streamgages for which data were available to calculate estimated carbon fluxes from exorheic basins. Values presented in parentheses represent the 5th and 95th confidence intervals. Total exports and total yields were calculated by summing dissolved inorganic carbon (DIC) and total organic carbon (TOC). gC/m<sup>2</sup>/yr, grams of carbon per square meter per year; TgC/yr, teragrams of carbon per year]

Waterway	Number of sites		Estimated total export, in TgC/yr	Estimated total yield, in gC/m <sup>2</sup> /yr	Estimated flux as DIC, as percentage of total export
	DIC yields	TOC yields			
Atlantic Ocean	55	52	4.1 (3.7, 4.6)	5.3 (4.8, 5.9)	50
Great Lakes	30	20	5.4 (5.3, 5.6)	18.7 (18.3, 19.1)	85
Gulf of Mexico	36	36	26.3 (18.0, 34.6)	6.45 (4.41, 8.49)	75
Rainy River	1	1	0.2 (0.1, 0.3)	11.6 (6.3, 16.8)	38
<b>All regions</b>	<b>122</b>	<b>109</b>	<b>36.5 (28.1, 44.8)</b>	<b>6.4 (5.0, 7.9)</b>	<b>74</b>

River was the single largest source of carbon to the coastal ocean (22.1 TgC/yr), and therefore, the majority of carbon export from the Eastern United States was to the Gulf of Mexico, which received 26.3 TgC/yr. The Great Lakes received 5.4 TgC/yr, whereas the Atlantic Ocean received 4.1 TgC/yr. The Rainy River in the Mixed Wood Shield ecoregion exported 0.2 TgC/yr.

The estimated total fluxes (table 5–1), calculated using the Ecoregion Dataset, were highest in the Southeastern USA Plains ecoregion (5.6 TgC/yr) and lowest in the Atlantic Highlands ecoregion (0.2 TgC/yr). The estimated mean yields were highest in the Ozark, Ouachita-Appalachian Forests ecoregion (10.7 gC/m<sup>2</sup>/yr) and lowest in the Atlantic Highlands ecoregion (1.2 gC/m<sup>2</sup>/yr; fig. 5–1; table 5–1). The mean DIC concentration in the Central USA Plains ecoregion (51 milligrams per liter (mg/L)) was eight times higher than the estimated mean DIC concentration in the Atlantic Highlands ecoregion (6 mg/L). The range of TOC concentrations were narrower, with the highest estimated mean concentration in the Mississippi Alluvial and Southeast USA Coastal Plains ecoregion (16 mg/L) and the lowest in the Atlantic Highlands ecoregion (4 mg/L). There was substantial variability in the mean runoff among the ecoregions, with the greatest mean runoff in the Atlantic Highlands ecoregion (627 millimeters per year (mm/yr)) and the smallest mean runoff was in the Mixed Wood Shield ecoregion (297 mm/yr).

#### 5.4.2. CO<sub>2</sub> Flux From Riverine Systems

The mean concentration of dissolved CO<sub>2</sub> in streams and rivers across the Eastern United States exceeded atmospheric concentrations, indicating that these ecosystems represent sources of carbon to the atmosphere. Mean *p*CO<sub>2</sub> concentration was greatest in the Southeastern USA Plains ecoregion at 4,902 micro-atmospheres (µatm), which is 12.5 times greater than atmospheric *p*CO<sub>2</sub> concentration, and smallest in the Atlantic Highlands ecoregion at 2,088 µatm, which is 5.3 times greater than atmospheric *p*CO<sub>2</sub> concentration. The mean *p*CO<sub>2</sub> concentration

for all regions was 3,265 µatm, which was 8.3 times greater than atmospheric *p*CO<sub>2</sub> concentration (fig. 5–1).

Stream surface area ranged from 630 km<sup>2</sup> in the Mixed Wood Shield ecoregion (representing 0.3 percent of the total land surface area of the Eastern United States) to 5,617 km<sup>2</sup> in the Southeastern USA Plains ecoregion (0.56 percent; table 5–3). The total stream surface area for the Eastern United States was 16,467 km<sup>2</sup> representing 0.56 percent of the land surface. Stream and river surface area was greatest in the Mississippi Alluvial and Southeast Coastal Plain ecoregion at 23,465 km<sup>2</sup>, or 0.9 percent.

The total riverine vertical flux of carbon for the Eastern United States was 152.1 TgCO<sub>2</sub>-eq/yr with 5th and 95th percentiles of 101 and 211, respectively. Ecoregion specific fluxes ranged from a high of 49.4 TgCO<sub>2</sub>-eq/yr (5th and 95th percentiles of 33.7 to 70.3 TgCO<sub>2</sub>-eq/yr) in the Ozark, Ouachita-Appalachian Forests ecoregion to 2.2 TgCO<sub>2</sub>-eq/yr (5th and 95th percentiles of 1.1 to 3.7 TgCO<sub>2</sub>-eq/yr) in the Mixed Wood Shield ecoregion. Riverine flux on an area basis for ecoregions in the Eastern United States was 14 gC/m<sup>2</sup>/yr (5th and 95th percentiles of 7.9 and 17 gC/m<sup>2</sup>/yr, respectively), ranging from 2.93 gC/m<sup>2</sup>/yr (5th and 95th percentiles of 1.6 and 4.9 gC/m<sup>2</sup>/yr, respectively) in the Mixed Wood Shield ecoregion to 26.2 gC/m<sup>2</sup>/yr (with 5th and 95th percentiles of 17.9 and 37.3 gC/m<sup>2</sup>/yr, respectively) in the Ozark, Ouachita-Appalachian Forests ecoregion (fig. 5–1).

#### 5.4.3. CO<sub>2</sub> Flux From Lacustrine Systems

The estimated mean concentration of *p*CO<sub>2</sub> in lacustrine systems of the Eastern United States was 1,184 µatm with a median of 740 µatm, which was greater than atmospheric concentrations for all eastern ecoregions. Thus, all ecoregions were net sources of carbon to the atmosphere. The mean *p*CO<sub>2</sub> was greatest in the Southeastern USA Plains ecoregion at 1,866 µatm, which was 4.8 times greater than the atmospheric concentration of CO<sub>2</sub>, and smallest in the Mixed Wood Shield ecoregion at 714 µatm, which was 1.8 times greater than the atmospheric concentration of CO<sub>2</sub> (fig. 5–1).

**Table 5–3.** Estimated vertical fluxes and yields of CO<sub>2</sub> from riverine systems in the Eastern United States.

[Sites are U.S. Geological Survey streamgages for which data were available to calculate the estimated partial pressure of carbon dioxide (*p*CO<sub>2</sub>). Values presented in parentheses represent errors associated with total flux and total yield (fluxes normalized to watershed areas) at the 5th and 95th percentiles derived from a Monte Carlo simulation. Total yields were calculated by dividing the estimated total flux by the ecoregion area. gC/m<sup>2</sup>/yr, grams of carbon per square meter per year; km<sup>2</sup>, square kilometers; TgC/yr, teragrams of carbon per year]

Ecoregion	Number of sites	Stream area, in km <sup>2</sup>	Estimated total flux, in TgC/yr	Estimated total yield, in gC/m <sup>2</sup> /yr
Mixed Wood Shield	59	630	0.6 (0.3, 1.0)	2.9 (1.6, 4.9)
Atlantic Highlands	194	861	2.6 (1.6, 3.8)	13.1 (8.6, 20.2)
Mixed Wood Plains	367	1,598	2.8 (1.9, 3.8)	7.1 (5.0, 10.2)
Central USA Plains	223	807	1.1 (0.7, 1.6)	4.6 (3.1, 6.6)
Southeastern USA Plains	1,444	5,617	14.5 (9.9, 19.4)	14.0 (10.0, 19.4)
Ozark, Ouachita-Appalachian Forest	1,149	3,054	13.8 (9.2, 19.2)	26.2 (17.9, 37.3)
Mississippi Alluvial and Southeast USA Coastal Plains <sup>1</sup>	622	3,901	6.4 (3.9, 8.9)	14.5 (9.2, 20.7)
<b>Eastern United States (total)</b>	<b>4,040</b>	<b>16,467</b>	<b>41.6 (27.5, 57.7)</b>	<b>14.0 (7.9, 17.0)</b>

<sup>1</sup>Includes the Everglades and Texas-Louisiana Coastal Plain level II ecoregions for the analysis of this assessment.

The estimated mean flux of CO<sub>2</sub> across the air-water interface was primarily determined by the gradient between the dissolved and atmospheric concentrations of carbon. The estimated gas transfer velocity was less variable than the estimated  $p\text{CO}_2$  among all of the ecoregions—smallest in the Atlantic Highlands ecoregion (0.99 m/d) and greatest in the Central USA Plains ecoregion (1.21 m/d). The ecoregional estimates of total annual CO<sub>2</sub> flux from lacustrine systems (table 5–4) ranged from 0.3 TgC/yr (1.2 TgCO<sub>2</sub>-eq/yr) in the Central USA Plains ecoregion to 3.9 TgC/yr (14.3 TgCO<sub>2</sub>-eq/yr) in the Southeastern USA Plains ecoregion. The total CO<sub>2</sub> flux from the Eastern United States was estimated to be 9.7 TgC/yr (35.6 TgCO<sub>2</sub>-eq/yr). The estimated ecoregional flux values were directly related to the surface area of the lacustrine systems (table 5–4), which varied among the ecoregions, partially because of differences in regional morphology and climate but mainly due to differences in the size of the ecoregions.

In order to facilitate a direct comparison between lake and reservoir gas fluxes, lateral carbon transport, carbon burial, and terrestrial processes, the estimated CO<sub>2</sub> flux values were normalized to the total land surface area in each ecoregion to provide the carbon yield (fig. 5–1; table 5–4). The estimated carbon yields ranged from 1.1 gC/m<sup>2</sup>/yr in the Central USA Plains ecoregion to 4.6 gC/m<sup>2</sup>/yr in the Mixed Wood Plains and the Mississippi Alluvial and Southeast USA Coastal Plains ecoregions. The estimated mean carbon yield (expressed as CO<sub>2</sub> flux per unit of total land and water area) from lacustrine systems in the Eastern United States was 3.3 gC/m<sup>2</sup>/yr.

#### 5.4.4. Carbon Burial in Lacustrine Systems

The estimated net flux of carbon due to burial in lacustrine sediments of the Eastern United States was –9.2 TgC/yr (negative values represent a carbon sink; table 5–5). The Mixed Wood Shield and the Mississippi Alluvial and Southeast USA Coastal Plain ecoregions had the highest

estimated carbon burial rates, accounting for net fluxes of –2.5 TgC/yr and –2.7 TgC/yr, respectively. The Central USA Plains and the Ozark, Ouachita-Appalachian Forest ecoregions had the lowest estimated carbon burial rates, with net flux of –0.4 TgC/yr each (table 5–5).

When normalized to the area of each ecoregion (yield), the estimated net flux due to carbon burial in lacustrine systems was –3.1 gC/m<sup>2</sup>/yr (fig. 5–1; table 5–5). The ecoregion-normalized fluxes ranged from –0.8 gC/m<sup>2</sup>/yr in the Ozark, Ouachita-Appalachian Forest ecoregion to –11.9 gC/m<sup>2</sup>/yr in the Mixed Wood Shield ecoregion.

## 5.5. Discussion

### 5.5.1. Coastal Export, Lateral Transport, and CO<sub>2</sub> Flux From Riverine Systems

The highest riverine within-ecoregion lateral carbon fluxes and CO<sub>2</sub> emissions occurred in the Ozark, Ouachita-Appalachian Forests ecoregion. Moderate DIC and TOC concentrations (15.3 mg/L and 4 mg/L, respectively) coupled with high annual precipitation (1,218 mm/yr) and average annual runoff (average streamflow divided by drainage area, 533.8 mm/yr) produced within-ecoregion riverine lateral carbon fluxes of 10.7 gC/m<sup>2</sup>/yr. Elevated  $p\text{CO}_2$  concentrations (4,950  $\mu\text{atm}$ ) were also estimated for this ecoregion, where terrestrial soil processes may have a significant impact on stream water chemistry. Direct input of terrestrial soil and root respiration is often facilitated by increased levels of precipitation and water throughput as groundwater enters a stream environment (Jones and Mulholland, 1998). In fact, Jones and Mulholland (1998) measured  $p\text{CO}_2$  concentration in excess of 6,000  $\mu\text{atm}$  within forested headwater catchments of the Ozark, Ouachita-Appalachian Forests ecoregion, 20 percent greater than the  $p\text{CO}_2$  concentrations estimated across similar headwaters systems presented in this report. The high riverine

**Table 5–4.** Estimated vertical flux of carbon dioxide from lacustrine systems in the Eastern United States.

[Sites are from the 2007 National Lakes Assessment (U.S. Environmental Protection Agency, 2009). The data from the 2007 NLA were used in the calculation of the partial pressure of carbon dioxide ( $p\text{CO}_2$ ). Values presented in parentheses represent errors associated with total flux and total yield (fluxes normalized to watershed areas) at the bootstrapped 5th and 95th confidence intervals. Carbon yields were calculated by dividing the estimated total flux by the ecoregion area. gC/m<sup>2</sup>/yr, grams of carbon per square meter per year; km<sup>2</sup>, square kilometers; TgC/yr, teragrams of carbon per year]

Ecoregion	Number of sites	Lake and reservoir area, in km <sup>2</sup>	Estimated total flux, in TgC/yr	Estimated total yield, in gC/m <sup>2</sup> /yr
Mixed Wood Shield	58	12,300	0.7 (0.4, 1.2)	3.5 (1.8, 6.0)
Atlantic Highlands	62	5,170	0.5 (0.3, 0.7)	2.7 (1.8, 3.9)
Mixed Wood Plain	143	11,700	1.7 (1.4, 2.2)	4.6 (3.6, 5.8)
Central USA Plains	37	3,170	0.3 (0.1, 0.4)	1.1 (0.6, 1.8)
Southeastern USA Plains	124	17,400	3.9 (2.9, 5.1)	3.9 (2.9, 5.1)
Ozark, Ouachita-Appalachian Forests	72	7,080	0.7 (0.5, 0.9)	1.4 (0.9, 1.8)
Mississippi Alluvial and Southeast USA Coastal Plains <sup>1</sup>	53	19,800	1.9 (1.2, 3.4)	4.6 (2.6, 7.6)
<b>Eastern United States (total)</b>	<b>549</b>	<b>76,620</b>	<b>9.7 (6.8, 13.9)</b>	<b>3.3 (2.9, 4.0)</b>

<sup>1</sup>Includes the Everglades and Texas-Louisiana Coastal Plain level II ecoregions for the analysis of this assessment.

**Table 5-5.** Estimated carbon burial in lacustrine sediments in the Eastern United States.

[Sites were those in the 2007 National Lakes Assessment (U.S. Environmental Protection Agency, 2009) that were used to develop a regression equation to estimate carbon concentrations in sediment. Values presented in parentheses represent errors associated with total flux and total yield (fluxes normalized to watershed areas) at the bootstrapped 5th and 95th confidence intervals. Carbon yields were calculated by dividing the estimated total flux divided by the ecoregion area. gC/m<sup>2</sup>/yr, grams of carbon per square meter per year; TgC/yr, teragrams of carbon per year]

Ecoregion	Number of sites	Estimated total flux, in TgC/yr	Estimated total yield, in gC/m <sup>2</sup> /yr
Mixed Wood Shield	21	-2.5 (-1.2, -3.7)	-11.9 (-6.0, -17.9)
Atlantic Highlands	47	-0.6 (-0.3, -1.0)	-3.4 (-1.7, -5.1)
Mixed Wood Plains	73	-1.4 (-0.7, -2.1)	-3.7 (-1.9, -5.6)
Central USA Plains	30	-0.4 (-0.2, -0.5)	-1.5 (-0.8, -2.3)
Southeastern USA Plains	95	-1.3 (-0.6, -1.9)	-1.3 (-0.6, -2.0)
Ozark, Ouachita-Appalachian Forests	53	-0.4 (-0.2, -0.7)	-0.8 (-0.4, -1.3)
Mississippi Alluvial and Southeast USA Coastal Plains <sup>1</sup>	31	-2.7 (-1.3, -4.0)	-6.2 (-3.1, -9.3)
<b>Eastern United States (total)</b>	<b>350</b>	<b>-9.2 (-4.6, -13.8)</b>	<b>-3.1 (-1.6, -4.7)</b>

<sup>1</sup>Includes the Everglades and Texas-Louisiana Coastal Plain level II ecoregions for the analysis of this assessment.

CO<sub>2</sub> emissions in the Ozark, Ouachita-Appalachian Forests ecoregion were also likely related to physical parameters of the riverine systems in this ecoregion. The slopes of streambeds in the headwaters were high, averaging 3 percent, which when coupled with high stream velocities, resulted in gas transfer velocities upwards of 22 m/d. The combination of elevated CO<sub>2</sub> concentrations and gas transfer rates resulted in large areal riverine CO<sub>2</sub> flux estimates of 26.2 gC/m<sup>2</sup>/yr in this ecoregion.

Similarly, the riverine CO<sub>2</sub> yield of 13.1 gC/m<sup>2</sup>/yr calculated for the Atlantic Highlands ecoregion, which includes much of the White Mountains throughout New England, was a result of the physical characteristics of the landscape. Estimated headwater slope averaged 3.5 percent, and calculated gas transfer rates were 25.6 m/d. The differences in climate, with a mean annual temperature of 6.1 °C in the Atlantic Highlands ecoregion compared with 12.6 °C for the Ozark, Ouachita-Appalachian Forests ecoregion, could explain the change in flux from 2.6 TgC/yr to 13.8 TgC/yr between the two ecoregions, respectively. At the lower temperatures that are characteristic of the Atlantic Highlands ecoregion, the mineralization and soil weathering rates are comparatively low, which would also lower the carbon yields (Post and others, 1982; Lauerwald and others, 2012). Additionally, the dilute water chemistry of this ecoregion also likely played a role in low riverine CO<sub>2</sub> emissions, as there were relatively low pCO<sub>2</sub> concentrations (2,088 microatmospheres) in the Atlantic Highlands ecoregion.

The headwaters of the Susquehanna River, one of the larger rivers in the Northeastern United States, are in the Atlantic Highlands and the Ozark, Ouachita-Appalachian Forests ecoregions. Coastal exports from this river are ultimately delivered to the Chesapeake Bay. This river accounted for about 1 percent of the total coastal carbon exports in the Eastern United States, with a total carbon yield of 5.8 gC/m<sup>2</sup>/yr. This value represents an average of the carbon yields of the three ecoregions that this river encounters along its flow path: the Atlantic Highlands ecoregion (main branch of the Susquehanna River), the Ozark, Ouachita-Appalachian Forests ecoregion (west branch of the Susquehanna River),

and the Southeastern USA Plains ecoregion (coastal outlet), which have ecoregional yields of 1.2 g/m<sup>2</sup>/yr, 10.7 g/m<sup>2</sup>/yr, and 5.6 g/m<sup>2</sup>/yr, respectively. These coastal export values for the Eastern United States are similar to previously reported (Mulholland and Watts, 1982; Shih and others, 2010) estimated TOC export values for the North Atlantic (3.4 gC/m<sup>2</sup>/yr) and southern Atlantic gulf (5.9 gC/m<sup>2</sup>/yr).

The Mississippi Alluvial and Southeast USA Coastal Plains ecoregion had the highest riverine pCO<sub>2</sub> concentrations at 4,902 µatm. The riverine DIC (15.2 mg/L) and TOC (16 mg/L) concentrations for the ecoregion were also high, indicating that both inorganic and organic carbon could have contributed to the high pCO<sub>2</sub> values. Additionally, the coastal outlet of the Mississippi River is in the Mississippi Alluvial and Southeast USA Coastal Plains ecoregion, and the combination of the Mississippi River and Atchafalaya River Basins represented more than 60 percent of the total carbon export from the Eastern United States. The flux of 20.6 TgC/yr estimated for the Mississippi River Basin is similar to reported flux values (Raymond and Cole, 2003; Turner and Rabalais, 2004). The high average concentrations and fluxes in this southern ecoregion may be supported by direct inputs from highly productive wetland and riparian vegetation that cover more than 30 percent of the total land area and average annual precipitation exceeds 1.3 m. Additionally, the areal extent of streams and rivers within the Mississippi Alluvial and Southeast USA Coastal Plains ecoregion was the greatest across the Eastern United States at about 1 percent of the total ecoregion area. The connectivity of wetland and riparian sources of dissolved carbon gasses to stream and river ecosystems has not been well established along spatial and temporal gradients; however, a study in other wetland-dominated systems suggests very high concentrations of CO<sub>2</sub> at these riparian interfaces (Clilverd and others, 2008). Although research does suggest that, in regions with high groundwater recharge rates, the penetration of root respiration derived CO<sub>2</sub> from wetlands can be enhanced (Hunt and others, 1999), the analysis presented in this chapter is unable to quantify this effects across ecoregions.

The Mixed Wood Shield (6.4 gC/m<sup>2</sup>/yr), Mixed Wood Plains (5.5 gC/m<sup>2</sup>/yr), and Central USA Plains (9.8 gC/m<sup>2</sup>/yr) ecoregions had substantial within-ecoregion lateral carbon fluxes. The Mixed Wood Shield ecoregion, which is dominated by wetlands and forests, represented an ecoregion where total carbon was divided relatively equally between DIC and TOC. Both these major land cover classes (forests and wetlands) deliver substantial amounts of organic matter to riverine systems (Mulholland, 2003; Creed and others, 2008). In contrast, the Mixed Wood Plains and Central USA Plains ecoregions had more than 80 percent total carbon export as DIC. Fluvial export of terrestrial alkalinity is a major component of riverine DIC concentrations (Raymond and Cole, 2003; Stets and Striegl, 2012), but sedimentary rock coverage in either ecoregion was not substantial (less than 10 percent). However, agricultural lands and urban development did dominate the land cover in this ecoregion; these two landscape types have been linked with elevated DIC concentrations (Barnes and Raymond, 2009). Interestingly, the magnitude of riverine CO<sub>2</sub> emissions was not as high in these two ecoregions, most likely because of the flat topography of these glacially impacted ecoregions.

### 5.5.2. CO<sub>2</sub> Flux From and Carbon Burial in Lacustrine Systems

Similar to the riverine flux results, the average lacustrine CO<sub>2</sub> emissions (4.6 gC/m<sup>2</sup>/yr) and carbon burial fluxes (−6.2 gC/m<sup>2</sup>/yr) were high in the Mississippi Alluvial and Southeast USA Coastal Plains ecoregion. However, unlike the riverine CO<sub>2</sub> emissions, the northern ecoregions of the Eastern United States (Mixed Wood Shield and Mixed Wood Plains ecoregions) also had relatively high lacustrine CO<sub>2</sub> emissions (4.6 gC/m<sup>2</sup>/yr and 3.5 gC/m<sup>2</sup>/yr, respectively) and carbon burial fluxes (−11.9 gC/m<sup>2</sup>/yr and −3.7 gC/m<sup>2</sup>/yr, respectively). The high fluxes in these ecoregions reflected the size and density of lakes in those areas. The southern part of the Eastern United States contains a higher density of smaller water bodies, many of which are artificial, compared with the northern part of the Eastern United States where there is a relatively low density of lakes, but the lakes that are present have large surface areas, particularly in the Mixed Wood Shield ecoregion. Water body area alone explained 60 percent of the variation in carbon burial rates among ecoregions.

In general, the ecoregions with higher CO<sub>2</sub> emissions were also ecoregions with high carbon burial rates, indicating that excess carbon entering lacustrine systems that is not processed and emitted as CO<sub>2</sub> may otherwise be buried. Lacustrine systems with higher carbon burial rates also had a strong positive correlation between ecoregional average soil organic carbon and sediment carbon concentration. Higher lacustrine burial rates were related to the prevalence of wetlands particularly in the Mixed Wood Shield and the Mississippi Alluvial and Southeast USA Coastal Plains ecoregions. As with the riverine fluxes, this reflects the

importance of allochthonous (terrestrially derived) inputs of carbon to lakes and reservoirs in freshwater carbon budgets (Stets and others, 2009).

Variations in total annual carbon burial among ecoregions reflected differences in the sedimentation rates and sediment carbon concentrations of lacustrine systems as well as the prevalence and size of water bodies within each ecoregion. In the Eastern United States, sedimentation rates in reservoirs were highest in the Central USA Plains ecoregion, where the dominant land use was cultivated crops, a land cover that is associated with high erosion rates (Crowder, 1987; McIntyre, 1993). These results further emphasize the important influence that land cover can have on inland water carbon fluxes, as the relationship between high within-ecoregion lateral fluxes for the Central USA Plains ecoregion was also linked to the combined effects of agricultural lands and urban development in the previous section.

Regions with higher total lacustrine CO<sub>2</sub> emissions (table 5–4) tended to also exhibit higher total riverine CO<sub>2</sub> emissions (table 5–3). A notable exception is the Ozark, Ouachita-Appalachian Forests ecoregion, which had relatively low lacustrine emissions. This was likely due to the greater abundance of streams relative to lakes and reservoirs in this mountainous region. Lacustrine CO<sub>2</sub> emissions (table 5–4) normalized to ecoregion area (yields) produced values that range from 6 to 52 percent of lateral inorganic carbon flux and from 28 to 126 percent of lateral organic carbon flux (table 5–1). Although there was not a strong relationship between the magnitude of lateral fluxes and lake emissions, there was a positive relationship between the fraction of the lateral flux present as inorganic carbon (table 5–1) and ecoregional CO<sub>2</sub> yield from lakes and reservoirs, so that ecoregions with high proportions of total carbon as DIC had low CO<sub>2</sub> emissions. This suggests that the carbon composition, as indicated by the ratio of DIC to TOC, rather than the overall amount of allochthonous-derived carbon, controlled lacustrine CO<sub>2</sub> flux.

### 5.5.3. Summary and Conclusions of Carbon Storage From Inland Aquatic Systems

The considerable variability in the estimated inland waters' carbon fluxes among the seven ecoregions in the Eastern United States was likely due to the differences in the size and abundance of water bodies, topography, climate, and land cover associated with each ecoregion. In general, those ecoregions across the Eastern United States that had the highest annual temperature, natural vegetation cover, and precipitation had the highest total carbon fluxes, suggesting strong linkages across the terrestrial to aquatic interface. Overall, these results highlight the impact that climate and land cover can have on annual carbon transfer, storage, and flux from inland waters.

Riverine systems and lacustrine systems covered 0.55 and 2.6 percent of the total ecoregional area of the

Eastern United States, respectively, excluding the Laurentian Great Lakes. Despite the small surface area that these inland waters cover, they accounted for considerable carbon losses. Riverine  $\text{CO}_2$  emissions were the largest carbon sources to the atmosphere ( $14 \text{ gC/m}^2/\text{yr}$ ). Additionally, a total of  $6.3 \text{ gC/m}^2/\text{yr}$  as DIC and TOC was exported to coastal areas. The lacustrine  $\text{CO}_2$  losses ( $3.3 \text{ gC/m}^2/\text{yr}$ ) were balanced by nearly equivalent fluxes of carbon buried in lacustrine sediments ( $-3.1 \text{ gC/m}^2/\text{yr}$ ). Accounting for the three carbon loss terms (riverine and lacustrine  $\text{CO}_2$  loss, and lateral carbon coastal export) and one sequestration term (lacustrine carbon burial) resulted in a net inland waters' carbon yield of  $23.5 \text{ gC/m}^2/\text{yr}$ .

The results presented in this study indicate that the magnitude of aquatic fluxes in inland waters is significant, and that integration of these fluxes into the traditional terrestrial carbon cycle is needed. In this study, the terrestrial NEP value defined as carbon stored in terrestrial biomass, soil organic carbon, or harvested wood is equivalent to  $99.9 \text{ gC/m}^2/\text{yr}$  (chap. 7). The sum of carbon transported, emitted, or buried in aquatic ecosystems ( $29.7 \text{ g C/m}^2/\text{yr}$ ) was equivalent to about 30 percent of this terrestrial NEP estimate. This percentage value must be interpreted with caution, as it is possible that some of the carbon considered as a part of the terrestrial soil organic carbon pool, may in fact have been lost to lacustrine and riverine systems via erosion or leaching processes, which would already be accounted for in the inland aquatic

ecosystems' yield values. However, this comparison indicates that the linkage between terrestrial and aquatic ecosystems is critically important to understand fully the role natural ecosystems play in greenhouse-gas storage and cycling.

This chapter focused on current carbon fluxes from inland aquatic systems, but projected climate and land-use changes are likely to influence aquatic fluxes in future decades. Predicted changes to the hydrologic cycle include increased precipitation and streamflow (Mearns and others, 2003; Hayhoe and others, 2007; Huntington and others, 2009), reduction in the number of ice cover days on lakes and rivers (Magnuson and others, 2000; Jensen and others, 2007), and decreases in snow depth (Hayhoe and others, 2007; Burakowski and others, 2008). Delivery of carbon to aquatic ecosystems will also be changed by expected alterations to both terrestrial and aquatic biogeochemical cycling of carbon. Increases in net primary productivity (Freeman and others, 2004; Wrona and others, 2006) and organic matter decomposition rates (Davidson and Janssens 2006; Craine and others, 2010), as well as land-use changes such as urbanization and changes in agricultural management practices (Raymond and Cole, 2003; Barnes and Raymond, 2009; Aufdenkampe and others, 2011) are all likely to affect the amount and composition of carbon delivered to aquatic systems. Coupling both hydrologic and biogeochemical reactions in a systematic fashion over space and time will be key to accurately predicting changes in the magnitude of aquatic carbon fluxes in the future.