Appendix E. Methods for Assessing Carbon Stocks, Carbon Sequestration, and Greenhouse-Gas Fluxes of Aquatic Ecosystems

E.1. Introduction

Inland and coastal waters are globally important locations of biogeochemical carbon cycling, carbon sequestration and carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) exchange with the atmosphere. Although inland aquatic ecosystems represent less than 3 percent of the total land area of the United States, they have greatly accelerated areal rates of carbon cycling relative to terrestrial ecosystems and may dominate greenhouse-gas (GHG) fluxes and carbon sequestration locally and regionally. Globally, the mass of carbon exported by inland waters to oceans annually rivals terrestrial net ecosystem exchange (NEE; Sarmiento and Gruber, 2006), and annual carbon burial in inland water sediments is comparable to that of annual carbon burial in coastal ocean sediments (Cole and others, 2007). When evaluating the importance of coastal, estuarine, and inland waters in the carbon cycle, three major factors should be considered:

8. Stream and river delivery of inorganic carbon (IC) and organic carbon (OC) from terrestrial uplands; through lowlands, ponds, lakes, and reservoirs; and to coastal areas and oceans (termed "lateral transport")

9. Biogeochemical production, consumption, sequestration, and pass-through of dissolved, particulate, and gaseous carbon by ponds, lakes, and reservoirs

10. Biogeochemical production, consumption, sequestration, and pass-through of dissolved, particulate, and gaseous carbon by coastal waters and estuaries

The importance of inland waters in the carbon cycle tends to be overlooked in terrestrial ecosystem models and global climate models, partly because of their size. Most water bodies are much smaller than the individual grid cells used as accounting units for regional-scale models. This problem is compounded by the fact that the numbers of water bodies increase exponentially as water-body size decreases (Downing and others, 2006) and that rates of carbon sequestration (Downing and others, 2008) and carbon-gas exchange, particularly methane emission (Michmerhuizen and others, 1996), are thought to increase as water-body size decreases. Consequently, if a water body is large enough to be detected at the pixel scale for terrestrial ecosystem modeling, the rates of carbon sequestration and carbon-gas exchange associated with that water body are likely to be smaller than global or regional averages. For these reasons, accurate regional modeling of carbon sequestration and gas exchange currently (2010) requires independent assessment of lateral transport to and from those regions, accurate accounting of the areal extent and size distribution of water bodies within regions, and assignment of regionally explicit biogeochemical rates of carbon sequestration and gas exchange that encompass the size distribution of streams, rivers, ponds, lakes, and reservoirs within those regions.

The carbon mass balance of estuaries and coastal areas of the Nation also is poorly quantified. Estuaries and coastal areas are some of the most biologically productive areas of the world, and the delivery of terrestrial carbon and nutrients to them by lateral transport and coastal erosion substantially enhances that production. In addition, local currents, temperature, bottom slope, and biogeochemical reactions all affect the quantity and form of particulate and dissolved carbon that will be sequestered in coastal areas, pass through to oceans, or be converted to greenhouse gases and emitted to the atmosphere. These and many other physical, chemical and biological factors controlling carbon cycling in near-shore areas vary substantially with space and time, complicating a national assessment of carbon sequestration and flux. Processes in coastal areas often are overlooked or underestimated in ocean carbon-cycling models because ocean models normally are operated at relatively coarse spatial resolution, and inclusion of coastal pixels confounds remotely sensed data and model execution (Dunne and others, 2005, 2007). Because coastal areas represent the confluence of terrestrial and oceanic processes, most ocean carbon sequestration occurs in the coastal zone, and terrestrial processes may dramatically alter coastal and estuarine processes, impacts of terrestrial management actions and carbon processes in the coastal ocean should be carefully examined (Hedges and Keil, 1995; Seitzinger and others, 2005). Owing to coastal groundwater discharge, carbon fluxes also have received relatively little attention, but Cole and others (2007) estimated that, globally, groundwater conveys dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) loads making up about 25 percent of the total carbon flux from land to sea.

In the sections that follow, a methodology for national assessment is presented for lateral transport of carbon, carbon sequestration, and greenhouse-gas exchange associated with inland and coastal waters. Methods are proposed for projection of the assessment into the future to account for ongoing and anticipated land-cover and climate change. In this report, aquatic carbon is grouped into four general categories:

- DOC, which is composed of all the dissolved fraction of organic carbon molecules that result from the production and decomposition of living matter (dissolved is operationally defined as the fraction that passes a 0.45 or 0.2 micrometer filter)

- DIC, which is composed of the aqueous carbon anions bicarbonate (HCO_3^-) and carbonate (CO_3^{-2}), carbonic acid, and dissolved CO_2

- Particulate organic carbon (POC), which is composed mostly of plant and animal debris, but also includes organic colloids, precipitates, and DOC adsorbed to particle surfaces
- Particulate inorganic carbon (PIC), which is composed of mechanically eroded sediments derived from carbonate rocks and carbonate precipitates

DOC and DIC represent most of the total carbon mass in lateral transport, whereas POC and PIC represent most of the carbon stored in inland waters and coastal sediments. Except in areas where old DOC is released from the terrestrial environment (such as from petroleum hydrocarbons, glacial melt, or permafrost thaw), most DOC tends to be modern in age and represents recently produced photosynthate that is leached from decomposing plant debris and soil organic matter. DIC is produced primarily by weathering of carbonate and silicate rocks and fine particles, where one-half of the carbon in DIC produced by carbonate weathering and all of the carbon in DIC produced by silicate weathering is derived from ecosystem respiration or atmospheric CO_2, and is therefore modern. The DOC and DIC exported from terrestrial landscapes are largely unaccounted for in terrestrial NEE or net ecosystem production (NEP) measurements, but regionally they may represent more than 5 percent of total ecosystem production (Striegl and others, 2007). POC includes recently produced plant and animal debris and some older organic carbon debris that has eroded from landscapes and is carried by water. POC that settles to streambeds or lake bottoms may serve as a food source for grazing organisms and microbes or be sequestered. Except for lakes and ponds having recent precipitation of carbonates, PIC plays a relatively unimportant role in the sequestration of modern carbon, as it mostly comprises carbon from old marine carbonates.

E.2. Transport of Carbon by Streams and Rivers

E.2.1. Lateral Transport

Lateral or hydrologic transport of carbon includes the delivery of dissolved and particulate carbon by streams and rivers from terrestrial landscapes to inland water bodies, coastal waters, and oceans. It also includes delivery of dissolved carbon by groundwater discharge to inland water bodies and coasts. Water is the carrier of all lateral carbon transport; therefore, direct calculation of lateral carbon fluxes requires quantitative understanding of water discharge and of the seasonal relations between water discharge and the concentrations of the aqueous carbon species (DOC, DIC, POC, PIC) being transported. Inferential methods for estimating carbon flux based on land-cover characteristics and hydrologic systems modeling of flow based on geomorphic and climatic conditions are promising, but currently (2010) are not fully coupled with carbon chemistry. The most accurate way to assess lateral transport, therefore, is to develop statistical relations between historical flow and chemistry data, and then empirically derive daily loads (mass carbon per time) for each carbon species (Striegl and others, 2007). There are multivariate statistical programs, such as the U.S. Geological Survey (USGS) Load Estimator (LOADEST) program, which are designed to do this for streams and rivers (Runkel and others, 2004). Estimates of groundwater flux are less accurate because groundwater-flow rates and chemistry generally are not measured; however, groundwater contributions to total carbon flux for large areas, such as the coastal United States, can be assumed to be small relative to surface-water flux.

E.2.2. Estimation of Lateral Transport

The LOADEST program (U.S. Geological Survey, 2010b) associates daily water-discharge values with constituent concentrations measured for a range of discharge conditions and develops statistical concentration-to-discharge relations for the constituent of concern. Based on these relations, it simulates concentrations for days without measurements, and then integrates discharge and concentration to estimate the total constituent load for the flow period analyzed. The accuracy of the estimates depends on the accuracy of the water discharge and constituent concentration measurements, adequate coverage of concentration measurements for a full range of flow conditions and seasons, and stability in concentration-to-discharge relations. Generally, at least 13 concentration measurements are required for LOADEST to produce accurate estimates; more are better, especially where concentration discharge relations vary seasonally. Sample collection during storm events is particularly important because most suspended sediment is transported during storms (Cohn and others, 1989; Hicks and others, 2000). If the LOADEST program is applied for estimation of lateral transport from streams and rivers that have not been streamgaged or sampled for concentrations of carbon species, the accuracy will be degraded based on additional uncertainties associated with the regression techniques for estimation of discharge and carbon concentration in those rivers.

The “spatially referenced regressions on watershed attributes” (SPARROW) model (U.S. Geological Survey, 2010e) uses these same techniques to estimate constituent loads (Schwarz and others, 2006, 2008). This model has the additional advantage of generating flow and concentrations based on land-use and land-cover characteristics and climatic data. It has been extensively applied for estimation of nitrogen and phosphorus loads and currently (2010) is under development for carbon species, particularly DOC. Additional detail on the SPARROW modeling approach is described in section E.4.3 of this report.

E.2.3. Data Needs and Availability

Estimating carbon loads requires flow and water-chemistry data collected at identical or close locations during identical periods. These data are archived in the National Water Information System (NWIS; U.S. Geological Survey, 2010f). Nationally, the USGS has collected data on daily streamflow at more than 25,000 sites and periodic flow information at more than 45,000 sites. Water-chemistry data are much more sparse, such that the total number of stations having more than 10 years of record of flow, DIC, and DOC concentration data is about 200 sites. There are many more sites having shorter or partial records.

A first step in the assessment of lateral carbon flux is to extract data from NWIS at locations where streamflow, and DIC, DOC, POC, or PIC data have been collected. These data will be assembled into a working database for further analysis. Carbon-concentration data are most prevalent for carbonate alkalinity, from which DIC can be calculated, followed by DOC, POC, and PIC. For organic carbon, older datasets commonly have only total organic carbon concentration (TOC), which by definition is DOC + POC, but operationally is commonly closer to DOC. Where concentration data are missing for a particular carbon species, it will be necessary to statistically estimate concentrations from other available water-chemistry data.

E.2.4. Approach: Nationwide Assessment of Lateral Flux

A first goal of the data analysis will be to identify key streamgaging stations from throughout the United States where carbon loads can be calculated and carbon concentration-to-discharge relations can be established. These key stations will represent large aggregated basins that drain directly to coastal areas, such as the Mississippi and Columbia River Basins (fig. E1), and smaller basins that represent specific land-use or land-cover types and (or) ecoregions. Basins of the conterminous United States are mapped in four orders of hydrologic units, including 18 regions, 204 subregions, 324 accounting units, and 2,111 cataloging units (U.S. Geological Survey, 2010a). Alaska, Hawaii, and Puerto Rico are similarly divided. Approximately 308 hydrologic units drain directly to coastal areas of the United States, ranging from a few tens of square kilometers to the Mississippi River Basin. The assessment eventually will assign carbon lateral flux values to all of these units.

Seasonal and annual loads (mass of carbon over time) and yields (mass of carbon over basin area over time) will be determined for the key streamgaging stations using LOADEST and SPARROW. The mass flux of carbon is primarily determined by water discharge, so concentration-to-discharge and

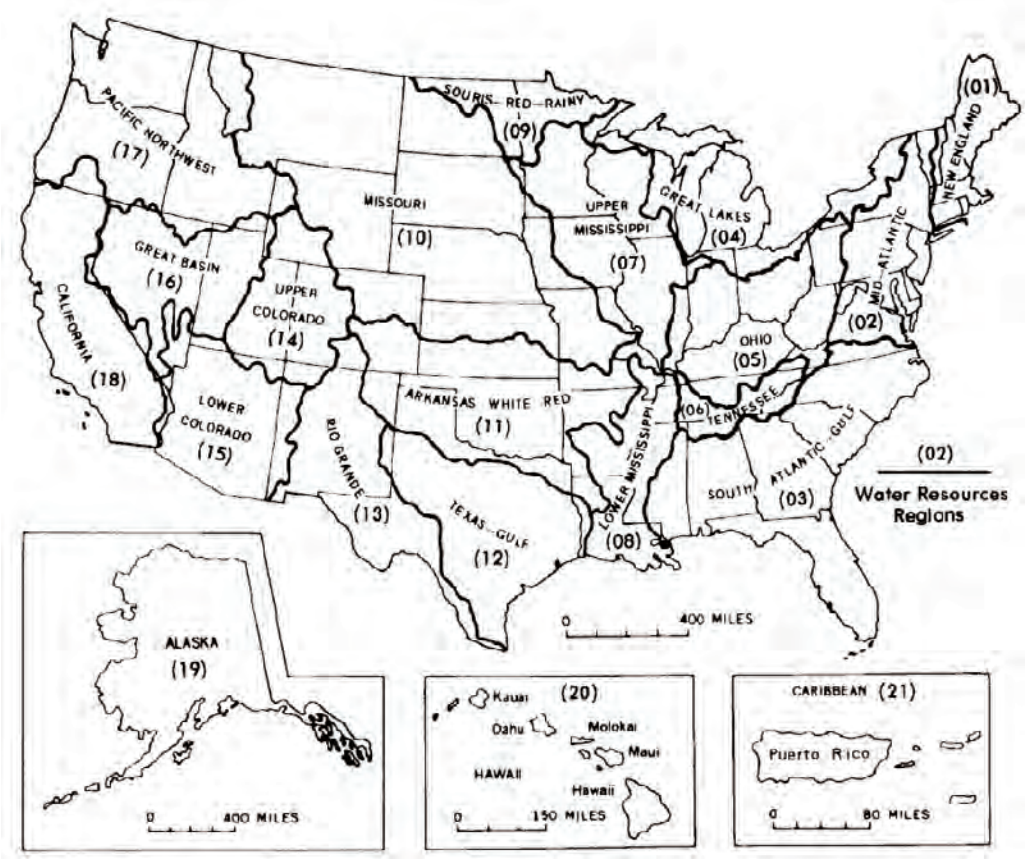

Figure E1. Map showing the water-resource regions of the United States that will be used as units for aquatic assessment (rivers, lakes, coastal regions). From Seaber and others, 1987, figure 2.

carbon yield-to-water yield relations also will be determined. These relations will be used for gap analysis to estimate fluxes from adjacent basins that are missing carbon-concentration data. Regression techniques will be used to estimate discharge for ungaged basins that are likely to transport substantial carbon to the coast, as in Hirsch and others (1982).

E.2.5. Coupling of Lateral Flux With Terrestrial Models

Currently (2010), the General Ensemble Modeling System (GEMS) and other terrestrial ecosystem models solve carbon mass balance in one-dimensional grid cells; they do not solve for lateral flow of water and carbon between cells. One goal of this assessment is to eventually couple hydrologic and terrestrial models so that water discharge and carbon flux can be estimated based on land use, land cover, physiography, and climate. The NWIS, LOADEST, and SPARROW analysis of lateral carbon flux will provide empirical validation for the development of these model attributes.

E.2.6. Projections of Lateral Flux

Water discharge is the primary determinant of lateral carbon transport from basins, and therefore needs to be accurately projected for estimation of future carbon flux. This will require projection of water discharge from downscaled climate predictions and application of flow-generation models, such as the Precipitation-Runoff Modeling System (PRMS) (Leavesley and others, 1983; U.S. Geological Survey, 2010d). Developing relations between lateral carbon flux and land use and land cover (LULC) and the coupling of these relations with GEMS or models such as SPARROW will further refine these projections. Developing such modeling capabilities should be a goal for future assessments.

E.2.7. GHG Fluxes From Rivers

In addition to the downstream transport of dissolved and particulate carbon, streams and rivers commonly are supersaturated with CO_2 and CH_4 relative to the atmosphere and emit greenhouse gases to the atmosphere along their entire courses (Cole and others, 2007). This can be attributed to within-stream biological cycling of carbon (Ritchie, 1989) and also to supersaturated groundwater and surface runoff contributing to streamflow.

E.3. Lakes and Impoundments

Inland waters are an important component of the global carbon cycle, but often are ignored in global climate models because they make up only a small part of the surface of continents, about 3 percent (Downing and others, 2006). Recent studies have shown, however, that fluxes of carbon from terrestrial to aquatic systems are substantial; for comparison, they are similar in magnitude to net ecosystem production of the terrestrial biosphere (about 2 petagrams per year (Pg/yr) of carbon), and thus, should not be ignored in global carbon budgets (Randerson and others, 2002; Cole and others, 2007). Although inland waters make up only a small fraction of total continental area, they are extremely active in the transport and storage of carbon received from the terrestrial environment (Cole and others, 2007; Tranvik and others, 2009). Pools of carbon stored in freshwater sediments also are large; approximately 820 petagrams (Pg) of carbon were stored in lake sediments during the Holocene (Einsele and others, 2001), which is comparable to the amount of carbon currently (2010) stored in the surface meter of soils (approximately 1,395 to 1,576 Pg) and terrestrial biomass (460 Pg) (Post and others, 1982; Raich and Schlesinger, 1992; Eswaran and others, 1993).

Humans have had a profound effect on hydrologic systems and sediment transport during the last several hundred years. Two of the main human affects are increased erosion, primarily related to deforestation and tilled agriculture, and construction of dams to form impoundments (Mann, 1985, 1986; Davidson and others, 1993; Paul and others, 1997; Renwick and others, 2005). Impoundments serve many functions; reservoirs commonly are used for hydroelectric power generation, recreation, flood control, and to store water for drinking and irrigation; ponds are smaller impoundments (usually less than or equal to 1 square kilometer) that typically are used for sediment retention, urban stormwater control, or to provide water for livestock. Impoundments have caused increased storage of sediment on the continents by creating pools of slow-moving water, where sediment that previously was carried in suspension by streams and rivers instead settles out and accumulates (Meade, 1982; Stallard, 1998). This alteration of the hydrologic system represents a substantial diversion of sediment that previously was exported to the ocean; it is estimated that sediment delivery to the oceans has been reduced approximately 50 percent by impoundments (Smith and others, 2005).

Organic matter makes up a small, but important, fraction of material that is eroded from upland areas and redeposited in colluvium or alluvium, or downstream in lakes or impoundments; in the Mississippi River Basin, for example, organic carbon averages 1.5 percent in erosional and depositional areas (Smith and others, 2005). Most organic carbon that is deposited in impoundments remains there for the life of the impoundment (tens to hundreds of years) because impoundment sediments usually are anoxic, which prevents oxidation of the organic matter (Tranvik and others, 2009); thus, burial of organic carbon in impoundment sediments can represent an important mechanism for carbon sequestration. Lakes can sequester organic carbon by burial as well; however, most of the carbon that is buried in lakes is autochthonous material that is produced by phytoplankton and aquatic macrophytes in the lake (Dean and Gorham, 1998). Tranvik and others (2009) estimated global burial of organic carbon in lakes and

impoundments may account for 0.6 Pg/yr of carbon. This compares with organic carbon burial in oceans of 0.1 Pg/yr of carbon (Dean and Gorham, 1998) and net uptake of carbon by the terrestrial biosphere of 1 to 3 Pg/yr of carbon (Sundquist, 1993).

Organic-carbon-burial rates in lakes and impoundments are inversely related to water-body size (Smith and others, 2002; Downing and others, 2008); this is because of increased productivity in shallow eutrophic ponds and high rates of erosion and sedimentation in agricultural areas, where small farm ponds are common. Although ponds are small, they are extremely numerous, so their cumulative effect on the global carbon budget could be substantial. Renwick and others (2005) estimated that there may be up to 8 to 9 million ponds in the conterminous United States alone, and their number has been increasing by 1 to 2 percent annually in agricultural parts of the United States (Downing and others, 2006).

Lakes and impoundments emit substantial amounts of CO_2 and CH_4, and small amounts of N_2O to the atmosphere, which contribute to greenhouse-gas warming. Global CO_2 and CH_4 fluxes from reservoirs account for 4 percent of total anthropogenic CO_2 emissions and 20 percent of total anthropogenic CH_4 emissions, respectively (St. Louis and others, 2000). The balance between carbon burial and GHG emissions determines whether or not lakes and impoundments are net sinks or net sources to global warming (Hanson and others, 2004). Global emissions of CO_2 from lakes and reservoirs have been estimated at approximately 0.8 Pg/yr of carbon (Tranvik and others, 2009); for comparison, deforestation releases 1.6 to 2 Pg/yr (Sundquist, 1993; DeFries and others, 2002; Houghton, 2003; Sundquist and others, 2008). Methane emissions from lakes and impoundments could be even more important than CO_2 in terms of greenhouse-gas potential. Methane is a powerful greenhouse gas, with 25 times the warming potential of CO_2, and accounting for 20 percent of the anthropogenic greenhouse-gas effect (Cicerone and Oremland, 1988; Wuebbles and Hayhoe, 2002). Global emissions of methane from reservoirs have been estimated to be 70 teragrams per year (Tg/yr) of CH_4, accounting for 7 percent of anthropogenic warming (St. Louis and others, 2000). Methane emissions from lakes add another 8 to 48 Tg/yr CH_4 to the atmosphere (Bastviken and others, 2004). Together, methane emissions from lakes and reservoirs are similar in magnitude to those from other anthropogenic sources, including fossil-fuel combustion (100 Tg/yr CH_4), waste management (90 Tg/yr CH_4), enteric fermentation (85 Tg/yr CH_4), rice paddies (60 Tg/yr CH_4), and biomass burning (40 Tg/yr CH_4) (St. Louis and others, 2000, and references therein).

The following section of this appendix describes the methodology for assessment of carbon sequestration in and greenhouse-gas fluxes from lakes and impoundments in the United States.

E.3.1. Carbon Burial in Lakes and Impoundments

Net storage of carbon in lakes and impoundments reflects a balance between carbon burial in sediments and GHG emissions from the surfaces and outlets of the water bodies. Estimation of carbon burial in lakes and impoundments requires several steps using a combination of geographic information systems (GIS), remote sensing, and statistical analyses, which are outlined in figure E2. To determine carbon burial in lakes and impoundments, it is necessary to quantify the total area of lakes and impoundments within specified size classes, sedimentation rates, and organic carbon concentrations in sediments.

The statistical distribution of water bodies within assessment units (U.S. Environmental Protection Agency (EPA) Level II ecoregions modified from Omernik (1987)) will be analyzed in a GIS framework to quantify their number and cumulative area within each of ten size classes (fig. E2). Input datasets will include the National Land Cover Dataset (NLCD) and the National Hydrography Dataset (NHD+). The NLCD is a nationally consistent land-cover

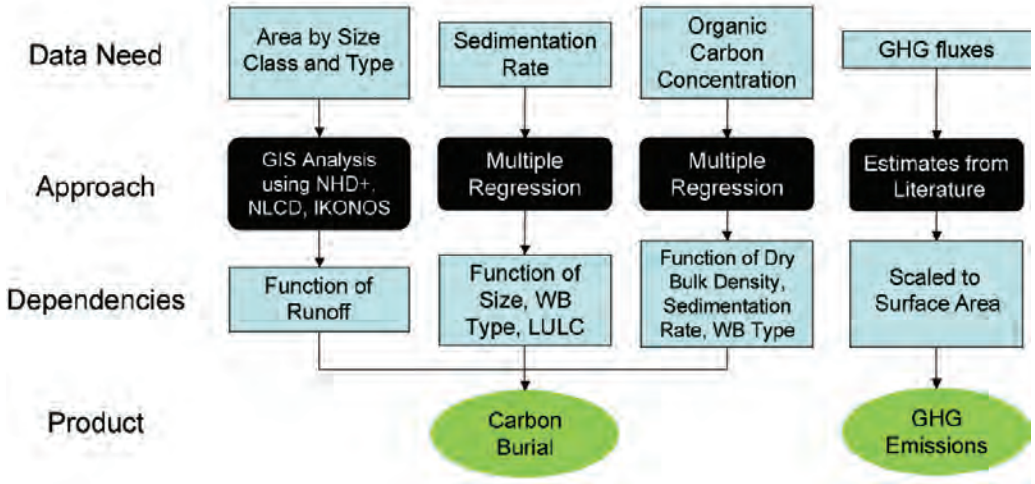

Figure E2. Schematic diagram showing key components of the methodology for assessing carbon sequestration in and greenhouse-gas fluxes from lakes and impoundments. Examples of key dependencies are given. GHG, greenhouse gas; IKONOS, Earth-observing satellite; LULC, land use and land cover; NHD+, National Hydrography Dataset Plus; NLCD, National Land Cover Database; WB, water body.

classification scheme derived from Landsat Thematic Mapper satellite data. It is one of the primary datasets used by other components of the assessment, and thus, will be the primary dataset used to determine the statistical distribution and surface area of water bodies. The NHD+ is a GIS layer developed by the USGS that depicts the Nation's interconnected network of rivers, streams, lakes, impoundments, and canals. The NHD+ will be used to validate the information on water bodies in the NLCD. The NLCD and NHD+ layers display information at 30-meter (m) resolution, which is useful for identifying water bodies larger than approximately 0.001 square kilometers (km^2). Because of the potential importance of carbon cycling in smaller water bodies, the feasibility of mapping those as small as 0.0001 km^2 will be investigated using a variety of techniques and datasets. It may be possible to map small water bodies using a combination of 10-m-resolution digital elevation models (DEMs) and 15-m panchromatic Landsat imagery, which cover most of the Nation. GeoEye and IKONOS are Earth observing satellites providing multispectral images at 2- to 4-m resolution, which can be used to identify water bodies, but the images are not available for the entire United States. Light detection and ranging (LIDAR) data collected using airborne surveys and synthetic aperture radar data collected using the Japanese Earth Resources Satellite 1 (JERS-1) have shown substantial promise in the identification and mapping of small water bodies (Telmer and Costa, 2007), but coverage is sparse in the United States.

The ratio of lakes to impoundments in each assessment unit will be determined by manually classifying a randomly selected subset of 200 water bodies based on visual inspection of high-resolution satellite imagery overlain on NLCD layers. The lake-to-impoundment ratio will be combined with water-body-area information to estimate the cumulative area of lakes and impoundments within each assessment unit. This information is needed because lakes and impoundments tend to have different sedimentation rates and sediment organic carbon concentrations, reflecting differences in land use, autochthonous production, and other processes.

The second primary task when estimating carbon burial in lakes and impoundments is to quantify sedimentation rates (fig. E2). Relatively few direct measurements of sedimentation rates in lakes and impoundments are available; this is an important data gap that will limit the accuracy of carbon-burial estimates. Initial estimates of sedimentation rates will be derived from data compiled from published sources and databases; these data will be used to estimate probability distribution functions (PDFs) representing the statistical distribution of measured sedimentation rates, which will be scaled to lake and impoundment surface areas. Most lake-sedimentation data are from dated lake-sediment cores (Dean and Gorham, 1998; Cole and others, 2007); most impoundment sedimentation-rate data are from repeat bathymetric surveys. Although there is no central repository for lake-sediment core data, impoundment sediment-rate data are stored in the national Reservoir Sedimentation (RESSED) database (Advisory Committee on Water Information, Subcommittee on Sedimentation, undated). The RESSED database includes data from approximately 1,800 reservoirs; however, this is less than 0.2 percent of the total number of impoundments in the United States (Ackerman and others, 2009). Additional data collection on lake and reservoir sedimentation rates could improve the accuracy of this assessment.

It may be possible to improve on the initial sedimentation rate estimates by using statistical relations between sedimentation rates and water-body size, water-body type (lake versus impoundment), and land use (Wetzel, 1990, 2001; Smith and others, 2001, 2002). Smith and others (2001, 2002), for example, reported that sedimentation rates vary inversely with water-body size and tend to be greater in impoundments than in lakes. Lakes and impoundments in basins with substantial tilled agriculture may be expected to have greater sedimentation rates than those in basins that are largely undisturbed (McIntyre, 1993). Correlations between sedimentation rates, water-body characteristics, and land use will be analyzed for lakes and impoundments in each assessment unit, and if significant relations are identified, multiple regression models will be developed to estimate sedimentation rates at unsampled water bodies throughout the assessment unit. Development of statistical relations in some assessment units may be limited by the scarcity of available sedimentation-rate data. Additional data collection could improve the reliability of statistical models used to estimate sedimentation and carbon-burial rates in unsampled water bodies.

OC concentrations in lake and impoundment sediments reflect the OC concentrations in upland sediments from which they are derived, plus particulate carbon derived from primary production in the water bodies (Smith and others, 2005). OC concentrations tend to be greater in lake sediments—where autochthonous production is relatively important—than in impoundment sediments (Mulholland and Elwood, 1982; Ritchie, 1989; Dean and Gorham, 1998). OC concentrations in lake sediments will be estimated from data in the literature. If sufficient data exist, then a PDF will be developed for OC in lake sediments; otherwise, a simple median concentration will be used. OC concentrations in impoundment sediments will be approximated by estimating median OC concentrations of soil in areas upslope and within a specified distance from each water body. Soil organic carbon (SOC) concentrations will be derived from a GIS layer of soil carbon provided by USGS (Bliss and others, 2009). Although it would be preferable to define a basin boundary and estimate SOC concentrations within that area, identifying and mapping basin boundaries for the large number of water bodies in the United States (on the order of 2.6 to 9 million; Renwick and others, 2005) is not operationally feasible. The simplification of the upland area providing sediment to downstream lakes and impoundments is likely to reduce the explanatory power of the predictive equations.

Burial of OC in lakes and impoundments (OC burial) will be calculated for each size class and type of water body using the following equation:

$$OC \text{ burial} = \text{Total water body area} \times \text{sedimentation rate} \times OC \text{ concentration} \quad \text{(E1)}$$

Sedimentation rate and OC concentrations will be represented by PDFs in the initial analysis. If valid statistical models can be developed for estimating sedimentation rates and OC concentrations based on water-body size and type, they will be used as input to equation E1. Results will be aggregated by EPA Level II ecoregion for consistency with other components of the assessment.

E.3.2. Alternate Method for Calculating Carbon Burial in Freshwater Aquatic Systems

As a check on results from the carbon-burial estimates for lakes and impoundments outlined above, carbon burial also will be estimated using an independent mass-balance method, as in Smith and others (2005). The method begins with calculating a sediment budget for a river basin and solving for sediment storage (S):

$$E - T = S \quad \text{(E2)}$$

where E is sediment erosion determined for the basin in GEMS from the two-dimensional Unit Stream Power Erosion and Deposition (USPED) model (Mitas and Mitasova, 1998);

T is sediment transported to the ocean, calculated in LOADEST from river discharge and suspended-sediment concentrations (Runkel and others, 2004); and

S is sediment storage, which includes redeposition of eroded sediments, primarily in alluvium, colluvium, and impoundments.

Sediment export to oceans is a relatively small component of the equation; Smith and others (2005) estimated that about 90 percent of eroded sediment is redeposited in depositional environments, and about 10 percent is exported to the ocean.

The equation for erosion, transport, and redeposition of OC is similar, but requires multiplying each of the terms in the sediment budget equation by the OC concentration (OC percent) of each sediment pool, and includes a residual term to account for oxidation of OC during transport and storage and replacement of eroded SOC in soil:

$$E \times OC \text{ percent} - T \times OC \text{ percent} = S \times OC \text{ percent} \pm \text{residual} \quad \text{(E3)}$$

The right side of equation E.3 represents total carbon burial in inland water sediments ± residual. The OC percent of eroded sediment is assumed to be the same as the OC percent of redeposited sediment, whereas the OC percent of sediment transported to the ocean is approximately twice as high, based on analyses by Ritchie (1989) and Smith and others (2005). Oxidation of OC usually is relatively minor, accounting for about 5 percent of the eroded OC budget (Smith and others, 2005). Replacement of eroded organic matter accounts for approximately 10 percent of the OC budget for the Mississippi River Basin (Smith and others, 2005).

These mass-balance calculations provide bounds on the amount of OC that may be stored in inland water sediments; it is recognized that these sediments include lakes and impoundments, as well as fluvial and colluvial systems.

E.3.3. GHG Fluxes From Lakes and Impoundments

Fluxes of greenhouse gases (CO_2, CH_4, N_2O) from lakes and impoundments will be estimated based on GHG fluxes reported in the literature. Because of the paucity of available data on CH_4 and N_2O fluxes from lakes and impoundments, a PDF approach will be used and emissions will be scaled to lake and impoundment surface areas. This necessarily simplistic approach will have large uncertainties associated with results, but could be refined in the future if sufficient data become available to build empirical models of GHG fluxes, as in Bastviken and others (2004) and in St. Louis and others (2000). These studies indicate that GHG emissions from lakes and impoundments are positively related to lake area, which is used as a surrogate for lake depth (Michmerhuizen and others, 1996; St. Louis and others, 2000; Bastviken

and others, 2004). GHG emissions also appear to vary with temperature, based on observations of GHG emissions in the tropics, which were an order of magnitude greater than GHG emissions from temperate reservoirs (St. Louis and others, 2000).

E.3.4. Error Estimation

It is anticipated that uncertainties in carbon burial in and GHG fluxes from lakes and impoundments will be large because of spatial variability in processes and rates controlling carbon cycling; accounting for this variability using a variety of explanatory variables (for example, basin characteristics or nutrient loads) is difficult in empirical models built on sparse data. In some cases, two independent approaches will be used to estimate fluxes, which can serve as a check on results. The mass-balance calculations, for example, will provide an upper bound on OC burial in lakes and impoundments.

PDFs will be used to represent the statistical distribution of input data, such as sedimentation rates, OC concentrations in sediments, and GHG fluxes from lakes and impoundments. The spread, or variability, of the input data affects the range of possible outcomes; this range is quantifiable using the PDF approach, and will provide information about the uncertainty of estimated carbon burial and GHG emissions rates.

Uncertainty in the empirical models will be evaluated based on the standard errors of the model slopes and intercepts. Bootstrapping or Monte Carlo approaches could be used to evaluate the importance of variations in input datasets on model results; however, these approaches require a minimum number of observations (for example, 20) to provide meaningful results (Efron, 1981; Efron and Tibshirani, 1993), and it is anticipated that relatively few assessment units will have sufficient data. Additional data collection could allow the use of bootstrapping or Monte Carlo approaches in the future, which would improve the uncertainty analysis.

Uncertainty in sediment and OC mass-balance calculations stems from errors in calculation of sediment and OC fluxes in rivers and errors in calculated erosion rates (Smith and others, 2005). To estimate river fluxes of sediment and OC accurately, samples must be collected for a range of hydrologic conditions using appropriate sampling methods. Collecting some samples during storm events is particularly important because most suspended sediment is transported during storms (Cohn and others, 1989; Hicks and others, 2000). Errors in estimated erosion rates are difficult to quantify, but it is assumed the mean standard error of the estimates is near zero (Smith and others, 2001).

E.3.5. Data Needs, Availability, and Gaps

Sedimentation rates and OC concentrations in sediments are key variables for calculating carbon-burial rates in lakes and impoundments, but data are sparse. Measurements of sedimentation rates in lakes are not coordinated at the national level; measurements of sedimentation rates in impoundments are stored in the national RESSED database, but are not collected at sufficient temporal and spatial resolution to support accurate estimation of OC burial for the assessment. It is recommended that these measurements be expanded, a routine monitoring plan developed, and the RESSED database be used by the U.S. Department of Interior (DOI) and other government agencies as the primary repository for these data.

Despite the importance of GHG fluxes from lakes and impoundments in the global carbon and GHG budgets, measurements are sparse and uncoordinated, and there is no centralized database for these data. Methane emissions from the outlets of reservoirs may be particularly important, but cannot be quantified at regional or national scale with current (2010) information. It is recommended that a Federal monitoring program be initiated to coordinate and conduct GHG flux measurements from lakes and impoundments in support of future carbon assessments.

E.3.6. Projections of Future Fluxes To and From Lakes and Impoundments

Future changes in streamflow, land use, and other management actions have the potential to alter carbon burial in or GHG fluxes from aquatic systems, including lakes and impoundments. Streamflow is a major driver of carbon and nutrient fluxes in rivers, as discussed in section E.2.6 in this report, and efforts are underway to develop models for projecting streamflow and carbon fluxes under various climate-change scenarios.

Management actions can have complex effects, sometimes creating offsetting benefits in terms of carbon sequestration. Land-use conversion from tilled agriculture to no-till or forest, for example, is likely to cause an increase in carbon sequestration on land, but will reduce the amount of carbon buried in lakes and impoundments because of decreased erosion (table E1). Reducing nutrient runoff from agricultural lands through best management practices (BMPs) will reduce eutrophication and CH_4 and N_2O emissions from inland and coastal waters, but also might cause a decrease in carbon burial because of reduced POC loads in rivers. Understanding the complex effects of these management actions is an area of active research by USGS and other researchers. Adding the capability of simulating the effects of these management actions to existing models is a goal of the assessment.

E.4. Coastal and Estuarine Systems

E.4.1. Carbon Sequestration in Coastal and Estuarine Systems

Coastal and estuarine systems are sites where terrestrial and deep-ocean fluxes of nutrients to the surface ocean combine to fuel intense primary productivity. More than 90

percent of global algal productivity occurs in coastal zones (including estuaries), with sufficient amounts of algal carbon sequestered to make coastal areas important sinks in the global carbon cycle (Dunne and others, 2007). Coastal areas also are sites that receive riverborne terrestrial exports of particulate and dissolved organic material, a fraction of which also is preserved in coastal marine sediments or is transported into the deep ocean. Globally, the magnitude of carbon sequestration in coastal oceans is on the same scale as net terrestrial ecosystem exchange and lateral flux of carbon to the oceans (fig. E3). Because only a small fraction of algal production and terrestrial inputs are preserved, and because coastal upwelling contributes CO_2 from the deep oceans, carbon-preservation processes in coastal oceans may be obscured and difficult to quantify (Hales and others, 2006).

There are two major processes acting to sequester carbon in coastal and estuarine sediments and coastal-ocean waters—direct burial of OC in sediments, and particulate transport of OC from the surface to deep oceans (Sarmiento and Gruber, 2002). The latter commonly is referred to as the biological pump. Both processes are strongly related to phytoplankton productivity in the coastal surface oceans, both are coupled to sediment supply from the terrestrial system, and both result in sequestration of CO_2 from the atmosphere for decadal to millennial time scales.

Carbon preserved by coastal ocean processes is from autochthonous primary production and from terrestrial inputs. Coastal primary production is fueled by nutrients supplied in terrestrial export, regeneration of nutrients in sediments and the water column, and by upwelling of nutrient-rich deep waters. The plankton production supported by externally supplied nutrients—the "new" production—represents potential net removal of CO_2 from the atmosphere. The export of this production into the deep ocean and into coastal sediments is strongly tied to total production, with higher productivity increasing export (Wassman, 1990). Other factors such as water depth and phytoplankton size also have been linked with export (Dunne and others, 2005) with larger exports observed for populations of large phytoplankton, such as those produced in nutrient-rich coastal areas.

Primary production export from the surface ocean to below the mixed layer—the biological pump—is a major mechanism for sequestration of carbon in coastal oceans (Sarmiento and Gruber, 2002; Hales and others, 2006). Primary production in the surface ocean is transported from the mixed layer into the deep ocean as settling particles, with the transported carbon sequestered from free exchange with the atmosphere for periods of decades to centuries, depending on ocean circulation (Sarmiento and Gruber, 2002; Gnanadesikan and Marinov, 2008). Particle flux has been estimated to range from 0.7 to 1.5 Pg/yr (Dunne and others, 2007;

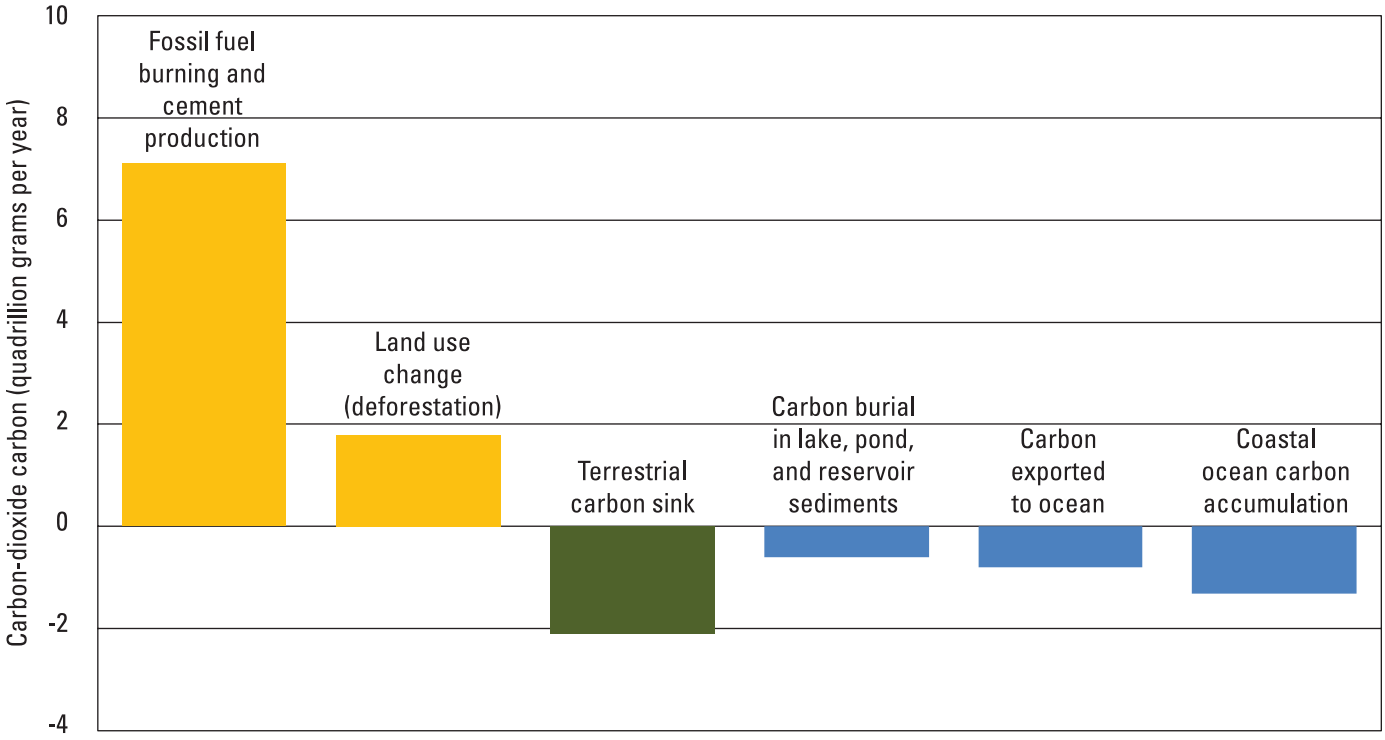

Figure E3. Chart showing the comparison of coastal carbon-sequestration processes to other important sources and sinks. Data from Hedges and Keil (1995), Muller-Karger and others (2005), Dunne and others (2007), Intergovernmental Panel on Climate Change (2007), and Tranvik and others (2009).

Muller-Karger and others, 2005). Coastal carbon preservation in large measure is, therefore, directly and immediately affected by changes in nutrient export from terrestrial systems.

Historical changes in the nutrient supply to coastal oceans related to changes in land use and land cover—such as fertilizer use, increased urbanization, and wetland restoration—likely have altered coastal carbon preservation and will continue to affect coastal carbon preservation to a greater degree in the future (Billen and Garnier, 2007; Seitzinger and Mayorga, 2008). There also is abundant evidence suggesting that submarine groundwater discharge conveys significant amounts of nutrients to coastal systems (Slomp and Van Cappellen, 2004), comparable to the nutrient loads delivered by surface water in some watersheds with large nitrogen-loading rates and permeable soils (for example, Valiela and others, 1997, 2000; Kroeger, Swarzenski, Crusius, and others, 2007; Kroeger, Swarzenski, Greenwood, and others, 2007). It is important to note that much of this groundwater is quite young (less than 20 years old), and may represent source areas amenable to management.

As for nutrients, changes in sediment supply also can affect carbon preservation in coastal and estuarine systems. Rivers in the conterminous United States export an estimated 5 to 7 Tg/yr of carbon to the oceans in the form of POC (Pacala and others, 2001), some of which is directly preserved through burial (Hedges and others, 1997; Blair and others, 2004). More importantly, however, is the flux of sediment, which is estimated to be more than 1 Pg/yr (Aulenbach and others, 2007). Sediment supply is a significant control on estuarine and coastal carbon sequestration because the lithogenic minerals in sediments increase the particle floc densities and settling rate, thereby increasing the efficiency of the biological pump (Armstrong and others, 2002). Benthic carbon preservation also is affected because higher rates of burial result in the preservation of a greater fraction of the associated organic material (Boudreau and Ruddick, 1991; Hedges and Keil, 1995; Dagg and others, 2004). Significant changes in the sediment delivery to the coastal oceans have occurred during the past several decades, altering patterns of burial (for example, Vorosmarty and others, 2003; Leithold and others, 2005; Syvitski and others, 2005). Pressures from increasing population, changes in land use, and changes in patterns of precipitation also will result in changes in sediment discharge (Wilkinson and McElroy, 2007).

Burial of POC—largely derived from phytoplankton—in marine sediments is a major sink in the global carbon budget. Historically, estimates for ocean sediment burial have been approximately 0.15 Pg/yr (Hedges and Keil, 1995; Sarmiento and Gruber, 2002; Muller-Karger and others, 2005). More recent estimates, which explicitly include biogeochemical processes occurring in coastal systems, suggest that this flux may be twice as great (0.32 pg/yr) (Dunne and others, 2007). Coastal sedimentation accounts for 85 percent of global sediment POC burial (Hedges and Keil, 1995; Dunne and others, 2007), with two-thirds of this burial (one-half of the global oceanic carbon burial) occurring in deltaic sediments of large rivers with high productivity and rapid sediment-accumulation rates (Blair and others, 2004). Much of the remaining burial in coastal oceans occurs as the result of episodic inputs from small, mountainous river systems that often occur in tectonically active zones where rates of geologic uplift are high (Milliman and Syvitski, 1992; Blair and others, 2003; Leithold and others, 2005; Wheatcroft and others, 2010). For example, the Eel River in California accounts for 15 percent of the sediment flux from the conterminous United States.

In summary, carbon burial in coastal sediments or accumulation in the deep ocean is directly related to the riverborne flux of nutrients (increases coastal primary production) and sediment (increases the efficiency of benthic burial and the biological pump of carbon into the deep ocean). The coastal carbon-sequestration methodology thus includes a terrestrial-flux component related to land use, a model of coastal primary production that is sensitive to changing nutrient inputs, and a process model that explicitly accounts for controlling processes in carbon remineralization such as degradation during sinking, ballasting, bioturbation, and burial (Dunne and others, 2005). The modeling approach used here is similar to a sensitivity analysis responding to changes in terrestrial inputs, and thus no seaward boundary is defined; however, because local conditions such as water-column depth and depositional environment are important elements that control sequestration, the estimates will be conducted individually for large terrestrial inputs, and regionally for smaller ones.

E.4.2. Methane and Nitrous-Oxide Fluxes in Coastal and Estuarine Systems

Changes in production, uptake, and release of methane and nitrous oxide in intertidal sediments and estuarine or coastal waters and sediments also can be substantially affected by changes in nutrient fluxes from the terrestrial system (Seitzinger and Nixon; 1985; Seitzinger and Kroeze, 1998), as can groundwater inputs (Bange, 2006; Hirota and others, 2007).

Surface waters of estuaries and coastal waters are typically supersaturated with respect to GHG, and are thus sources to the atmosphere. These rates and controlling processes, however, are understudied on a national scale, and are likely underestimated. At present (2010), there is insufficient knowledge of CH_4 and N_2O fluxes in estuaries and coastal waters in the United States to make satisfactory estimates, or to develop mechanistic models of the fluxes. There is ample evidence, however, that the fluxes are likely to be of substantial size in terms of global warming potential (GWP) relative to carbon and GHG fluxes in other ecosystems, and the fluxes are likely to change in response to human actions, including intentional management to reduce GHG fluxes, and unintended environmental changes that may alter the rates of flux, such as changes in nitrogen loads, sediment-carbon loads, wetland coverage, and the occurrence of hypoxia associated with eutrophication and climate change.

Nitrous oxide.—Owing to increasing nitrogen loading from fertilizer applications to watersheds, wastewater disposal, and atmospheric deposition, estuaries are among the most intensely fertilized ecosystems on earth. Typical fertilizer application rates to turf (about 110 kilograms of nitrogen per hectare per year; Valiela and others, 1997) and to crops (a wide range, but a reasonable average is about 140 kilograms of nitrogen per hectare per year; Valiela and others, 1997) are commonly exceeded by the rates of nitrogen loading to estuaries (for example, Chesapeake Bay main stem, 141 kilograms of nitrogen per hectare per year; Hudson River and Raritan Bay, 900 kilograms of nitrogen per hectare per year; Connecticut River, 3,705 kilograms of nitrogen per hectare per year; Bricker and others, 2007). Because of nearby terrestrial nitrogen sources, global estuarine N_2O fluxes are estimated to be about 7 to 61 percent of total marine fluxes (Capone, 1991; Bange, 1996; Seitzinger and Kroeze, 1998; Nevison, 2004). At the same time, recent studies suggest that agricultural and soil N_2O fluxes may be overestimated (Bange, 2006), in part because soil N_2O consumption has not been appropriately considered (Chapuis-Lardy and others, 2007; Neftel and others, 2007). Thus, values reported by Bange (2006) indicate that estuarine N_2O fluxes may be in the range of 4 to 25 percent of the total global flux from all sources. Further, as argued by Nevison (2000), measurements of N_2O fluxes from estuaries and from groundwater are critical needs for improvement of Intergovernmental Panel on Climate Change (IPCC) methodology for N_2O fluxes from agriculture. Recent literature (Nevison, 2000, and references therein) reports that estimates of the groundwater contribution to N_2O fluxes owing to leaching of nitrogen from agriculture may need to be revised downward, and that estuarine N_2O fluxes may need to be revised upward to perhaps 25 percent of the N_2O flux because of leaching loss of agricultural nitrogen.

In addition to fluxes from estuaries, it is likely that coastal waters outside of estuaries contribute significantly to fluxes, and furthermore that those fluxes will change in response to changes in anthropogenic nitrogen pollution and possibly to climate change. Part of the nitrogen loaded to landscapes ultimately transits to continental-shelf waters in discharges from rivers, groundwater, and estuaries, and there it fuels denitrification and production of new organic matter (Sietzinger and Giblin, 1996; Seitzinger and Kroeze, 1998; Seitzinger and others, 2006). The increasing anthropogenic nitrogen and associated new organic matter can be expected to fuel production of N_2O (Bange, 2006). In an increasing number of locations (fewer than 400 documented global locations), eutrophication owing to increasing nitrogen loads is severe enough to produce low-oxygen "dead zones" in estuaries and on continental shelves (Diaz and Rosenberg, 2008), and that process may substantially enhance N_2O fluxes on continental shelves (Naqvi and others, 2000). Bange (2006) compiled published data on N_2O fluxes to the atmosphere from European estuaries and coastal waters and found that much greater flux densities existed within estuaries, but that the larger surface areas of the non-estuary coastal waters resulted in about 40 percent of the total coastal flux.

Methane.—A global estimate of estuarine CH_4 flux has been attempted (Middelburg and others, 2002). The conclusions based on a compilation of existing data suggested that estuaries are consistently a source of CH_4 to the atmosphere, amounting to about 9 percent of the global marine source. It is likely, however, that estuarine CH_4 fluxes are severely underestimated and are significant to global fluxes (Bange, 2006). It is clear that important sources of CH_4 fluxes from estuaries are direct inputs from rivers (Middelburg and others, 2002) and groundwater (Bugna and others, 1996; Crusius and others, 2008; Santos and others, 2009); tidal exchanges with salt marshes, mangroves, and intertidal sand and mud flats (Middelburg and others, 2002; Savvichev and others, 2004; Barnes and others, 2006; Ferron and others, 2007); and production in estuarine sediments (Abril and Iversen, 2002; Kitidis and others, 2007). There are two reasons to conclude that estuarine CH_4 fluxes are underestimated:

- The majority of research attempts to measure dissolved CH_4 concentrations in estuarine surface water focused primarily on the open waters of estuaries, farthest from the nearshore sources listed above, and likely after much of the flux to the atmosphere has already occurred.

- Most of the studies considered in the global flux estimate did not include fluxes from sediments to the atmosphere caused by ebullition of biogenic gas bubbles commonly composed primarily of CH_4.

Neglect of fluxes caused by ebullitions (bubbles) is likely to dramatically underestimate fluxes because, in the few cases where such fluxes have been measured, they typically comprised 50 to more than 90 percent of fluxes from sediment (Hammond and others, 1975; Martens and Klump, 1980; Chanton and others, 1989; Hovland, 1993; Shalini and others, 2006; Rajkumar and others, 2008). Further, the importance of ebullitive fluxes is magnified by the fact that such fluxes largely escape oxidation in the sediment and water column (for instance, Martens and Klump (1980) estimated that 85 percent of CH_4 in bubbles survived transit through 7.5 m of water), whereas much of the diffusive flux from sediments is consumed by oxidation before flux to the atmosphere. Fluxes owing to the release of bubbles are likely to be particularly important in shallow (less than 5 m) waters (Joyce and Jewell, 2003), and releases are episodic on tidal and seasonal time scales (Chanton and others, 1989), making them difficult to measure and likely to be missed by oceanographic cruises (Hovland, 1993).

Rajkumar and others (2008) provide an example of a study where diffusive and ebullitive fluxes were measured and scaled to an entire estuary. In a 42-kilometer-long mangrove-fringed estuary with a water-surface area of 690 hectares (ha), ebullitive fluxes comprised more than 90 percent of the CH_4 flux. In terms of GWP, the CH_4 flux was 453 moles CO_2-equivalents per square meter per year. Comparing this to the

rates of carbon sequestration in U.S. forests and nonpermafrost peatlands, which are -2.9 and -1.0 moles carbon per square meter per year, respectively (U.S. Climate Change Science Program, 2007), this single estuary has a CH_4 flux equivalent to the GWP of carbon sequestration in about 107,000 ha of forest, or 313,000 ha of peatland.

As discussed with regard to coastal N_2O fluxes, it is likely that coastal waters outside of estuaries contribute significantly to CH_4 fluxes as well. For example, Bange (2006) also compiled published data on CH_4 fluxes from European estuaries and coastal waters, and similarly found much higher flux densities within estuaries. Still, fluxes from nonestuary coastal waters once again were responsible for about 40 percent of the total coastal flux.

Potential for change.—GHG fluxes from estuaries and coasts are likely evolving in response to environmental changes and human actions, including changes in nitrogen and phosphorus loading; inputs of GHG from rivers, groundwater, and wetlands; delivery of sediment; wetland coverage because of removal, restoration, or sea-level rise; and sediment carbon inventory because of dredging. Climate change can be expected to alter estuarine and coastal GHG fluxes in as yet unquantified ways because of sea-level rise and temperature increases. In recent decades, the areal coverage and intensity of coastal dead zones (hypoxic and anoxic zones) has increased dramatically in the United States and worldwide because of increasing nutrient loading (Diaz and Rosenburg, 2008), and climate change is expected to exacerbate that process (Justic and others, 2003; Boesch and others, 2007). Eutrophication and associated increases in OC production and low dissolved oxygen conditions both are likely to increase CH_4 production (Giani and Ahrensfeld, 2002) and decrease CH_4 oxidation (consumption) in estuaries. N_2O fluxes are expected to increase in response to increasing nitrogen supply: Seitzinger and Kroeze (1998) suggest that the proportion of the nitrogen released to aquatic environments that is converted to atmospheric N_2O depends on the nitrogen loading rate—from about 0.3 percent under conditions of low nitrogen loading, to 3 to 6 percent with higher nitrogen loading. Hypoxic and anoxic zones may be particularly important sources of N_2O (Naqvi and others, 2000). Because CH_4 fluxes from some estuaries and coasts may be large, and the assessment is focused on changes during the next four decades, it is worth noting that on a 20-year time horizon, the GWP of CH_4 in CO_2 equivalents is estimated at 72 rather than the 25 equivalents typically considered on a 100-year time horizon (Intergovernmental Panel on Climate Change, 2007).

Coastal groundwater as a source.—GHG fluxes from coastal groundwater also have received little attention, but data do exist indicating that concentrations of N_2O and CH_4 are at times quite elevated in coastal groundwater (Butler and others, 1987; LaMontagne and others, 2003; Santos and others, 2009). Further, the global inventory of N_2O in groundwater is a large term, comprising perhaps 10 to 20 percent of biogenic N_2O (Ronen and others, 1988; Haag and Kaupenjohann, 2001). Correlations between radon activity in estuaries as a tracer of groundwater discharge and concentrations of dissolved CH_4 (Bugna and others, 1996; Santos and others, 2009) and N_2O (Crusius and others, 2008) suggest that groundwater is a dominant source for those dissolved gases in some estuaries. Finally, coastal groundwater may interact in important ways with CH_4 production in estuarine sediments. Several authors have noted associations between the presence of discharging fresh groundwater in pore waters and elevated CH_4 concentrations in shallow sediments, suggesting reduced sulfate inhibition of methanogenesis at low-salinity water or, in some cases, delivery to the estuary of terrestrial groundwater that is enriched in dissolved methane owing to onshore aquifer properties and the influence of freshwater wetlands and hydric soils (Hill and others, 1992; Bratton and others, 2004; Kogan and Paull, 2005). The assessment will, therefore, explicitly consider groundwater as a source for coastal GHG.

E.4.3. Methodology for Assessing and Projecting Carbon Sequestration and Greenhouse-Gas Fluxes From Coastal and Estuarine Systems

There are three subsections to the coastal and estuarine assessment methodology. The first subsection describes the methods used to assess the terrestrial supply of dissolved and particulate organic carbon, nutrients, and sediments to the coastal oceans. The second subsection describes the methods used to assess the role of estuaries and coastal processes in carbon storage. The third subsection describes a method for estimating the GHG fluxes from coastal and estuarine waters, intertidal sediments, and tidal systems not covered in the wetland assessment.

It is explicitly recognized that wetland restoration and destruction as well as changes caused by sea level rise will substantially affect carbon storage, carbon sequestration, and GHG production along coastal margins in the terrestrial to aquatic transition zone. Because the methods used to assess wetlands and sea-level rise are contained within the models used to assess terrestrial processes (as discussed in appendixes C and D in this report), these methods are not described here. Nevertheless, the effects of changes to coastal and estuarine wetlands and changes because of sea-level rise are represented in the coastal and estuarine methodology as it affects nutrient, carbon, and sediment fluxes.

The goal of the coastal and estuarine assessment is to assess the magnitude of linkages between terrestrial land use, coastal carbon sequestration, and GHG production, as driven by changes in flux of water, nutrients, sediment, and carbon from the continent. The coastal and estuarine assessment focuses exclusively on the carbon-sequestration and GHG production functions of estuaries and coastal systems that are presently (2010) affected or may be affected by changes in terrestrial processes responding to changing management, land use, population, or climate. Given that the modeled processes differ by coastal geomorphology and continental flux, the

assessment will be segmented into physiographic regions, but the seaward spatial boundary will remain undefined.

The methods for assessment of coastal and estuarine processes are broken down into four parts, according to the methods used—surface-water fluxes of carbon, nutrients and sediments to estuaries and coasts; groundwater fluxes to estuaries and coasts; carbon preservation in coastal waters; and, greenhouse-gas (methane and nitrous oxide) release or uptake.

E.4.3.1. Surface-Water Fluxes of Carbon, Nutrients, and Sediments

The methods used to assess the carbon sequestration and GHG productions in coastal and estuarine systems require determination of the terrestrial fluxes that affect these processes. Current (2010) fluxes and future potential fluxes under different climate and land-use scenarios will be assessed using a hybrid modeling approach (SPARROW) that combines process-based and statistical models to calculate constituent fluxes from rivers (head of tide) to estuaries and the coastal zone across the United States. Datasets that drive the SPARROW model will include the LULC data generated as part of the assessment effort described in chapter 3 and appendix B of this report. Modeled data will be produced for all coastal and inland hydrologic units (HUC) that produce runoff to estuaries in the United States, and will be developed for DOC, POC, total suspended sediments (TSS), nitrogen (organic and inorganic) and phosphorus (organic and inorganic). The assessment also will incorporate estimates of the submarine groundwater flux to estuaries from coastal basins via modeled or literature values where available. This broader methodology will not consider inorganic carbon (dissolved CO_2 or particulate) or micronutrients (silica, iron) at this time.

The goals of this part of the assessment are to estimate the mean annual flux of POC, TSS, and nutrients from hydrologic unit (HUC) basins across the United States to the head of tide; estimate the mean annual flux of particulate carbon, TSS, and nutrients from coastal landscapes below the head of tide; and develop new SPARROW models for key constituents that affect coastal carbon cycling, including organic nutrients, POC, and carbon degradation. The lateral-flux estimates described earlier will be conducted in coordination with these assessments.

A variety of modeling approaches have been used to estimate constituent contaminant sources and loads in basins including process-based and statistical models with a range of complexities (Alexander, Elliot, and others, 2002; Schwarz and others, 2006). Process-based (mechanistic) models, such as the Hydrological Simulation Program-Fortran (HSPF) (Bicknell and others, 2001) and the Soil and Water Assessment Tool (SWAT) (Srinivasan and others, 1993), use a detailed set of equations that attempt to describe relevant processes affecting water and constituent transport. These models typically have a complex mass-balance structure that requires a large number of input parameters and a priori assumptions about the dominant processes and reactions rates (Schwarz and others, 2006). In addition, these models often lack robust measures of uncertainty in model coefficients and predictions and suffer from challenges in extrapolating the results of small catchment models and field-scale measurements to larger spatial scales; however, these models are based on physical processes occurring in basins and drainage networks and theoretically would be applicable across a broad range of sites with detailed input data.

In comparison, statistical models have a simple correlative mathematical structure and use empirical relations, such as linear regression between stream measurements (load, concentration) and source or landscape drivers. Examples of purely statistical models include regressions of nitrogen export from large basins on population density (Peierls and others, 1991), net anthropogenic sources (Howarth and others, 1996), and atmospheric deposition (Howarth and others, 1996; Jaworski and others, 1997). Although these models can be applied in basins of various sizes and can incorporate uncertainty estimates, they typically use a "black box" approach that lacks a mechanistic explanation of the processes affecting contaminant transport (Schwartz and others, 2006). In addition, these models also lack spatial detail on the distribution of sources and sinks within basins and do not allow for assessing the relative importance of terrestrial versus aquatic processes.

Hybrid modeling approaches (SPARROW: Smith and others, 1997; Global NEWS: Seitzinger and others, 2005; PolFlow: de Wit, 2001) expand on simple statistical models by adding process-based model structure to develop relations with spatially referenced properties. For example, SPARROW has process-based mass-transport components for water flow paths, in-stream processing, and mass-balance constraints on model inputs, losses, and outputs (Schwarz and others, 2006). Parameters are estimated for monitoring stations with sufficient records for discharge and water-quality parameters (including capturing the dynamic range) by spatially correlating stream data with georeferenced data on constituent sources (atmospheric deposition, fertilizers, human and animal wastes) and delivery factors (precipitation, topography, vegetation, soils, water routing). Parameter estimation ensures that the calibrated model will not be more complex than can be supported by the data.

SPARROW has been included in several model comparison studies with process-based and statistical models. These include comparisons of total nitrogen (TN) loading with the models at the national scale and for the Chesapeake Bay Basin (Alexander and others, 2001). Alexander, Johnes, and others (2002) and Seitzinger and others (2002) also compared statistical and hybrid models for the northeastern United States, with results typically showing general agreement between models and literature estimates, but lower estimates of uncertainty with SPARROW in comparison to many other models (Alexander, Johnes, and others, 2002).

In this part of the assessment, SPARROW will be used to model the delivery of terrestrial carbon and other constituents in rivers to the coastal zone. Understanding carbon transport requires models that cover the conterminous United States

and estimate the loading of key constituents to estuaries and coastal systems. A number of previous studies have used the SPARROW model for national-scale assessments of TN and total phosphorus (TP) sources and loads throughout the conterminous United States (Smith and others, 2003; Alexander and others, 2001). Separate regional studies of TN and TP loads also have been conducted in the Chesapeake Bay Basin (Preston and Brakebill, 1999; Brakebill and Preston, 2003; Roberts and Prince, 2010), the Mississippi River and tributaries (Alexander and others, 2008; Robertson and others, 2009) and New England (Moore and others, 2004). Although most studies to date have focused on TN and TP, SPARROW models also have also been developed for a range of parameters including *E. coli* (Puri and others, 2009), suspended sediment (Schwarz and others, 2006), and national estimates of total organic carbon, and dissolved solids (Anning and others, 2007).

SPARROW model parameters are estimated with nonlinear regression techniques by spatially correlating constituent flux estimates at monitoring stations with geospatial datasets on constituent sources and factors affecting constituent fate and transport. The calibrated models are used to predict flux and estimate source contributions for stream reaches throughout a river network (Schwarz and others, 2006). Data for in-stream nutrient loads at monitoring sites, nutrient sources, and land-surface characteristics are assigned to each stream reach in a digital stream-reach network that provides continuity between upstream and downstream loads. Mean annual loads typically are used from a large number of sites according to site-selection criteria, including the minimum number of observations at each station, maximum prediction accuracy of plus or minus 50 percent of mean annual load, and sufficient coverage of basin-attribute data (Schwarz and others, 2006; Alexander and others, 2008). Statistical approaches such as LOADEST (Runkel and others, 2004) and Fluxmaster (Schwarz and others, 2006) then are used to develop a time-series flow model and estimate the water-quality model (Schwarz and others, 2006).

Geospatial datasets are required as explanatory data in the SPARROW model as described in Schwarz and others (2006). The stream reach (and its incremental contributing drainage basin) is the basic spatial unit used to estimate and apply SPARROW models, and data collected at different spatial scales (for example, census block data, county fertilizer application) are converted to the stream-reach scale using GIS techniques (Schwarz and others, 2006).

To accomplish this assessment, monitoring data and geospatial datasets will be collected and evaluated for use in SPARROW models of constituent transport to the head of tide. Potential data sources are included in tables 3.7. and 3.10. in this report. The assessment will use land-use and land-cover data generated from the "forecasting scenarios of future land-cover" (FORE–SCE) model described in appendix B of this report to 2050 at 250-m grid-cell resolution, will evaluate existing data, test assumptions, and develop correlations between parameters such as fertilizer-application rates and atmospheric deposition over time. The assessment also will include uncertainty estimates for parameters that have significant assumptions or are difficult to evaluate. Given that most SPARROW models are developed for studies of TN and TP, additional data types or sources may be required for models of other constituents affecting terrestrial-carbon contributions to estuaries and coastal systems.

SPARROW output contains prediction results paired with measures of accuracy in stream reaches. Constituent transport is predicted as fluxes (mass over time) at the reach and incremental basin scale with statistics on the prediction results (standard errors, prediction intervals). Fluxes then are used to derive constituent yields (mass over area over time), flow weighted concentrations (mass over volume) and contribution by sources (Schwarz and others, 2006). The temporal scale for data output in the current (2010) SPARROW structure is long-term mean-annual or mean-seasonal flux (mass per unit time) of constituents, the response variable of the model.

In the assessment, the transport of constituents to the head of tide will focus on an annual time scale and will be referenced to a specific year as described in Schwarz and others (2006); however, the development of parameter-estimation methods for applying the SPARROW model at shorter time steps (for example, seasonal or monthly; Schwarz and others, 2006) will be evaluated early in the study with existing TN and TP to develop a more mechanistic understanding of processes, fluxes, and temporal variability that will inform future model development and interpretation of annual-scale results. A number of terrestrially derived constituents affect carbon cycling in estuaries, and therefore need to be included in model output. Critical constituents currently (2010) modeled by SPARROW or in development include DOC, TSS, TN, and TP. The current (2010) methodology also will use SPARROW modeling to predict the form of dissolved nitrogen (inorganic versus organic) and POC transport since both are critical to carbon cycling in estuaries and coastal systems.

E.4.3.2. Groundwater Fluxes of Carbon and Nutrients

The SPARROW model and streamgage data do not estimate coastal groundwater loads. To adequately estimate nutrient loads to coastal waters, the assessment must explicitly estimate and model those inputs using a land use and geological typology approach. Nitrogen loads to estuaries and coasts from coastal groundwater discharge will be estimated using existing information on discharges and loads, and a typological approach to scale site-specific rates to larger sections of the United States coast. A number of published USGS reports include hydrological modeling estimates of groundwater discharge rates from specific basins, commonly using various versions of USGS's groundwater-flow model (MODFLOW) or related groundwater models (U.S. Geological Survey, 2010c) (for example, Scorca and Monti (2001)] for the north shore of Long Island; Monti and Scorca (2003) for the south shore of Long Island; Sanford and others (2008) for the Chesapeake Bay; and Masterson and others (2006) for Rhode Island). Discharge results of those studies will be applied, as a proportion

of total rainfall to the catchment, to neighboring locations of similar climate and geology. Where available, results will be compared to estimates of fresh groundwater discharge at particular locations published in journal articles. Concentrations of nitrogen, carbon, and GHG in discharging groundwater will be estimated based on published and unpublished data, including Kroeger and others (1999), Bratton and others (2004, 2009), Crusius and others (2005), Cole and others (2006), Kroeger, Cole, and Valiela (2006), Kroeger, Cole, York, and Valiela (2006), Kroeger, Swarzenski, Crusius, and others (2007), Swarzenski and others (2007), and Kroeger and Charette (2008), at selected east coast sites and with USGS monitoring data for several thousand wells available through the USGS's National Water Information System (NWIS). The NWIS data will be selected based on well depth and proximity to the coast, and their suitability as an indication of concentrations in discharging groundwater will be assessed based on comparisons to USGS data on concentrations measured at the coast. Nitrogen concentrations and loads in groundwater will be further estimated based on application of a modified version of Nitrogen Loading Model (NLM) (Valiela and others, 1997, 2000). NLM is an empirical, land-use-based model of groundwater nitrogen loads to estuaries. The model will be applied to nearshore parts of basins not accounted for in SPARROW and streamgage estimates of river discharge and nitrogen loads.

E.4.3.3. Carbon Preservation in Coastal Systems

Carbon preservation in carbon systems also will use a hybrid modeling approach, and will be conducted in two tiers. The goals of this part of the assessment are (1) to quantify the mean annual burial flux of carbon to the sediments in coastal and estuarine environments, (2) to estimate the mean annual net flux of terrestrially supported, phytoplankton-derived, "new" production into the sediments and across the thermocline into the deep ocean; and (3) to develop a new modeling structure for coastal carbon cycling that incorporates variations in terrestrial inputs, POC degradation, burial, and transport to the deep ocean.

The conceptual modeling structure for this effort (fig. E4) starts with the effects of changing nutrient flux from terrestrial systems on productivity (and hypoxia) in coastal waters. Sediment POC inputs from rivers will contribute to the flux of carbon to the sediments, but will also act to ballast algal production, increasing transport through the mixed layer. Depending on the water depth and local currents, the particles are transported to the sediment surface or to below the thermocline, where the carbon is essentially sequestered (Hales and others, 2006). Particles arriving at the sediment surface are subject to continued degradation and resuspension until they are buried below the penetration of oxygen in the sediments, after which the carbon is presumed to be sequestered (Hedges and Keil, 1995; Hartnett and others, 1998).

The first major process to be modeled is carbon accumulation in coastal sediments, which, as discussed above, is a function of coastal productivity and sediment-accumulation rate. The vast majority of carbon preserved in the ocean is marine derived and occurs in coastal sediments, mainly in deltas (Hedges and Keil, 1995). The initial assessment of carbon sequestration occurring in these systems will be based on the sediment-flux values provided by section E.2 ("Transport of Carbon by Streams and Rivers") of this report, using values for carbon content provided in Hedges and Keil (1995) and other relevant publications with data on carbon content and grain-size distribution in major deltas of the

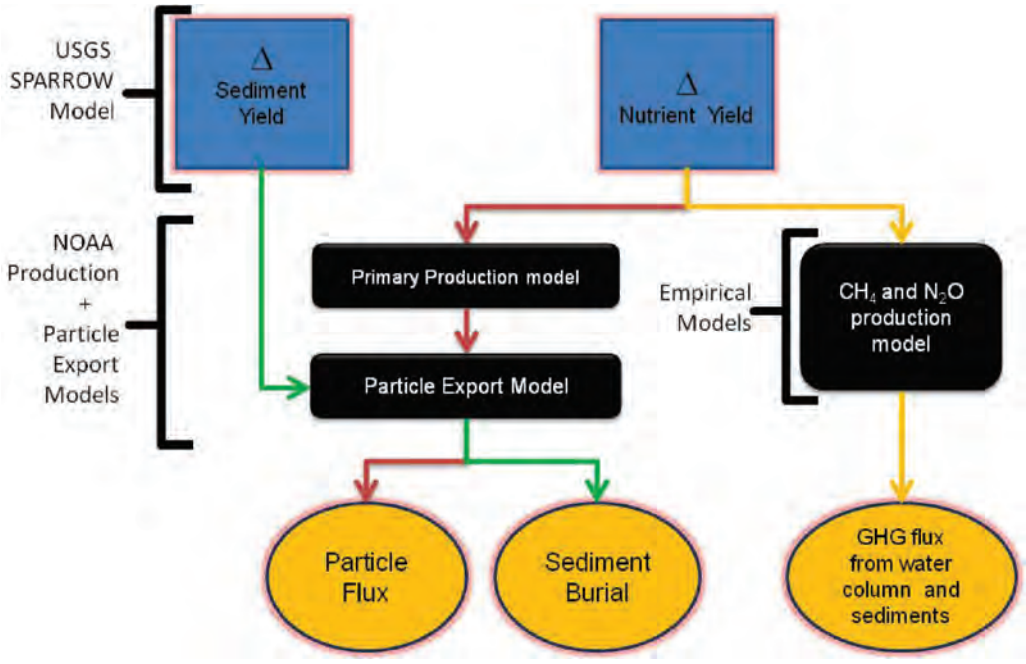

Figure E4. Diagram showing the modeling structure for coastal carbon-sequestration processes.

United States. The previously published estimates of carbon accumulation are based on an assumed partitioning between deltaic and coastal sediments, with the correspondingly different carbon content in the depositional sites.

The same assumptions as presented in Hedges and Keil (1995) initially will be used until a diffusional model is implemented in conjunction with a sedimentation model (discussed below). It is anticipated that under some IPCC SRES scenarios (Nakicenovic and others, 2000), ocean warming will increase stratification and induce additional hypoxia (Levin and others, 2009). Our estimates will be adjusted based on the anticipated extent of hypoxic areas in many major river deltas (Howarth, 2008; Rabouille and others, 2008), whereby sediments underlying these suboxic zones will exhibit elevated levels of carbon preservation because of matrix protection and reduced microbial activity (Bergamaschi and others, 1997).

The second process to be modeled is phytoplankton biomass flux across the thermocline based on models developed in the National Oceanic and Atmospheric Administration (NOAA) Geophysical Fluid Dynamics Laboratory (Dunne and others, 2005) and conducted in collaboration with the NOAA team. They have developed a combined statistical-mechanistic model using global data that estimates phytoplankton size distribution and grazing from primary productivity, temperature, and a variety of other ecosystem variables. Ballasting, sinking rate, remineralization rate, and other relevant mechanistic variables also are included to assess the export of carbon from the photic zone. The model will be adapted for application in coastal areas and for the purpose of determining carbon flux to the sediments in shallow zones and below the thermocline in deeper zones.

This modeling approach divides the processes into productivity sediment preservation and biological pump contributions to carbon preservation. The first model component assesses the amount of coastal productivity supported by nutrient supply from rivers. Changes in nutrient supply can be caused by changes in population, discharge, agricultural practice, reforestation, and many other similar land-use-related or climate-related variables (Billen and Garnier, 2007), and will affect the primary productivity in adjacent coastal areas.

At present (2010), the assessment will calculate sediment, nutrient, and POC into coastal segments at monthly time increments. A discharge intensity factor will be used to assess dispersion, and an energetic factor to assess resuspension cycles—estimated as a function of bathymetry and wind energy—that affect the processing of organic carbon associated with particles (Burdige, 2005; Thunell and others, 2007). Resuspension owing to large events, such as hurricanes (Chen and others, 2009), is not taken into account.

The model will use monthly time increments to incorporate seasonality as well as river-ocean coherence, which can have a large effect on the fate of POC in coastal ocean systems (Wheatcroft and others, 2010). Dunne and others (2005, 2007) include a complete model description, model parameters, and equations. Data needs and sources are listed in table E1.

E.4.3.4. Net Production of Methane and Nitrous Oxide in Estuaries and Coastal Waters

N_2O and CH_4 fluxes from estuaries and coastal waters will be assessed based on empirical data on flux rates and will involve a geospatial approach to quantify coverage of key sources including salt marshes, mangroves, and intertidal areas. Where data are available, a regression approach will be taken to estimate flux rates based on spatial or temporal variations in controlling variables. In cases where insufficient data are available for a simple regression approach, information gaps initially will be filled with estimated unit values. For example, all fringing salt marsh initially will be estimated to contribute CH_4 to adjacent estuaries at the same (albeit poorly constrained) rate.

Terrestrial inputs of N_2O and CH_4 will be estimated through linkages to measured and modeled discharges and chemical composition of rivers and groundwater. Methanogenic aquifers will be identified based on proposed geological controls, with thin vadose zones resulting in methanogenesis. N_2O and CH_4 content of coastal groundwater and rivers will be estimated based on LULC regressions (appendix B of this report), geological setting, biogeochemical conditions, chemical data synthesized from published literature, USGS monitoring data for groundwater and rivers available through NWIS, and other data sources, as available. Future changes in terrestrial N_2O flux will be estimated based on modeled changes in nitrogen loads (SPARROW; NLM; Valiela and others, 1997, 2000), projected land-use changes, and an assumed proportion exported as N_2O (for example, Seitzinger and Kroeze, 1998). Where data are available, variables to be considered will include eutrophication status, nitrogen load, hypoxia and anoxia, wetland coverage and type, latitude, climate, terrestrial-sediment load, sediment carbon content, water depth, salinity, and temperature or season. The assessment will require limited new data collections and monitoring to fill knowledge and data gaps, and will require uncertainty estimates given the limited data availability on N_2O and CH_4 in rivers and groundwater.

N_2O flux to the atmosphere from the water column will be calculated as the sum of nitrification and denitrification rates, multiplied by the emission factor (EF), which is the proportion of the production rate of N_2O versus other products (nitrate or N_2) in those transformation processes (Seitzinger and Nixon, 1985; Seitzinger and Kroeze, 1998). The EF is calculated based on experiments showing that N_2O /N_2 as a product of sediment denitrification increased linearly with nitrogen load ($r^2 = 0.97$) and the EF for nitrification has been observed to vary from 0.3 to 30 percent (Goreau and others, 1980; Priscu and others, 1996). Thus, in the methodology, EF will be calculated as a fraction of total N transformation by denitrification and nitrification, and that fraction will increase with N load per unit area of estuary. The denitrification rate is assumed to be 50 percent of the nitrogen-loading rate, supported by a regression between those variables ($r^2 = 0.81$ versus inorganic nitrogen load; $r^2 = 0.7$ versus total nitrogen

Table E1. Examples of data requirements and sources for coastal and estuarine assessment.

[Partial list. Final sources will be selected in consultation with stakeholders and assessment team members. Abbreviations and acronyms are as follows: DEM, digital elevation model; DOC, dissolved organic carbon; GIS, geographic information system; HUC, hydrologic unit code; km, kilometer; lb/yr, pounds per year; LOADEST, Load Estimate; LULC, land use and land cover; m. meter; N, nitrogen; NADP, National Atmospheric Deposition Program; NCDC, National Climatic Data Center; NED, National Elevation Dataset; NHD, National Hydrography Dataset; NOAA, National Oceanic and Atmospheric Administration; NPCDI, National Coastal Pollutant Discharge Inventory; NPDES, National Pollutant Discharge Elimination System; NWIS, National Water Information System; POC, particulate organic carbon; ppt, parts per trillion; PRISM, "parameter-elevation regressions on independent slopes" model; SSURGO, Soil Survey Geographic Database; STATSGO, U.S. General Soil Map; STORET, Storage and Retrieval Data Warehouse; USDA, U.S. Department of Agriculture]

Type	File	Description	Source
Atmospheric nitrogen deposition			Wet deposition of nitrate-N from NADP (http://nadp.sws.uiuc.edu/).
Bathymetry	GIS	NOAA estuary bathymetry maps—includes 30-m DEM, Google Earth files, detailed metadata, images (soundings and nautical charts), estuary-footprint shape files, images	http://estuarinebathymetry.noaa.gov/finddata.html. http://coastalgeospatial.noaa.gov/data_gis.html.
Calculated constituent loads	Site specific		Data: NWIS (http://waterdata.usgs.gov/nwis), STORET (http://www.epa.gov/storet/), other sources. Calculations: LOADEST, Runkel and others, 2004 (http://water.usgs.gov/software/loadest/). Fluxmaster, Schwarz and others, 2006.
Climate (precipitation, air temperature)			PRISM (http://www.prism.oregonstate.edu/index.phtml). NCDC (http://lwf.ncdc.noaa.gov/oa/ncdc.html). Daymet (http://www.daymet.org/.
Coastal primary productivity	GIS	Primary productivity calculated from satellite chlorophyll data	http://www.csc.noaa.gov/digitalcoast/data/index.html.
Fertilizer use			Ruddy and others, 2006 (http://pubs.usgs.gov/sir/2006/5012/). http://coastalgeospatial.noaa.gov/data_table.html.
Population density			Provided by LULC modeling team. Derived 200-m U.S. Census Bureau datasets from 1990 and 2000 (http://www.census.gov/).
In-stream and water-column losses		First-order decay functions	Schwarz and others, 2006; Dunne and others, 2007; other primary literature sources.
Land use	GIS		Provided by LULC modeling team.
National estuarine eutrophication assessment	Website	Data on individual watersheds from other datasets	http://ian.umces.edu/neea/.
Nutrient, POC, DOC concentrations in rivers	Site specific		http://waterdata.usgs.gov/nwis.
Permitted waste discharges			NPDES (http://www.epa-echo.gov/echo/compliance_report_water_icp.html).
Physical and hydrologic characteristics	Data tables	Watershed areas (including land versus water), mean streamflow, mean monthly streamflow, tidal information	http://coastalgeospatial.noaa.gov/data_table.html.

Table E1. Examples of data requirements and sources for coastal and estuarine assessment.—Continued

Type	File	Description	Source
Physical features	GIS	NOAA GIS maps of shorelines, rivers, lakes, land use/land cover by (1) coastal (estuarine) watershed, (2) upstream (fluvial) watersheds, (3) Interior watersheds	http://coastalgeospatial.noaa.gov/data_gis.html. http://www.csc.noaa.gov/digitalcoast/data/ccapregional/.
Pollution sources	Tables	Data on non-point and point source loading (lbs/yr) for a wide range of nutrients and metals, as well as by land use and upstream sources	NPCDI; http://coastalgeospatial.noaa.gov/data_table.html.
Salinity zones	GIS	NOAA GIS data with average annual salinity zones by region—mixing zone (5–25 ppt), seawater zone (25 ppt), tidal fresh zone (0–5 ppt)	http://coastalgeospatial.noaa.gov/data_gis.html.
Soils (permeability, porosity)			1-km resolution data on soil permeability and porosity from USDA STATSGO and SSURGO database. STATSGO (http://soils.usda.gov/survey/geography/statsgo/). SSURGO (http://soils.usda.gov/survey/geography/ssurgo/).
Stream reaches	GIS		Enhanced River Reach File (ERF1) (Alexander and others, 1999) (http://water.usgs.gov/lookup/getspatial?erf1). NHD, http://nhd.usgs.gov/index.html. NED, http://gisdata.usgs.net/ned/.
Topography	GIS		Nolan and others, 2002 (http://water.usgs.gov/GIS/metadata/usgswrd/XML/erf1_2.xml).
Topography (slope, topographic indices)			Nolan and others, 2002 (http://water.usgs.gov/GIS/metadata/usgswrd/XML/erf1_2.xml).
Watershed boundary	GIS		Watershed Boundary Dataset (http://www.ncgc.nrcs.usda.gov/products/datasets/watershed/).
Temperature		Satellite-based surface	http://coastalgeospatial.noaa.gov/data_gis.html.
Wind speed and direction			http://coastalgeospatial.noaa.gov/data_gis.html.

load) (Seitzinger and Kroeze, 1998). The modeled pelagic nitrification rate is less constrained, and is assumed to be 1.2 times the denitrification rate based on observations in Narragansett Bay (Seitzinger and others, 1984). Benthic nitrification is not included, although the rate has been observed to be approximately equivalent to pelagic nitrification (Berounski and Nixon, 1993). For the methodology, the total dissolved nitrogen (TDN) loads will be estimated based on the sum of loads from rivers (from the SPARROW model), direct groundwater discharge (NLM groundwater nitrogen model), and atmospheric deposition (derived from National Atmospheric Deposition Program (NADP) data). Modeled N_2O flux rates from estuaries will be calculated as follows:

$$N_2O = EF \times (NIT + DENIT) \quad \text{(E4)}$$

calculated as $NIT = 1.2 \times DENIT$

$DENIT = 0.5 \times TDNinput$

$N_2O = EF \times 1.1 \times TDNinput$

where
- N_2O — N_2O flux (grams of nitrogen per year)
- EF — emission factor = $N_2O / N_2 = (1.12 \times 10^{-7}) \times$ kilograms of nitrogen per square kilometer of estuary per year
- NIT — pelagic nitrification rate (grams of nitrogen per year)
- DENIT — sediment denitrification rate (grams of nitrogen per year)
- TDNinput — external total dissolved nitrogen load from rivers plus groundwater plus atmospheric deposition (grams of nitrogen per year)

This simple empirical model is intended to produce coarse estimates of fluxes, and the availability of data to construct and validate the model is extremely limited. The model will therefore be updated continuously as additional validation data become available. Field research and monitoring will be required to further develop, test, validate, and calibrate the model.

E.4.4. Validation and Error Estimation

Bootstrap methods will be used in the SPARROW model to address uncertainties in parameters and correct for potential bias (Schwarz and others, 2006; Robertson and others, 2009). The model will provide statistics to evaluate model results for SPARROW assumptions (variance, spatial bias, and outliers) and measures of model fit (Schwartz and others, 2006). Monte Carlo methods will be used to estimate uncertainty in models of coastal productivity and carbon accumulation (Dunne and others, 2005). Models will be validated using continuous monitoring data such as that produced by the USGS National Stream Quality Accounting Network (NASQAN) and other programs. Parameter data will be validated by comparison to existing scientific literature. Modeled accumulation rates will be validated using existing and proposed core data.

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