Baseline Carbon Sequestration, Transport, and Emission From Inland Aquatic Ecosystems in the Western United States

By Sarah M. Stackpoole, David Butman, David W. Clow, Cory P. McDonald, Edward G. Stets, and Robert G. Striegl

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Chapter 10. Baseline Carbon Sequestration, Transport, and Emission From Inland Aquatic Ecosystems in the Western United States

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10.1. Highlights

- There was considerable variability in the estimated aquatic carbon fluxes among the five ecoregions in the Western United States, most likely because of differences in precipitation, levels of organic matter inputs, lithology, and topography.
- Inland aquatic ecosystems in the Western United States were both sources and sinks of carbon. Riverine and lacustrine systems were sources of carbon dioxide to the atmosphere, but lacustrine systems also buried carbon in sediments. Total aquatic carbon flux rates were estimated for all five ecoregions in the Western United States using empirical data from 1920 to 2011. The carbon dioxide efflux from lacustrine and riverine systems (combined) was estimated to be 28.1 teragrams of carbon per year (TgC/yr) (confidence interval from 16.8 to 48.7 TgC/yr). The dissolved inorganic and total organic carbon export from riverine systems was estimated to be 7.2 TgC/yr (confidence interval from 5.5 to 8.9 TgC/yr). The carbon burial in sediments of lacustrine systems was estimated to be −2.1 TgC/yr (confidence interval from −1.1 to −3.2 TgC/yr).
- The total aquatic yields (flux rates normalized by land area) for all five western ecoregions were estimated using empirical data from 1920 to 2011. The carbon dioxide efflux yield from riverine systems was estimated to be 14.0 grams of carbon per square meters per year ($gC/m^2/yr$; confidence interval from 6.0 to 17.1 $gC/m^2/yr$) and from lacustrine systems was estimated to be 0.5 $gC/m^2/yr$ (confidence interval from 0.0 to 1.0 $gC/m^2/yr$). The dissolved inorganic and total organic carbon export yield from riverine systems was estimated to be 3.4 $gC/m^2/yr$ (confidence interval from 2.6 to 4.2 $gC/m^2/yr$). The carbon burial yield in sediments of lacustrine systems was estimated to be −1.2 $gC/m^2/yr$ (confidence interval from −0.6 to −1.8 $gC/m^2/yr$).

10.2. Introduction

The aquatic ecosystems discussed in this chapter include streams, rivers, perennial ponds, lakes, and impoundments. Despite the small portion of the land surface area that they cover, lacustrine systems (perennial ponds, lakes, and impoundments) and riverine systems (rivers and streams) can play a major role in the regional and continental-scale carbon budgets (Dean and Gorham, 1998; Cole and others, 2007; Battin and others, 2008). These ecosystems are constantly exchanging carbon with the terrestrial and atmospheric environments, so they can be active sites for transport, transformation, and storage of carbon (Cole and others, 2007; Striegl and others, 2007; Tranvik and others, 2009).

Many processes affect the overall magnitude of fluxes in aquatic ecosystems and determine whether the system is a source or a sink of carbon. Estuarine and lacustrine systems can be sinks of carbon derived from both autochthonous sources (formed at the site of deposition) and allochthonous sources (formed outside of the site of deposition), and riverine systems can transport carbon from upland terrestrial systems to the ocean. Riverine and lacustrine systems, however, can also be supersaturated in carbon dioxide and, therefore, can be sources of carbon to the atmosphere (Kling and others, 1991; Cole and others, 1994, 2007; Aufkenkampe and others, 2011). Some important drivers of carbon fluxes in aquatic ecosystems include (1) timing and magnitude of precipitation and flow, (2) autochthonous and allochthonous carbon production, and (3) physical parameters such as topographic slope, air and water temperature, and seasonality (Michmerhuizen and others, 1996; Tranvik and others, 2009; Einola and others, 2011).

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Due to a shortage of empirical data and the lack of a coupled terrestrial and aquatic modeling framework, carbon fluxes and burial rates in the inland aquatic ecosystems of the Western United States were assessed separately from those of the terrestrial processes (chapters 5 and 9), as depicted in figure 1.2 of chapter 1 of this report. This chapter provides baseline estimates of carbon fluxes from inland aquatic systems that were calculated using empirical data spanning a time period from 1920 to 2011. More specifically, this chapter will provide estimates of (1) coastal export and within-ecoregion transport of both dissolved inorganic carbon (DIC) and total organic carbon (TOC) in riverine systems, (2) gaseous carbon emissions in the form of carbon dioxide from lacustrine and riverine systems, and (3) carbon burial rates in sediments of lacustrine systems. In contrast, the following chapter (chapter 11) supplies both baseline and projected changes in TOC fluxes from 1992 to 2050 to coastal areas and assesses the effect of nutrients and land cover on carbon burial rates in coastal estuaries, which are transition zones between the riverine and the oceanic systems.

The baseline estimates of carbon fluxes in inland aquatic ecosystems presented in this chapter benefited from two strengths in the methodology: (1) the estimated values were all based on large, spatially consistent datasets of water chemistry, flow, and sedimentation rates, and (2) the models made use of updated national hydrographic datasets in the conterminous United States, which improved the accuracy of these broad-scale fluxes. The value of computing these estimates is that it is possible to compare the relative magnitude of all fluxes across ecoregions, where changes in physiography and land-use associated with each ecoregion can have a large effect on carbon storage, transport, and loss to the atmosphere. Additionally, these baseline estimates can be used in an integrated analysis (chapter 12) to estimate an overall regional carbon budget that encompasses all of the ecosystems in the Western United States.

10.3. Input Data and Methods

10.3.1. Lateral Carbon Transport in Riverine Systems

Lateral carbon fluxes in riverine systems included carbon derived from terrestrial ecosystems (forests, wetlands, agricultural lands), groundwater, and in-stream production (photosynthesis) minus the losses from sedimentation and carbon dioxide efflux to the atmosphere. Water-quality data were obtained from the National Water Information Service (NWIS) Web site (U.S. Geological Survey, 2012d). The dissolved inorganic carbon (DIC) concentration was estimated from pH, temperature, and either filtered or unfiltered alkalinity. The estimated total organic carbon (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 (in kilograms per day, kg/day) were estimated from water-quality and daily streamflow data using the U.S. Geological Survey's (USGS's) Load Estimator Model (LOADEST; Runkel and others, 2004). LOADEST is a multiple-regression Adjusted Maximum Likelihood Estimation (AMLE) model which uses measured DIC or TOC concentration values to calibrate a regression between constituent load, streamflow, seasonality, and time (equation 1).

$$\ln LOAD = a_0 + a_1 \ln Q + a_2 \ln Q^2 + a_3 \sin\left(2\prod dtime\right) + a_4 \cos\left(2\prod dtime\right) + a_5 dtime + a_6 dtime^2 + \varepsilon \quad (1)$$

where

$\ln LOAD$ was the natural log of the constituent load (kg/d),

Q was the discharge,

$dtime$ was time in decimal years, $a_0, a_1, \ldots a_n$ were regression coefficients, and

ε was 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. The models that were used to estimate loads for individual USGS stations varied in terms of coefficients and estimates of log load (equation 1), and the program was set to permit LOADEST to select the best of nine models based on Akaike's Information Criterion (Runkel and others, 2004). The estimated loads and their standard errors were used to develop 95-percent confidence intervals for various time periods. The model's performance was examined by reviewing its output, such as the AMLE's coefficient of determination (R^2) values and residuals (model error).

Two different datasets were used to estimate lateral TOC and DIC transport in riverine systems: the Coastal Export Dataset and the Ecoregional Comparison Dataset. The Coastal Export Dataset included data on NWIS sites located just upstream from the point where a river meets the coast or a national border. The coastal export of carbon was important to include in this assessment because the significant amounts of carbon transferred from terrestrial systems by rivers and delivered to coastal areas can help balance the overall regional or continental-scale carbon budgets (Schlesinger and Melack, 1981).

The Colorado River and the Rio Grande deliver carbon to the Gulf of California and western Gulf of Mexico, respectively. Carbon is delivered to the coastal Pacific Ocean from watersheds in California, Oregon, and Washington. The largest watershed is that of the Columbia River. In addition, several large endorheic basins (basins that do not drain to the ocean) exist in the Western United States, the largest of which is the Great Basin. Endorheic basins may contain streams and, although there is lateral carbon movement within them, they do not reach the ocean; therefore, the carbon from those streams was not included in estimates of lateral carbon flux to the coastal ocean. The total exorheic drainage area (basins that do drain to the ocean) in the Western United States was 1.66 million square kilometers (km^2). The Coastal Export Dataset included TOC and DIC export estimates from 36 sites in the Western United States (fig. 10.1*A*).

The carbon export to the ocean was estimated by summing the mean observed carbon export from individual sites and then correcting for the drainage area that was not represented by the watersheds included in the database (Stets and Striegl, 2012). The total carbon export estimate (Total E_C) was calculated using equation 2:

$$\text{Total } E_C = E_{C(IN)} \times \left(A_{TOT}/A_{IN}\right) \quad (2)$$

where

$E_{C(IN)}$ was the carbon export estimated from sites included in the database,

A_{TOT} was the total exorheic drainage area, and

A_{IN} was the total drainage for which lateral flux estimates could be made.

This correction assumed an equivalent areal carbon yield from the remaining (unmeasured) exorheic drainage area. This estimate was performed separately for the Colorado River, Rio Grande, and for basins draining to the coastal Pacific Ocean**.**

Fluxes calculated from streamgages located near coastal waters were assigned to an associated coastal receiving waters' region; however, some rivers within one receiving waters' region often crossed ecoregional boundaries, so they were not necessarily instructive about differences in carbon fluxes among the ecoregions. Because a primary goal of this assessment was to explore ecoregional variability in carbon storage and fluxes across all of the Western United States, a second dataset (the Ecoregional Comparison Dataset) was created to include drainage basins contained entirely within single ecoregions in order to characterize lateral carbon flux. This dataset also included fluxes that were estimated from streamgages located upstream from coastal areas. This dataset included DIC estimates from 333 sites and TOC estimates from 94 sites (fig. 10.1*B*). These estimates were derived from smaller drainage basins ranging in size from 1.1 to 16,000 km^2 and draining a total area of 327,902 km^2.

The methods used for uncertainty analysis were applied in a similar manner for results from both the Coastal Export and Ecoregional Comparison Datasets. Daily carbon fluxes (kg/d) were summed by ecoregion for each representative station's flux within either dataset. Then, daily fluxes were converted to annual fluxes (kilograms per year, kg/yr), and 95-percent confidence intervals were calculated from associated standard errors. Each flux value was connected to a USGS streamgage station, which had an associated drainage area (km^2). The drainage areas for fluxes included in a particular receiving waters' region or ecoregion were summed. The total DIC and TOC yields for an ecoregion (in grams of carbon per square meter per year, $gC/m^2/yr$) were calculated by dividing the summed ecoregional annual fluxes by the summed drainage areas. All of the ecoregion boundaries used in this chapter are consistent with those presented in chapter 1 and are slightly modified from the U.S. Environmental Protection Agency's (EPA's) level II ecoregions (EPA, 1999).

10.3.2. Carbon Dioxide Efflux From Riverine Systems

Three values were required to measure the gas fluxes from aquatic systems: (1) the concentration of dissolved carbon dioxide, (2) the gas transfer velocity (k), and (3) the surface area of the water body. The vertical efflux of carbon dioxide from riverine systems in the Western United States was modeled according to established methods (Butman and Raymond, 2011) and as outlined in equation 3:

$$CO_2 \text{ Flux} = \left(CO_{2\text{-water}} - CO_{2\text{-air}}\right) * kCO_2 * SA \quad (3)$$

where

CO_2 Flux was the total net emission of carbon dioxide from riverine systems of the Western United States (in teragrams of carbon per year, TgC/yr),

$CO_{2\text{-water}}$ was the riverine carbon dioxide concentration (in moles per liter, moles/L),

$CO_{2\text{-air}}$ was the carbon dioxide concentration in the atmosphere (in moles/L),

kCO_2 was the gas transfer velocity of carbon dioxide across the air-water interface (in meters per second, m/s), and

SA was the riverine surface area (in square meters, m^2).

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

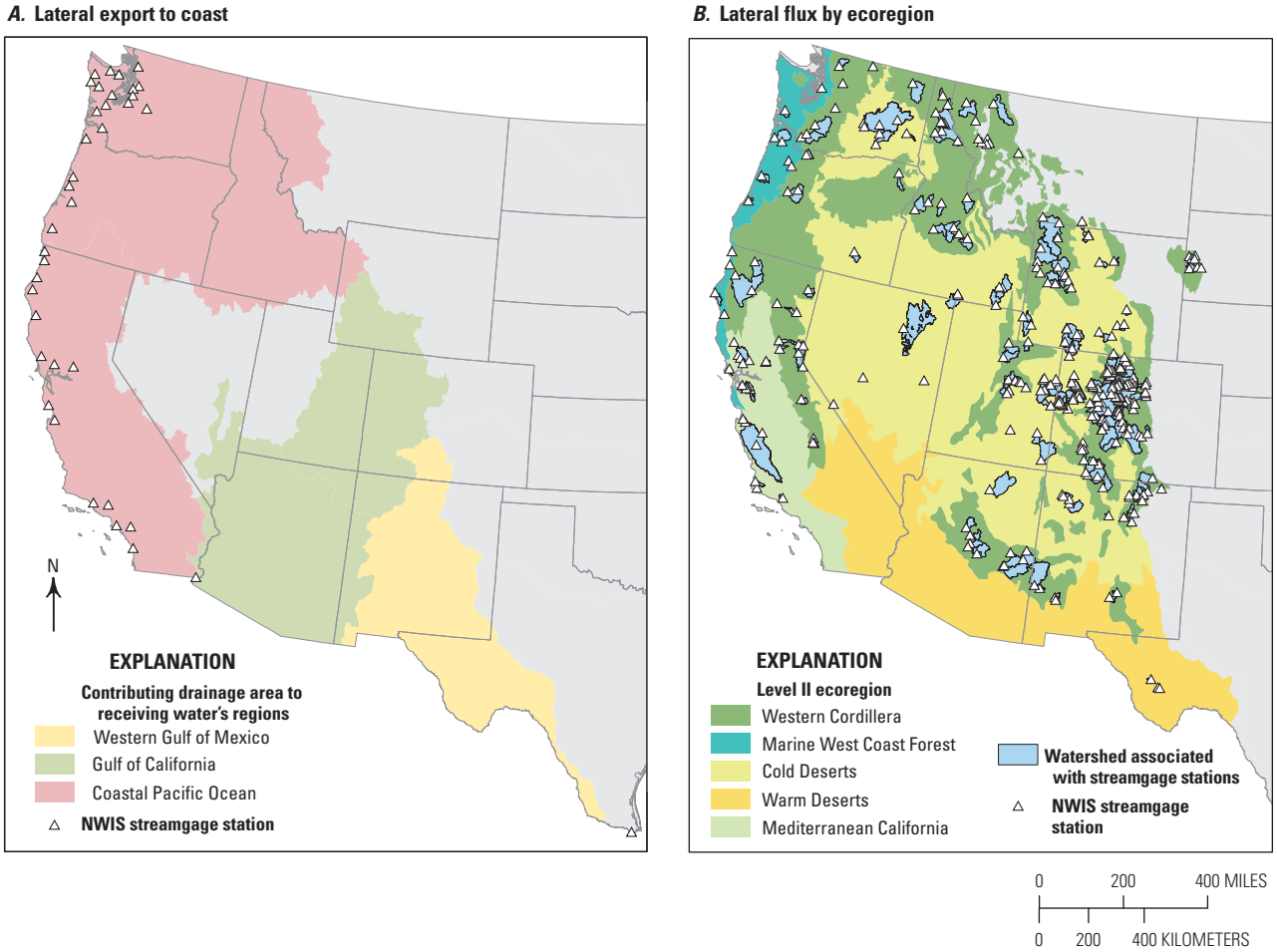

Figure 10.1. Maps showing the locations of the National Water Information System (NWIS) streamgage stations and associated drainage areas. *A*, Stations included in the Coastal Export Dataset. *B*, Stations included in the Ecoregional Comparison Dataset.

The dissolved carbon dioxide concentrations ($CO_{2\text{-water}}$) were estimated from riverine alkalinity data available through NWIS using the CO2SYS program[5] (van Heuven and others, 2009). CO2SYS linked parameters such as temperature, pH, and alkalinity to estimate the dissolved carbon dioxide concentrations by incorporating disassociation constants for carbonic acid (H_2CO_3) into its values. Disassociation constants are mathematical values that describe the tendency of a large molecule such as carbonic acid (H_2CO_3) to disassociate into smaller molecules such as bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), and carbon dioxide (CO_2) in an aqueous environment. The disassociation constants used in the CO2SYS equations for this assessment were from Millero (1979).

Water-chemistry data were collected from the late 1920s through 2011, and daily measurements of pH paired with temperature and alkalinity measurements were used to estimate dissolved carbon dioxide. For the five ecoregions in the Western United States, 1,545 USGS streamgaging-station locations had an adequate chemistry record, and their data were used for the carbon dioxide efflux estimate (fig. 10.2*B*). A minimum of 12 sampling dates was required for inclusion in this analysis. A total of 101,852 daily chemical measurements was identified. The concentration of carbon dioxide in the atmosphere ($CO_{2\text{-air}}$) was assumed to be constant at 390 ppm for all of the ecoregions in the Western United States in equation 3.

The gas transfer velocity (kCO_2), which is the rate of exchange of carbon dioxide across the air-water interface, was based on the physical parameters of stream slope and water velocity (Melching and Flores, 1999; Raymond and others, 2012). The average slope was derived from the NHDPlus datasets (Horizon Systems Corporation, 2005) for each stream order within each ecoregion in the Western United States. The average stream velocity estimates were based on hydraulic geometry parameters for each stream order. The stream discharge (volume of water per unit of time, in cubic

[5] Mathworks, Inc., Natick, Mass.

meters per second, m^3/s) was dependent on the width (m) and depth (m) of the stream channel as well as the velocity of the water moving within the stream (meters per second, m/s) (Leopold and Maddock, 1953; Park, 1977). The stream surface area (SA) in square meters (m^2) was calculated as the product of the average width and total length of the stream by stream order.

Error propagation and uncertainty analyses were performed for each component of equation 3. A bootstrapping technique outlined in Efron and Tibshirani (1993) and Butman and Raymond (2011) was used to estimate error. Bootstrap with replacement ($\alpha = 0.05$) was run for 1,000 iterations to calculate 95-percent confidence intervals for the concentrations of pCO_2 for each stream order within an ecoregion. Similarly, bootstrap with replacement was used 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 both the stream surface area and gas transfer velocity (R Development Core Team, 2008). The overall bias associated with the estimates of pCO_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 flux (TgC/yr) from riverine surfaces (equation 3). The 5^{th} to 95^{th} confidence intervals derived from the bootstrapping discussed above were used to constrain the Monte Carlo simulation for each parameter of equation 3. The total flux calculation was replicated 1,000 times. This approach was considered to be conservative as 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 efflux.

All of the estimates for the total carbon flux within an ecoregion were presented with the 5th and 95th confidence intervals derived from the Monte Carlo simulation. By using this conservative approach, the range of estimates generally had a high bias because of a slight positive skew in the distribution of pCO_2 concentration within a stream order and ecoregion. The mean concentrations were chosen over the median values because the broader spatial representation was better approximated by incorporating mean values in the Western United States. All of the estimates derived from the Monte Carlo simulation were adjusted to account for monthly temperatures below freezing because it was assumed that riverine efflux did not occur when monthly temperatures averaged below 0°C. This adjustment reduced the estimated efflux measurements for the Western Cordillera and the Cold Deserts ecoregions by 25 percent and 19 percent, respectively.

10.3.3. Carbon Dioxide Efflux From Lacustrine Systems

Water-chemistry data were obtained from the EPA's 2007 National Lakes Assessment (NLA; EPA, 2009a). 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 (EPA, 2009a). Of the 68,223 lakes and reservoirs in the conterminous United States, 1,028 met those criteria. Of those, 252 were located in the Western United States; their locations are shown in figure 10.2*C*.

Sampling took place during the summer of 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. Twenty-two lakes were sampled twice, and these replicates helped to increase the sample data accuracy. For the lakes that were sampled twice, the data were averaged. The data were assigned to one of the five ecoregions in the Western United States. The number of lakes ranged from 12 to 166 per ecoregion, or one lake for every 38,700 to 2,300 km^2 of total area (including both land and water).

Various biological, physical, and chemical indicators were measured during the NLA (EPA, 2009a), and only a subset of water-chemistry and physical data was used in this assessment: acid-neutralizing capacity (ANC, assumed to be equal to alkalinity), pH, temperature, and dissolved organic carbon (DOC). The final working dataset represented 260 observations from 245 sites.

The estimated carbon dioxide flux from lacustrine systems was calculated using the general equation 3. The estimated dissolved carbon dioxide (CO_{2water}) was computed using the equilibrium geochemical model PHREEQC (Parkhurst and Appelo, 1999). This model is similar to CO2SYS in that parameters such as water, temperature, pH, and alkalinity were used to estimate carbon dioxide concentrations.

The gas transfer velocity (k) for lacustrine systems is largely a function of windspeed (m/s) Cole and Caraco (1998). The estimated mean summer (June to September) wind speeds for each ecoregion were determined from the National Aeronautics and Space Administration's (NASA's) surface meteorology and solar energy data (NASA, 2012; Cory P. McDonald, USGS, unpub. data, 2012). The surface areas of lakes and reservoirs were tabulated for each ecoregion, as in McDonald and others (2012).

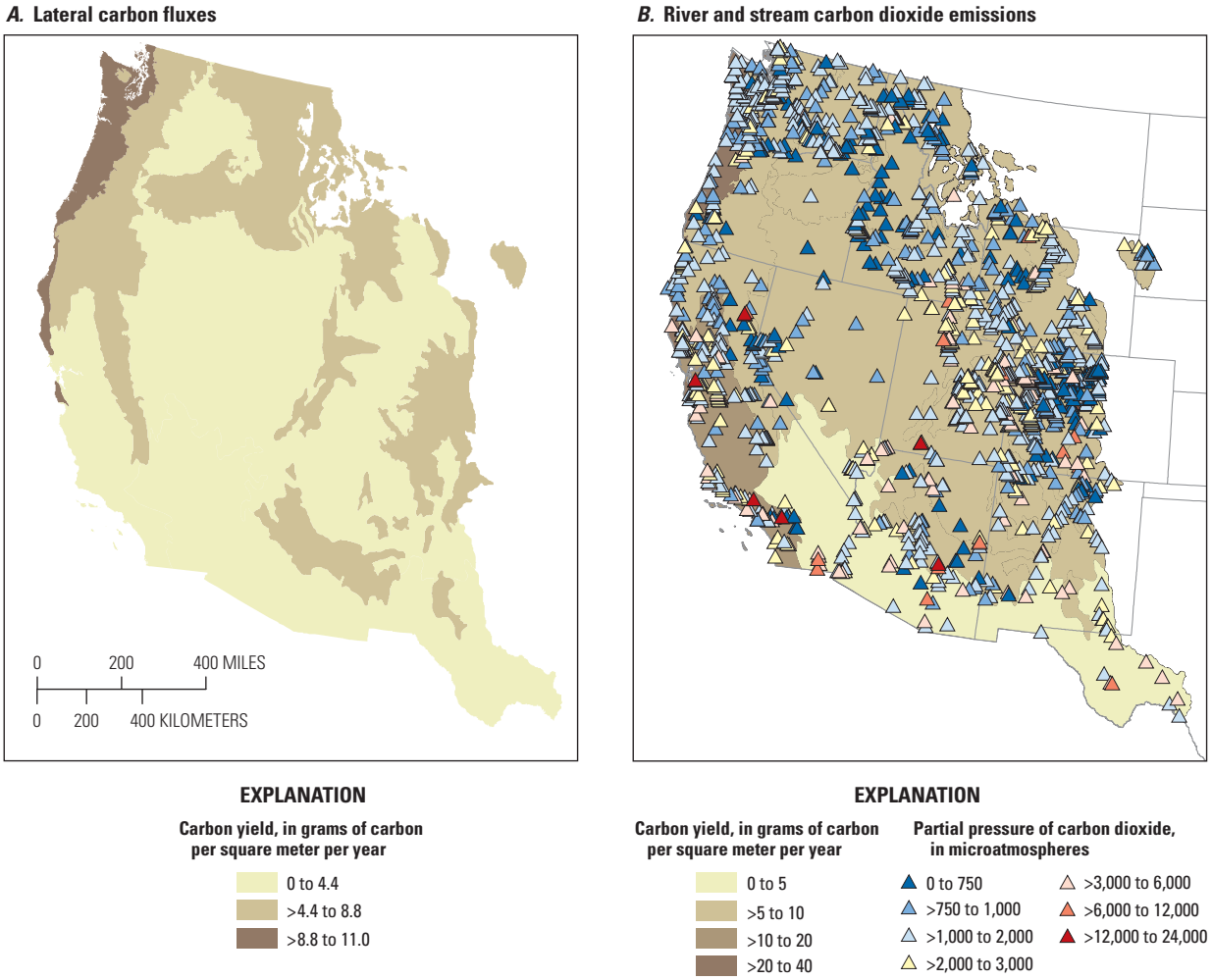

Figure 10.2. Maps showing the estimated relative magnitude of carbon yields, in grams of carbon per square meter per year ($gC/m^2/yr$). *A*, Lateral carbon fluxes in riverine systems. *B,* Carbon dioxide emissions from riverine systems. *C*, Carbon dioxide emissions from lacustrine systems. *D*, Carbon burial rates in lacustrine systems. Parts *B* to *D* show locations of calibrated sample data, and parts *B* and *C* also indicate the estimated relative magnitude of the partial pressure of carbon dioxide (pCO_2) concentrations at the sampling locations.

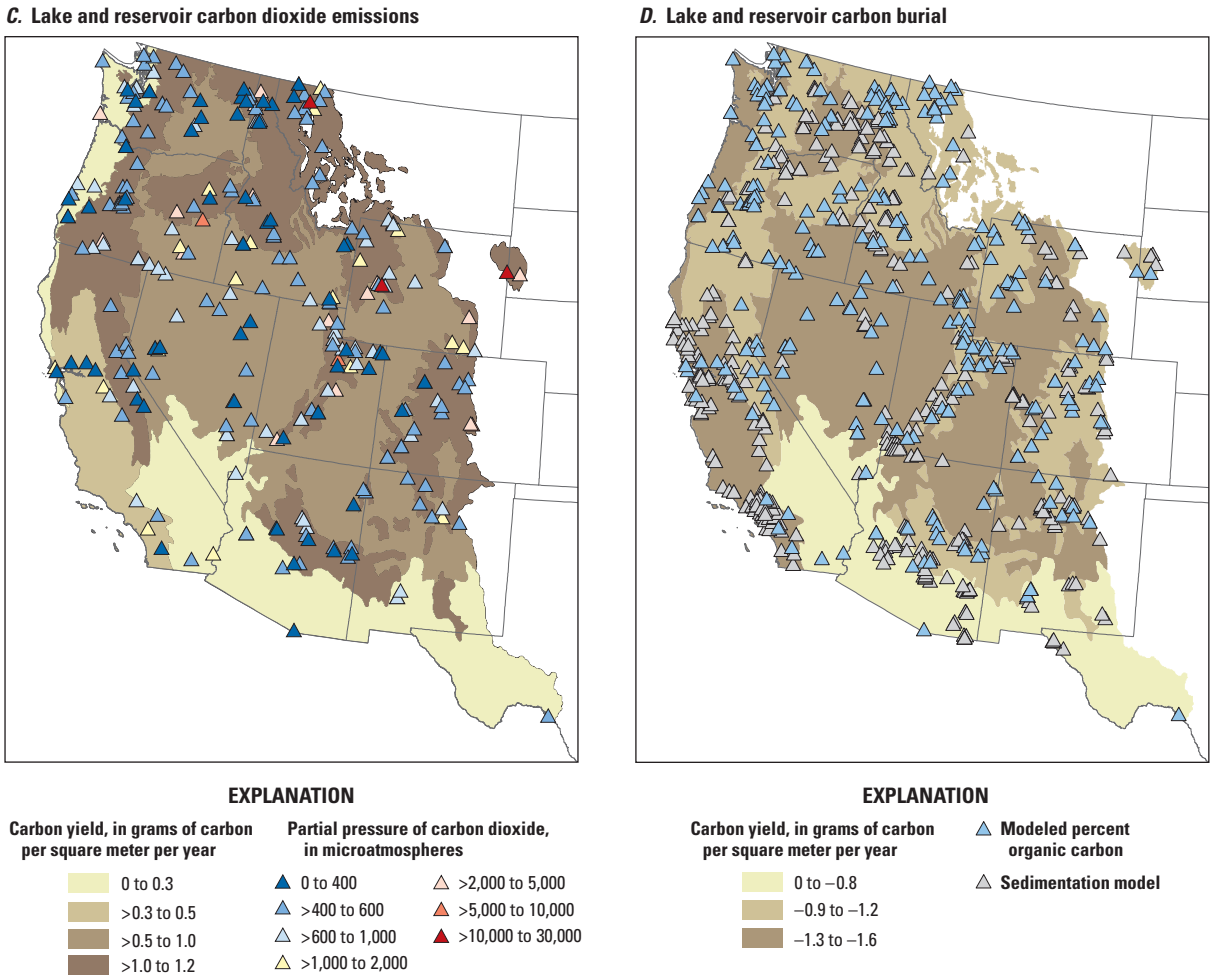

Figure 10.2.—Continued

Many of the parameters involved in these calculations violated normality assumptions; therefore, nonparametric confidence intervals (95 percent) 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 were likely to be systematic. For the two ecoregions with extended periods of below-freezing air temperatures (the Western Cordillera and the Cold Deserts), the lower confidence interval was adjusted by assuming that carbon dioxide only degasses (at the estimated rate) during the ice-free season. This approach was conservative because carbon dioxide stored under ice is released when the ice melts.

10.3.4. Carbon Burial in Lacustrine Systems

Carbon burial in lacustrine systems is a function of sedimentation rates, carbon concentrations in lacustrine sediments, and the areal extent of lacustrine systems:

$$C_{burial} = SedRt * C_{conc} * SA_{WB} * 10^{-12} \quad (4)$$

where

C_{burial} was the carbon burial rate (in TgC/yr),

SedRt was the sedimentation rate (in $gC/m^2/yr$),

C_{conc} was the concentration of carbon in sediments (in percent by dry weight),

SA_{WB} was the surface area of the water body (in m^2), and

10^{-12} was a conversion factor to convert from grams to teragrams.

Data on sedimentation rates and on 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. 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 a national-scale synoptic survey on the water quality of lacustrine systems.

The areal extents of lacustrine systems were derived from the high-resolution (1:24,000) USGS National Hydrography Dataset (NHD; USGS, 2012c). Both sedimentation rates in lakes and carbon concentrations in lake sediments are usually 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 visited during the 2007 NLA (EPA, 2009a) indicated that this classification scheme was correct 80 percent of the time; however, misclassification rates might have been higher for small water bodies (≤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; Advisory Committee on Water Information, Subcommittee on Sedimentation, 2012), which included sedimentation-rate data on over 1,800 georeferenced reservoirs in the United States (Mixon and others, 2008; Ackerman and others, 2009). The sedimentation rates in the RESSED database were estimated from repeat bathymetric surveys and were expressed in acre feet per year to facilitate the estimation of storage losses. 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 GIS analysis was performed to quantify these characteristics for each hydrologic unit (represented by a 12-digit hydrologic unit code, or 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 (coefficient of determination, $R^2=0.94$). The values for the net contributing area, however, 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 explanatory variables. The explanatory 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 ≤0.1. The multicollinearity among explanatory variables was evaluated using the variance inflation factor ($1/1–R^2$) (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 of the reservoirs in the NHD. The standard error of the equation was used to calculate uncertainty with 95-percent confidence intervals for the predicted sedimentation rates for sites in the validation dataset.

A national dataset of lake sedimentation rates does not exist; therefore, sedimentation rates were estimated on the basis of data in peer-reviewed literature. Lake sedimentation rates have been calculated for over 80 lakes around the world using ^{210}Pb and ^{137}Cs 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 North America, Europe, Africa, Asia, New Zealand, and Antarctica. The data were compiled and a statistical analysis was performed to characterize a probability distribution function (pdf) of lake sedimentation rates. A sedimentation rate was assigned to each lake in the NHD 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. Each of these values was used to calculate a carbon burial rate using equation 4, providing a range of carbon burial estimates for each lake in the NHD. Uncertainty at the 95-percent confidence level was calculated as 2×F-pseudosigma, which is a nonparametric equivalent to the standard deviation when sample data have a normal distribution.

Carbon concentrations were measured on sediment samples collected from 697 water bodies during the 2007 NLA (EPA, 2009a). 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 Western United States. Uncertainty and model performance were evaluated as in the reservoir sedimentation-rate analysis.

10.4. Results

10.4.1. Lateral Carbon Transport in Riverine Systems

The total carbon export from exorheic basins, calculated using the Coastal Export Dataset, was estimated to be 7.2 (ranging from 5.5 to 8.9) TgC/yr (table 10.1), with more than 75 percent of the export occurring as DIC. The carbon exported to the western Gulf of Mexico and the Gulf of California was a small proportion of this total, estimated at approximately 0.1 TgC/yr (table 10.1); the remainder, an estimated 7.1 TgC/yr, was exported to the coastal Pacific Ocean (table 10.1). The Columbia River exported the highest carbon load in this region at an estimated 3.1 TgC/yr. The Klamath River, which had the next highest load, carried approximately one-tenth the carbon load of the Columbia River at an estimated 0.32 TgC/yr.

Table 10.1. Estimated carbon exports, carbon yields (fluxes normalized to watershed areas), and percentages of the total export as dissolved inorganic carbon organized by the three main receiving waters' regions in the Western United States.

[Sites represent U.S. Geological Survey streamgaging stations for which data were available to calculate estimated carbon fluxes from exorheic basins. The 95-percent confidence intervals for the yields and exports are given in the parentheses. The estimated total exports and yields were calculated by summing the dissolved inorganic carbon (DIC) and total organic carbon (TOC). $gC/m^2/yr$, grams of carbon per square meter per year; TgC/yr, teragrams of carbon per year]

Receiving water's region	Number of sites	Estimated total export (95-percent confidence interval) (TgC/yr)	Estimated total yield (95-percent confidence interval) ($gC/m^2/yr$)	Estimated flux as dissolved inorganic carbon (percent of total export)
Coastal Pacific Ocean	35	7.10 (5.42, 8.78)	6.29 (5.90, 6.68)	77
Western Gulf of Mexico[1]	1	0.020 (0.011, 0.028)	0.06 (0.05, 0.07)	79
Gulf of California[2]	1	0.076 (0.074, 0.079)	0.12 (0.10, 0.13)	93
All regions	37	7.20 (5.52, 8.88)	3.38 (2.59, 4.17)	77

[1] Rio Grande, partially drains the South-Central Semi-Arid Prairies ecoregion of the Great Plains region.

[2] Colorado River.

The estimated carbon yields and fluxes, calculated using the Ecoregional Comparison Dataset, were highest in the Marine West Coast Forest ecoregion and lowest in the Warm Deserts ecoregion (table 10.2; fig. 10.2*A*). The Marine West Coast Forest ecoregion had a relatively high estimated total carbon yield, but the estimated total export was low because of the ecoregion's small area, which is approximately 10 times smaller than the Western Cordillera ecoregion. Conversely, the Cold Deserts had a relatively high estimated export value because of its extensive land surface area, which is the largest in the Western United States at 1,055,715 km^2. The estimated dissolved inorganic carbon was between 65 and 75 percent of the estimated total carbon export from all regions.

Much of the variability in ecoregional estimates can be explained by differences in the mean runoff and in mean DIC and TOC concentrations. There was substantial variability in the mean runoff among the ecoregions (ranging from an estimated 14 to 1,259 millimeters per year, or mm/yr). The greatest mean runoff was estimated in the Marine West Coast Forest and the Western Cordillera ecoregions and the smallest amount was in the Warm Deserts ecoregion. For each of the ecoregions, the estimated mean DIC concentrations were higher than the estimated mean TOC concentrations, but the estimated mean DIC concentrations in the Cold Deserts ecoregion (62.4 milligrams per liter, or mg/L) were nearly eight times higher than the estimated mean DIC concentrations in the Marine West Coast Forest ecoregion (8.7 mg/L).

10.4.2. Carbon Dioxide Efflux From Riverine Systems

The estimated mean concentration of dissolved carbon dioxide in riverine systems across the Western United States exceeded atmospheric concentrations, indicating that these ecosystems were sources of carbon to the atmosphere. The estimated mean pCO_2 concentration was greatest in the Warm Deserts at 2,391 microatmospheres (µatm; 6.1 times greater than the atmospheric concentrations of carbon dioxide) and smallest in the Western Cordillera at 1,357 µatm (3.4 times greater than the atmospheric concentrations of carbon dioxide). The estimated mean pCO_2 for all five ecoregions combined was 1,893 µatm (3.4 times greater than the atmospheric concentrations of carbon dioxide) (fig. 10.2*C*).

Stream surface areas ranged from 365 km^2 in the Mediterranean California ecoregion to 2,336 km^2 in the Western Cordillera (table 10.3), which was from 0.22 to 0.27 percent of the total area of the ecoregion, respectively. Although its total area was small, the percentage of area covered by riverine systems in the Marine West Coast Forest was the highest of all the ecoregions at 0.73 percent. The total stream surface area for the Western United States region was 6,076 km^2, which was 0.23 percent of the region's area.

Table 10.2. Estimated carbon fluxes, yields (fluxes normalized to watershed areas), and percentages of total flux as dissolved inorganic carbon from riverine systems in the Western United States.

[Sites represent U.S. Geological Survey streamgaging stations in both endorheic and exorheic basins for which data were available to calculate estimated dissolved inorganic carbon (DIC) and total organic carbon (TOC) fluxes, respectively. The 95-percent confidence intervals for the yields and exports are presented in parentheses. The estimated total fluxes and yields were calculated by summing the estimated DIC and TOC. An asterisk (*) indicates DIC values only. $gC/m^2/yr$, grams of carbon per square meter per year; NA, not available; TgC/yr, teragrams of carbon per year]

Ecoregion	Number of sites (DIC fluxes, TOC fluxes)	Estimated total flux (95-percent confidence interval) (TgC/yr)	Estimated total yield (95-percent confidence interval) ($gC/m^2/yr$)	Estimated flux as dissoved inorganic carbon (percent of total flux)
Western Cordillera	224, 61	4.57 (4.15, 5.09)	5.23 (4.76, 5.83)	74
Marine West Coast Forest	11, 6	0.9 (0.68, 0.1.38)	11.0 (7.97, 16.24)	66
Cold Deserts	72, 23	2.41 (2.00, 2.9)	2.29 (1.9, 2.75)	80
Warm Deserts	3, NA	1.00 (0.85, 1.18)*	2.17 (1.83, 2.55)*	NA
Mediterranean California	23, 4	0.43 (0.25, 0.86)	2.61 (1.54, 5.20)	75
Western United States (total)	333, 94	9.35 (7.93, 11.41)	3.64 (3.18, 4.33)	

Table 10.3. Estimated vertical effluxes and yields of carbon dioxide from riverine systems in the five ecoregions of the Western United States.

[Sites are U.S. Geological Survey streamgaging stations for which data were available to calculate the estimated pCO_2. Errors associated with both the total flux and areal flux estimates are presented in parentheses and represent the 5th and 95th percentiles derived from Monte Carlo simulation. Estimated carbon yields were calculated by dividing the estimated total flux by the ecoregion area. $gC/m^2/yr$, grams of carbon per square meter per year; km^2, square kilometers; TgC/yr, teragrams of carbon per year]

Ecoregion	Number of sites	Stream area (km^2)	Estimated total flux (5th and 95th percentiles) (TgC/yr)	Estimated total yield (5th and 95th percentiles) ($gC/m^2/yr$)
Western Cordillera	518	2,336	11.76 (7.3, 21.0)	9.87 (8.4, 24.1)
Marine West Coast Forest	151	619	4.04 (2.0, 7.37)	35.72 (23.7, 86.5)
Cold Deserts	607	2,305	6.15 (4.1, 9.1)	7.16 (3.9, 8.7)
Warm Deserts	107	451	1.53 (0.8, 2.9)	3.57 (1.8, 6.1)
Mediterranean California	162	365	2.65 (1.5, 5.0)	17.1 (8.8, 30.5)
Western United States (total)	1,545	6,076	26.13 (15.7, 45.4)	14.03 (6.0, 17.1)

The estimated total riverine vertical carbon efflux for the Western United States was converted to carbon dioxide equivalent, which produced a value of 95.6 teragrams of carbon dioxide equivalent per year ($TgCO_{2\text{-}eq}/yr$; confidence interval from 57.0 to 166.3 $TgCO_{2\text{-}eq}/yr$). The estimated carbon efflux ranged from a high of 43.1 $TgCO_{2\text{-}eq}/yr$ (confidence interval from 26.7 to 77.0 $TgCO_{2\text{-}eq}/yr$) in the Western Cordillera to a low of 5.5 $TgCO_{2\text{-}eq}/yr$ (confidence interval from 2.9 to 10.6 $TgCO_{2\text{-}eq}/yr$) in the Warm Deserts (table 10.3). The estimated riverine efflux for the Western United States on a per-unit-of-area basis was 14.0 $gC/m^2/yr$ (confidence interval from 7.2 to 20.63 $gC/m^2/yr$); on an ecoregional basis, the estimated efflux ranged from 3.6 $gC/m^2/yr$ (confidence interval from 1.8 to 6.1 $gC/m^2/yr$) in the Warm Deserts to 35.7 $gC/m^2/yr$ (confidence interval from 23.7 to 86.6 $gC/m^2/yr$) in the Marine West Coast Forest.

10.4.3. Carbon Dioxide Efflux from Lacustrine Systems

The estimated mean concentration of pCO_2 in lacustrine systems of the Western United States was 733 µatm (fig. 10.2*C*), which was greater than the atmospheric concentrations for all of the ecoregions; this estimated mean pCO_2 indicated that the lakes generally were sources of carbon to the atmosphere. The estimated mean pCO_2 was greatest in the Western Cordillera at 1,036 µatm (2.7 times greater than the atmospheric concentration of carbon) and smallest in the Marine West Coast Forest at 599 µatm (1.5 times greater than the atmospheric concentration of carbon).

The estimated flux of carbon dioxide across the air-water interface was primarily determined by the gradient between the dissolved and atmospheric concentrations of carbon. The greatest flux was estimated for the Western Cordillera at 106 $gC/m^2/yr$ (or 389 $gCO_{2\text{-}eq}/m^2/yr$), and the smallest flux was estimated for the Marine West Coast Forest at 36.5 $gC/m^2/yr$ (or 134 $gCO_{2\text{-}eq}/m^2/yr$). These fluxes were given as the mass flow per unit of area of the water surface. The estimated mean flux across the air-water interface for all of the ecoregions was 58 grams of carbon per square meter per day ($gC/m^2/d$), or 219 grams of carbon dioxide equivalent per square meter per day ($gCO_{2\text{-}eq}/m^2/d$). The estimated gas transfer velocity was less variable than the estimated pCO_2 among all of the ecoregions—smallest in Western Cordillera (0.93 meters per day, or m/d) and greatest in the Warm Deserts (1.22 m/d).

The ecoregional estimates of total annual carbon dioxide efflux from lacustrine systems (table 10.4) ranged from 0.02 TgC/yr in the Marine West Coast Forest to 1.0 TgC/yr in the Western Cordillera, or from 0.1 to 3.6 $TgCO_{2\text{-}eq}/yr$, respectively. The total carbon dioxide efflux from the Western United States was estimated to be 2.1 TgC/yr (95-percent confidence interval of 1.1 to 3.3 TgC/yr), or 7.6 $TgCO_{2\text{-}eq}/yr$. The estimated ecoregional efflux values were directly related to the surface area of the lacustrine systems (table 10.4), which varied among the ecoregions, partially because of differences in regional morphology and climate but mainly because of differences in the size of the ecoregions.

Table 10.4. Estimated vertical flux of carbon dioxide from lacustrine systems in the five ecoregions of the Western United States.

[Sites are from the 2007 National Lakes Assessment (EPA, 2009a). The data from the 2007 NLA were used in the calculation of pCO_2. Errors associated with both the estimated total flux and yield are presented in parentheses. They represent the bootstrapped 5th and 95th confidence intervals. Estimated carbon yields were calculated by dividing the estimated total flux by the ecoregion area. $gC/m^2/yr$, grams of carbon per square meter per year; km^2, square kilometers; TgC/yr, teragrams of carbon per year]

Ecoregion	Number of sites	Lake and reservoir area (km^2)	Estimated total flux (5th and 95th confidence intervals) (TgC/yr)	Estimated total yield (5th and 95th confidence intervals) ($gC/m^2/yr$)
Western Cordillera	137	9,410	0.99 (0.63, 1.28)	1.15 (0.73, 1.49)
Marine West Coast Forest	18	689	0.02 (0.00, 0.08)	0.29 (–0.01, 1.00)
Cold Deserts	68	13,500	0.88 (0.43, 1.54)	0.84 (0.41, 1.47)
Warm Deserts	10	2,630	0.12 (0.06, 0.17)	0.25 (0.14, 0.37)
Mediterranean California	12	1910	0.07 (0.00, 0.16)	0.46 (0.00, 1.02)
Western United States (total)	245	28,139	2.08 (1.13, 3.25)	0.80 (0.43, 1.24)

In order to facilitate a direct comparison between lake and reservoir gas fluxes, lateral carbon transport, carbon burial, and terrestrial processes, the estimated carbon dioxide flux values were normalized to the total land surface area in each ecoregion to provide the carbon yield (table 10.4, fig. 10.2*C*). The estimated carbon yields ranged from 0.3 $gC/m^2/yr$ in the Warm Deserts ecoregion to 1.1 $gC/m^2/yr$ in the Western Cordillera ecoregon. The estimated mean carbon yield (expressed as carbon dioxide efflux per unit of area) from lacustrine systems in the Western United States was 0.6 $gC/m^2/yr$.

10.4.4. Carbon Burial in Lacustrine Systems

The estimated total annual carbon burial rate in lacustrine systems of the Western United States was −2.42 TgC/yr and varied substantially among ecoregions (table 10.5; fig. 10.2*D*). The Western Cordillera ecoregion had the highest estimated carbon burial rate of −1.14 TgC/yr (confidence interval from –1.71 to –0.57), and the Marine West Coast Forest ecoregion had the lowest estimated carbon burial rate of −0.10 TgC/yr (confidence interval from –0.15 to –0.05). The estimated carbon yield in lacustrine systems, normalized by ecoregion area, was −1.2 $gC/m^2/yr$ (confidence interval from –1.8 to −0.6 $gC/m^2/yr$). The estimated yields ranged from −0.4 $gC/m^2/yr$ (confidence interval from −0.8 to −0.3 $gC/m^2/yr$) in the Warm Deserts ecoregion to −1.3 $gC/m^2/yr$ (confidence interval from −2.0 to −0.7 $gC/m^2/yr$) in the Marine West Coast Forest ecoregion.

The estimated sedimentation rates in reservoirs in the Western United States ranged from 8,622 to 10,068 $gC/m^2/yr$ (TgC/yr normalized to the area of the water body). The lowest estimated rates were in the Warm Deserts ecoregion, and the highest estimated rates were in the Western Cordillera and Cold Deserts ecoregions. The estimated sedimentation rates for lakes compiled from the literature followed an exponential distribution, with an abundance of lakes having low rates and relatively few having high rates. The estimated mean mass sedimentation rates in the lakes were much lower than those in reservoirs, with the mean lake sedimentation rate estimated to be 2,488 $gC/m^2/yr$.

The carbon concentrations in lacustrine sediments varied substantially among the ecoregions of the Western United States. Sediment concentrations were highest in the Marine West Coast Forest ecoregion (11.4 percent) and relatively low in the Warm Deserts ecoregion (5.0 percent). The specific carbon burial rates (rates normalized to the area of a water body) indicated the intensity of carbon cycling in lacustrine systems. The estimated specific carbon burial rates (per unit of area) were highest in the Marine West Coast Forest at −147 $gC/m^2/yr$ (confidence interval from –222 to –72) and lowest in the Warm Deserts at −84 $gC/m^2/yr$ (confidence interval from –126 to –42).

Overall, the estimated specific carbon burial rates were strongly correlated with the estimated amounts of soil organic carbon (SOC, in gC/m^2) near the water bodies; the R^2 value between estimated carbon burial rates in reservoirs and estimated SOC was 0.96 (p-value=0.01), and the R^2 value between estimated carbon burial rates in lakes and estimated SOC was 0.99 (p-value=<0.001). These results

Table 10.5. Estimated carbon burial rates in lacustrine sediments in the five ecoregions of the Western United States.

[Sites are from the 2007 National Lakes Assessment dataset (EPA, 2009a), which was used to estimate carbon concentrations in sediment. The 95-percent confidence intervals associated with the estimated total fluxes and yields are presented in parentheses. Estimated carbon yields were calculated by dividing the estimated total flux divided by the ecoregion area. $gC/m^2/yr$, grams of carbon per square meter per year; TgC/yr, teragrams of carbon per year]

Ecoregion	Number of sites	Estimated total flux (95-percent confidence interval) (TgC/yr)	Estimated total yield (95-percent confidence interval) ($gC/m^2/yr$)
Western Cordillera	71	−1.14 (−1.82, −0.57)	−1.1 (−1.8, −0.6)
Marine West Coast Forest	10	−0.10 (−0.15, −0.05)	−1.3 (−2.0, −0.7)
Cold Deserts	46	−0.74 (−1.07, −0.36)	−1.3 (−2.0, −0.7)
Warm Deserts	7	−0.20 (−0.26, −0.09)	−0.4 (−0.8, −0.3)
Mediterranean California	4	−0.24 (−0.35, −0.12)	−1.3 (−2.0, −0.7)
Western United States (total)	138	−2.42 (−3.65, −1.22)	−1.2 (−1.8, −0.6)

indicate strong connections between SOC, lacustrine sediment carbon concentrations, and carbon burial rates in lacustrine systems. Of the five ecoregions in the Western United States, the Marine West Coast Forest had the highest estimated SOC (1,824 gC/m^2) and the highest estimated specific carbon burial rates (−147 $gC/m^2/yr$). The Warm Deserts had the lowest estimated SOC (246 gC/m^2) and lowest estimated specific carbon burial rates (−84 $gC/m^2/yr$). In reservoirs, the estimated specific carbon burial rates were positively correlated to the prevalence of forests in nearby areas ($R^2=0.79$, p-value$=0.04$); in lakes, the specific carbon burial rates were more strongly associated with wetlands ($R^2=0.78$, p-value$=0.05$).

10.5. Discussion

10.5.1. Coastal Export, Lateral Transport, and Carbon Dioxide Efflux From Riverine Systems

The coastal export values represented the estimated amount of carbon that exited the terrestrial landscape and was delivered to the coast. This carbon could potentially have been stored in the ocean or could have contributed to coastal ocean ecosystem processing. The Gulf of California and western Gulf of Mexico, both located adjacent to the drier regions of the Western United States, received waters from one dominant watershed, either the Colorado River or Rio Grande, respectively. The Pacific Northwest, however, experienced much higher precipitation, and many more river basins (about 30) delivered carbon to the receiving waters of the Pacific Ocean; in fact, the highest proportion of land area represented as riverine systems (0.73 percent) was found in the Marine West Coast Forest ecoregion, which was more than double the surface area represented by riverine systems in the other remaining ecoregions. One of the defining characteristics of the Marine West Coast Forest was the high rate of precipitation, and higher annual precipitation increased the transfer of carbon, in either organic or inorganic forms, from the terrestrial environment to streams and rivers (Omernik and Bailey, 1997).

Riverine systems in the Marine West Coast Forest delivered more carbon at a higher estimated rate per unit of area than either the Rio Grande or the Colorado River. Despite the geographic prominence of large river basins, such as the Colorado River and the Rio Grande, the large annual runoff in the Marine West Coast Forest caused this ecoregion to dominate carbon delivery such that even much smaller rivers with coastal endpoints in this ecoregion were important sources of carbon export to coastal areas. These rivers included (1) the Eel River in Scotia, California (drainage$=8{,}031$ km^2), (2) the Elder River near Branscomb, California (drainage$=17$ km^2), and (3) the Queets River near Clearwater, Washington (drainage$=1{,}148$ km^2). The Rio Grande, despite its large drainage size, had an annual runoff of only 1 mm/yr compared with annual runoff exceeding 3,000 mm/yr just from several rivers in coastal Washington.

The coastal carbon yields were defined as the amounts of carbon remaining after balancing the inputs and outputs within a watershed, which ranged in area between about 20 and 650,000 km^2. Many of the larger watersheds crossed ecoregional boundaries; for example, the Snake River's headwaters are in the Western Cordillera, but its flow path traverses the Cold Deserts twice before reaching the mainstem portion of the Columbia River, which ultimately meets

the Pacific Ocean in the Marine West Coast Forest. The headwaters of many of the larger rivers (such as the Rogue, Klamath, and Sacramento Rivers) that contribute to coastal fluxes in the Mediterranean California and Marine West Coast Forest ecoregions are located in the uplands of the Western Cordillera ecoregion. This spatial mismatch is important to consider in terms of ecoregional carbon budgets because rivers are not passive transporters of material, and much of the carbon from the headwater source may be transformed or lost before it reaches the ocean.

In order to estimate meaningful ecoregional lateral flux values, the Ecoregional Comparison Dataset included data only from watersheds that fell entirely within the ecoregional boundaries. The benefit of this approach was that the entire watershed, and therefore both the riverine carbon sources and sinks, were defined by the ecoregion's unique characteristics. By using this approach, the differences in flux based on climate, vegetation, and topography could be more easily discerned. This approach skewed the dataset toward smaller watersheds and rivers, but the larger watersheds of the Western United States—in particular, the Columbia River, the Colorado River, and the Rio Grande—were represented in the coastal export section well.

Both the estimated coastal export and ecoregional lateral-flux values demonstrated that runoff or precipitation was a major driver in the variability of both DIC and TOC yields (Amiotte-Suchet and Probst, 1995; Raymond and Oh, 2007; Hartmann, 2009). The two sets of results also highlighted the dominant role of DIC in total carbon export to the coast, as DIC was between 77 to 93 percent of all carbon exports and was between 65 and 80 percent of ecoregional lateral fluxes. In contrast, recent global carbon studies have suggested that the global TOC and DIC export was nearly equal (Meybeck, 1982; Amiotte-Suchet and Probst, 1995). The higher proportion of DIC in the Western United States reported in this study may have had several causes: (1) a large portion of the ecoregions were in dry and arid environments, so there was little contribution of organic matter to overall fluxes; (2) the presence of easily weathered carbonate bedrock contributed unusually high amounts of DIC to the streams; and (3) the high temperatures and the prevalence of dams and reservoirs increased the residence time of water within the streams, which encouraged the organic matter to be mineralized to DIC. In general, DIC was a smaller proportion of total carbon fluxes estimated from the Ecoregional Comparison Dataset than from the Coastal Export Dataset (tables 10.1 and 10.2). The in-stream processing of organic matter may have allowed DIC to become more prominent in the coastal export values.

The concentrations of riverine DIC were especially high in the Cold Deserts ecoregion relative to the other ecoregions, which could have been caused by lithology (Amiotte-Suchet and Probst, 1995; Hartmann, 2009; Moosdorf and others, 2011). For example, there is a large carbonate-rock aquifer that extends throughout the eastern part of the Great Basin, which includes much of the Cold Deserts (Harrill and Prudic, 1998). Chemical weathering and physical erosion releases carbon into rivers, and alkalinity for rivers overlying carbonate rocks can be nearly 20 times higher than for rivers overlying igneous or metamorphic rocks (Amiotte-Suchet and others, 2003).

Considering the variability of the DIC concentrations among the five ecoregions, variation in the estimated pCO_2 values in riverine systems was expected. The contact with groundwater in these carbonate systems (in particular, in the Cold Deserts, as indicated above) could have affected the DIC concentrations, which resulted in higher estimated in-stream pCO_2 concentrations. Additionally, the carbon dioxide efflux from streams and rivers was probably supported by carbon dioxide inputs either directly from the terrestrial environment or through mineralization of terrestrially derived organic matter. It should be noted that for each ecoregion, the estimated total carbon dioxide efflux from riverine systems was always higher than the estimated total lateral flux of DIC; that is, the amount of carbon dioxide being emitted from a stream was higher than the amount of dissolved inorganic carbon material in a stream. For now, the best explanations for this apparent imbalance are that (1) uncertainty in the estimated carbon dioxide fluxes inadvertently resulted in the higher values (field validation may provide more accurate measurements) and (2) the estimates were not fully integrated with terrestrial ecosystem models (further integration may help account for additional sources of carbon to riverine systems).

Additional variables other than lithology and terrestrially derived carbon dioxide are probably needed to explain the variation in dissolved carbon dioxide in streams and rivers across the ecoregions in the Western United States. In general, water sources at high elevations originate from snowmelt. A study by Wickland and others (2001) indicated that runoff from snowmelt, if originating from the surface of the snowpack, was in close equilibrium with the atmosphere; however, throughout the year, the sources of dissolved carbon dioxide at high elevations shifted from snowmelt runoff to water that was in contact with the carbon dioxide produced from soil respiration, thus causing the mean annual carbon dioxide concentration to remain well above atmospheric levels. In the Warm Deserts, where the estimated concentrations of pCO_2 were highest, groundwater may have contributed a significant proportion of dissolved carbon dioxide or carbonates to the estimated total riverine carbon flux.

The very high estimated per-unit-of-area fluxes of carbon from the Marine Western Coast Forest were again indicative of the relatively high estimated pCO_2 concentrations and a diverse landscape along the Coast Range. Estimated gas transfer velocities ranged from 3.2 to 54 m/d, and estimated dissolved carbon dioxide ranged from 3,214 µatm in first-order drainage systems down to 824 µatm at the terminus of the large rivers at the coast. The combination of high carbon

concentrations, high gas transfer velocities, and high stream surface area in a relatively small ecoregion resulted in the very high estimated per-unit-of-area flux estimate. The error analysis for the carbon dioxide flux in streams and rivers of the Marine West Coast Forest suggested an uncertainty in the estimate of up to 33 percent, which should be acknowledged when interpreting the reported values. In general, the very high estimated carbon dioxide flux from streams and rivers in the Western Cordillera was both a function of the steep terrain and relatively fast velocities associated with the Western Cordillera and Gila Mountains (in the Warm Deserts ecoregion). The estimated gas transfer velocities ranged from 10 to 80 m/d and most likely drove the high estimated gaseous flux.

10.5.2. Carbon Dioxide Efflux From and Carbon Burial in Lacustrine Systems

There was significant variability in the number and type of water bodies in each ecoregion. The Western Cordillera contained a balanced mix of natural and artificial lakes or reservoirs (50 percent of each), and the Marine West Coast Forest and Cold Deserts contained fewer natural water bodies (23 percent and 15 percent, respectively). The Warm Deserts and Mediterranean California included only artificial water bodies. The variability in the origin of the water body (natural or artificial) did not appear to be related to the variability in carbon dioxide efflux, however, because carbon dioxide efflux from lacustrine systems was greatest in the Western Cordillera and lowest in the Marine West Coast Forest, the two ecoregions with the most natural water bodies.

The estimated dissolved carbon dioxide in lacustrine systems was in excess of atmospheric concentrations; the excess dissolved carbon dioxide must ultimately have been derived from external inputs of either organic or inorganic carbon. A greater portion of the carbon dioxide in the lacustrine systems of the Western Cordillera appears to have originated from terrestrial organic carbon inputs relative to the other ecoregions. Water bodies in more arid regions (such as the Cold Deserts, Warm Deserts, and Mediterranean California) all exhibited relatively high estimated mean alkalinities (3,200, 2,700, and 2,000 microequivalents per liter, or μeq/L, respectively), suggesting that a large amount of inorganic carbon was delivered to the lacustrine systems from their watersheds. The estimated mean DIC concentrations determined from lateral fluxes in the ecoregional riverine systems supported this hypothesis. For example, the estimated mean riverine DIC concentrations in the Cold Deserts and Mediterranean California were relatively high (62.4 and 44.9 mg/L, respectively) compared to those in the Western Cordillera and Marine West Coast Forest (19.8 and 8.7 mg/L, respectively). Such hydrologic inputs of inorganic carbon have been demonstrated to contribute to dissolved carbon dioxide in some systems (Striegl and Michmerhuizen, 1998; Stets and others, 2009).

The mean alkalinity was lower in the Western Cordillera (1,100 μeq/L) despite the fact that the estimated pCO_2 was greatest in this region, which suggests that a greater fraction of the dissolved carbon dioxide was not derived from riverine inputs, but from the products of in-lake processing of terrestrial organic carbon. The extent to which organic carbon inputs drove carbon dioxide fluxes from lacustrine systems in the Marine West Coast Forest was not clear because both alkalinity (estimated mean = 500 μeq/L) and estimated mean pCO_2 were low. It should be noted that the estimated carbon burial rate (expressed on a watershed-area basis) was highest in the Marine West Coast Forest at 119 ± 60 gC/m^2/yr. In contrast, the comparable estimated carbon dioxide efflux from this same ecoregion was lower than any other ecoregion at 37 gC/m^2/yr. Additionally, this ecoregion had a high estimated riverine pCO_2 yield, implying that there was a considerable amount of carbon emitted from the stream environment per unit of area, which may be a factor in the low alkalinities of the downstream lacustrine systems.

The differences in the estimated total annual carbon burial in lacustrine systems among the five ecoregions reflected variations in the estimated specific carbon burial rates, which were controlled by (1) soil organic carbon (SOC), (2) vegetation, and (3) sedimentation rates. The estimated specific carbon burial rates were strongly correlated with the estimated amounts of SOC (gC/m^2) near the water bodies. Of the five ecoregions in the Western United States, the Marine West Coast Forest had the largest estimated amount of SOC (gC/m^2) and the highest estimated specific carbon burial rates. The Warm Deserts had the smallest estimated amount of SOC (gC/m^2) and lowest specific carbon burial rates. Regarding vegetation, the estimated specific carbon burial rates for reservoirs were positively correlated to the prevalence of forests in nearby areas; for lakes, the estimated carbon burial rates were more strongly associated with wetlands. Both types of vegetation (forests and wetlands) contributed to the accumulation of carbon in soils near the water bodies. Soil erosion in forested areas contributed allochthonous carbon, which is particularly important in reservoirs (St. Louis and others, 2000; Tranvik and others, 2009). Because wetlands are areas of active carbon cycling (Bridgham and others, 2006), they may contribute particulate and dissolved carbon to lakes. Finally, estimated sedimentation rates, particularly in reservoirs, were strongly related to the reservoir's area; larger reservoirs had higher estimated sediment accumulation rates.

10.5.3. Limitations and Uncertainties

The lateral flux values determined from the Ecoregional Comparison Dataset (table 10.2) represented only smaller watersheds, with boundaries that lay entirely within ecoregional boundaries. This bias was balanced by also providing estimates of larger western watersheds in the Western United States that drain to the Pacific coast in the Coastal Export Dataset. There was a paucity of data, however, for the smaller watersheds, and the values presented in table 10.2 represented only 0.05 to 25 percent of the total ecoregional area. Because of the limited dataset and the large extrapolation of these values, they should be interpreted with caution.

In this assessment, the estimated carbon dioxide efflux 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 m/d in the larger 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 carbon dioxide 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 could have caused an overestimation of the dissolved pCO_2 concentrations (Tischenko and others, 2006; Hunt and others, 2011). In typical naturally occurring fresh water, the only major contributor to noncarbonate alkalinity is organic acid, primarily humic and fulvic acids (Lozovik, 2005). The concentration of free organic ions was estimated for the lakes included in the 2007 NLA (EPA, 2009a) 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 prior to performing an analysis of pCO_2; however, an appropriate correction algorithm has not been developed for the dataset used for the flux calculation in riverine systems because of the limited locations of paired dissolved organic carbon and alkalinity measurements within the USGS's NWIS database. Because the current methodology for estimating alkalinity in riverine systems does not account for organic acids, some of the existing estimate of riverine fluxes may be high. Uncertainties in the estimates may be reduced by accounting for noncarbonate alkalinity (organic acids) when deriving pCO_2 concentration from total alkalinity measurements.

The stream and river surface-area estimates for each ecoregion ranged from 0.2 to 0.73 percent of the total area, and they are consistent with other published values (Downing and others, 2009; Aufdenkampe others, 2011); 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, in press). 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. Regional efforts to physically map first-order stream-surface areas in combination with scaling laws would reduce uncertainties.

The location of USGS streamgaging stations, which were used in calculating the hydraulic geometry coefficients, introduced a bias because the stations were placed in a location that was best suited for accurate discharge measurements (Leopold and Maddock, 1953; Park, 1977). Therefore these station locations most likely do not represent the entire range of variability in the relationships among stream depth, width, and velocity that exists along the flowpaths of rivers in the Western United States. The results from the Monte Carlo simulation suggested levels of uncertainty approaching 50 percent for the Western Cordillera and about 30 percent for each of the four 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 carbon dioxide 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 carbon dioxide efflux from lacustrine systems. In dimictic lakes (lakes that experience ice cover and mix completely in the spring and fall), carbon dioxide 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 pCO_2 dynamics was not included in the estimates, which most likely affected the results from the Western Cordillera and the Cold Deserts ecoregions, where lakes are at high elevations and mean air temperatures are below freezing for approximately 100 days each year. The Marine West Coast Forest, the Warm Deserts, and Mediterranean California ecoregions do not, on average, experience sustained below-freezing temperatures, but monomictic lakes (lakes that vertically mix once a year) potentially also experience one large degassing event per year.

10.6. Summary and Conclusions

There was great variability in estimated carbon fluxes among the aquatic ecosystems of the five ecoregions in the Western United States, most likely because of differences in (1) precipitation, (2) organic matter production, (3) lithology, and (4) physical characteristics of watersheds such as stream width and slope. The estimated total riverine carbon dioxide efflux in the Western United States was high (26.1 TgC/yr) relative to other aquatic ecosystems. Considering the additional estimated total carbon dioxide efflux from lacustrine systems (2.1 TgC/yr) and riverine export to coastal areas (7.2 TgC/yr), the sum of these losses totaled 35.4 TgC/yr. This loss was offset by an estimated total carbon burial rate of –2.4 TgC/yr in lacustrine systems.

Even though the extent of aquatic ecosystem fluxes presented in this chapter was extensive, it was not exhaustive. For example, it was not known how much carbon was produced by photosynthesis, lost by respiration, or buried in riverine systems; therefore, it was not possible to present a complete aquatic carbon budget for the Western United States, and the full impact of aquatic carbon fluxes on a terrestrial carbon budget could not be determined. The sum of losses from aquatic ecosystems listed above was equivalent to about 25 percent of the net ecosystem production (NEP) obtained by the terrestrial ecosystem component of this report (chapter 12). This value must be interpreted with caution; because the terrestrial and aquatic modeling systems were decoupled, it was not clear how much of the carbon dioxide efflux from riverine and lacustrine systems was already captured in a terrestrial carbon dioxide efflux value. This comparison does, however, indicate that the linkage between terrestrial and aquatic ecosystems is critically important to fully understand the role natural ecosystems play in greenhouse-gas storage and cycling. The relationship between aquatic and terrestrial ecosystem fluxes will be further explored in chapter 12.

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