

include denitrification that occurs over longer time scales (NO_3^- that is incorporated into biomass must first be mineralized and then nitrified before it can be converted to N_2), these direct measurements represent conservative estimates of denitrification rates. The N_2O yield from this series of experiments was very low, with only 0.04 to 5.6% of the total gaseous ^{15}N produced as N_2O (Beaulieu et al. 2011). Although the total N_2O produced increased with denitrification rates, Beaulieu et al. (2011) did not observe an increase in the proportional yield of N_2O with N loading, despite measuring gaseous end products across streams that varied widely in stream water NO_3^- concentrations. These observations suggest that streams provide ideal conditions for complete denitrification.

Hydrology constrains nitrogen assimilation and denitrification. Benthic algae and microbes are less able to assimilate N from the water column when flows (and thus fluxes) are high and scouring flows can remove most of algal standing stocks (Grimm and Fisher 1989). The capacity of river ecosystems to retain versus transport additional N depends not only on the biological capacity (set by either light or allochthonous carbon availability) but also on the timing of N delivery. Nitrogen that enters streams in stormflows will travel much farther downstream than nitrogen molecules that seep into the channel during baseflows (Shields et al. 2008).

River Phosphorus Cycling

Globally rivers transport $\sim 21 \times 10^{12}$ g of phosphorus to the oceans each year, with nearly all of this phosphorus in particulate form (Meybeck 1982, Ittekkot and Zhang 1989, Meybeck 1993). Only about 10% of the particulate phosphorus is biologically available; the rest is strongly bound to soil minerals (Meyer and Likens 1979, Ramirez and Rose 1992). For rivers without significant wastewater or fertilizer inputs, very little inorganic phosphorus is found in the water column. Phosphorus mineralized from organic matter is rapidly sorbed or assimilated, keeping P out of solution (Meyer 1979, Meyer and Likens 1979, Meyer 1980).

Because so little inorganic P remains in the water column in small streams, it is more difficult to measure its importance to ecosystem metabolism than in deepwater systems. P is less likely to be limiting to productivity and respiration in rivers than in deepwater habitats because P deposited in river sediments remains available to most river biota. Phosphorus spiraling is also more difficult to interpret than nitrogen spiraling, because a large proportion of inorganic phosphorus uptake may be through physical sorption (Demars 2008, Stutter et al. 2010). The abundance of physical retention features (debris dams and slow-moving pools) in stream channels explained >90% of the variation in phosphorus uptake rates across streams of the Hubbard Brook Valley (Warren et al. 2007), consistent with previous observations that sediment sorption and trapping are the dominant drivers of P uptake in these streams (Meyer and Likens 1979). Changes in biological demand can affect P uptake rates. Grazing invertebrates reduced P uptake rates by suppressing algal productivity in laboratory streams (Mulholland et al. 1983), while autumn litterfall increased P uptake into coarse particulate organic matter in Walker Branch (Mulholland et al. 1985).

ESTUARIES

When large rivers reach sea level, their rate of flow slows, drastically reducing their ability to carry sediment. The load of suspended materials is deposited in the river channel and on the continental shelf. Rivers carrying large sediment loads, such as the Mississippi, may form

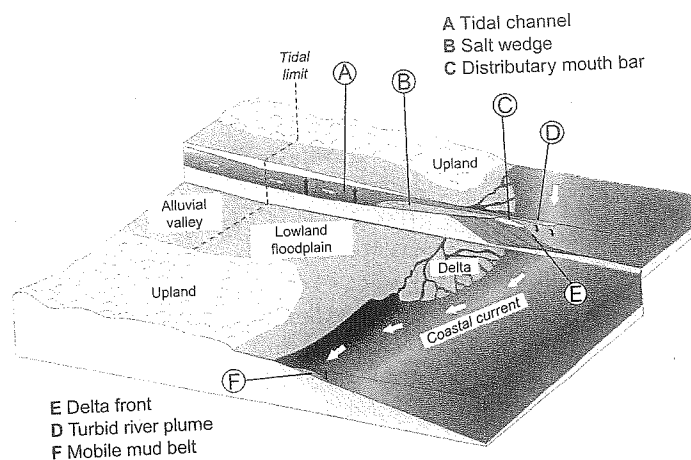


FIGURE 8.31 Generic diagram of a river estuary. The estuary boundaries are defined as the upper limit of the tidal influence within the river inflow to the coastal boundary of freshwater influence. Source: From Bianchi and Allison 2009. Used with permission of the National Academy of Sciences.

obvious deltas. The river channel is progressively confined and divided by deposited sediments, which may support broad, flat areas of salt marsh vegetation (Figure 8.31). The lower reaches of rivers and their salt marshes are subject to daily tidal inundation. An estuarine ecosystem consists of the river channel, to the maximum upstream extent of tidal influence, and the adjacent ocean waters, to the maximum seaward extent that they are affected by the addition of freshwater.

The estuary also includes any salt marshes that may develop along the shoreline. Estuaries are zones of mixing; within an estuary there is a strong gradient in salinity from land to sea. Estuaries are among the most challenging environments on Earth in which to study biogeochemistry, because, in addition to the underlying salinity gradient, turbulent mixing of fresh and saltwater within estuaries generates abrupt changes in temperature, salinity, pH, redox, and element concentrations with implications for biogeochemical cycling. Rivers were defined as running waters with a discharge of $> 500 \text{ L s}^{-1}$ (see Table 8.7).

Estuarine Water Budgets and Mixing

The mixing of freshwater from rivers and salt water from the sea occurs in the central channel of an estuary. If the estuary is well mixed, the transition from freshwater to seawater is gradual and progressive as one moves downstream. In many cases, inflowing freshwater may extend over a "wedge" of denser saltwater, creating a sharp vertical gradient in salinity throughout much of the estuary (Figure 8.32). In either case, this transition zone is an arena of rapid biogeochemical transformations and high productivity (Burton 1988, Dagg et al. 2004). Seawater has high pH (about 8.1), redox potential ($> +200 \text{ mV}$), and ionic strength (total dissolved ions) relative to freshwater (Figure 4.19; Table 9.1). The mixing of freshwater and seawater causes a rapid precipitation of the dissolved humic compounds carried by rivers. The cations in seawater replace H^+ on the exchange sites of the humic materials (Chapter 4), causing these materials to flocculate and sink to estuarine sediments (Sholkovitz 1976, Boyle et al. 1977).

Although humic acids make up only a small fraction of total riverine DOC, this flocculation is also responsible for the "salting out" of hydrocarbons and organometallic complexes which are precipitated in the estuary or within a short distance of the mouth of the river (Boyle et al.

TABLE 8.7 A Compilation of Literature Estimates of GPP, R, and NEP for Streams, Rivers, and Estuaries from Whole-Ecosystem Metabolism Estimates

Ecosystem	GPP (g Cm ⁻² d ⁻¹)	R (g Cm ⁻² d ⁻¹)	NEP (g Cm ⁻² d ⁻¹)	Global R (Pg Cy ⁻¹)	Global net heterotrophy (Pg Cy ⁻¹)
Streams (n = 62)	0.73±0.14 (0.02–5.62)	1.93±0.19 (0.29–8.16)	-1.20±0.15 (-5.86–2.51)	0.19	0.12
River (n = 37)	0.91±0.10 (0.06–2.28)	1.53±0.15 (0.20–3.54)	-0.66±0.11 (-2.06–1.60)	0.16	0.07
Estuaries (n = 31)	3.14±0.41 (0.72–10.4)	3.51±0.32 (0.83–7.58)	-0.39±0.21 (-2.98–2.86)	1.20	0.13

Note: Given is the mean standard error and the minimum and maximum in brackets. Ecosystems with the same superscript are not statistically different.

Source: Adapted from Battin et al. 2009.

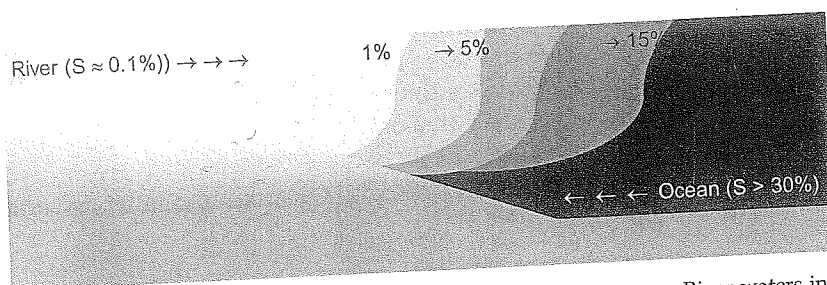


FIGURE 8.32 A diagram of a generic salinity gradient within a coastal estuary. River waters interacting with ocean waters lead to a gradient from fresh to full-strength ocean waters. The greater density of saltwater often leads to a salt wedge underlying a plume of less saline surface waters.

1974, Sholkovitz 1976, Jickells 1998, Turner and Millward 2002, Blair and Aller 2012). The flocculation of dissolved organic compounds and the deposition of larger plant debris account for a major portion of the organic carbon in estuarine sediments (Hedges et al. 1997, Blair and Aller 2012), and there is little evidence that organic matter from land contributes much to marine sediments beyond the continental shelf (Hedges and Parker 1976, Prahl et al. 1994, Hedges et al. 1997). As a result of the removal of terrestrial organic matter, the majority of the organic carbon in estuarine waters is composed of nonhumic substances, presumably resulting from net primary production in the estuary and its salt marshes (Fox 1983, Nixon et al. 1996).

Thermal stratification in estuaries is reinforced by salinity differences, such that thermohaline stratification separates more dilute, well-lit estuarine surface waters from darker and more saline bottom waters. Just as in lakes, this density gradient can lead to well-oxygenated and productive surface waters overlying deep waters where oxygen consumption can exceed diffusion. Together with enhanced nutrient loading, this density separation contributes to the widespread occurrence of coastal hypoxia (Diaz and Rosenberg 2008, Conley et al. 2009a).

Carbon Cycling in Estuaries

The inner reaches of estuaries receive large subsidies of organic matter from rivers. Despite having highly productive vegetation along their margins (mangroves, salt marshes) these regions are net heterotrophic because much of their metabolism is sustained by allochthonous carbon inputs from rivers, groundwaters, and, for many estuaries, urban wastewaters (Odum and Hoskin 1958, Odum and Wilson 1962, Heip et al. 1995, Kemp et al. 1997, Gattuso et al. 1998, Cai 2003, Gazeau et al. 2004, Wang and Cai 2004). As a result, most estuaries are supersaturated in CO_2 . In a synthesis of literature estimates of air-water CO_2 fluxes from 32 estuaries from around the world, Chen and Borges (2009) found only one reported instance where the estuary was a net sink for CO_2 , that is the air-water flux (FCO_2^{12}) was $3.9 \text{ mol C m}^{-2} \text{ yr}^{-1}$ (from Kone and Borges 2008). For the other estuaries FCO_2 values ranged from $-3.6 \text{ mol C m}^{-2} \text{ yr}^{-1}$ in Finland's Bothnian Bay (Algesten et al. 2004) to $-76 \text{ mol C m}^{-2} \text{ yr}^{-1}$ in Portugal's Douro estuary (Frankignoulle et al. 1998). While acknowledging the wide variation in reported FCO_2 values and uncertainties in the spatial extent of inner estuaries, mangroves, and marshes (Borges 2005, Borges et al. 2005), Chen and Borges (2009) estimate that globally, estuaries emit CO_2 of $\sim 0.50 \text{ Pg C yr}^{-1}$ to the atmosphere (Figure 8.33).

Mounting evidence based on pCO_2 measurements and mass-balance calculations seems to indicate that the continental shelves are sinks for atmospheric CO_2 (Borges 2005, Chen and Borges 2009). Annual FCO_2 estimates on continental shelves average $\sim 1.1 \text{ mol CO}_2 \text{ m}^{-2} \text{ yr}^{-1}$, which, scaled to a global continental shelf area of $26 \times 10^6 \text{ km}^2$, yields an annual CO_2 uptake of about $0.35 \text{ Pg C yr}^{-1}$ (Chen and Borges 2009). Because of their much greater spatial extent, coastal shelves more than offset the atmospheric CO_2 released from inner estuaries and their fringing marshes and mangroves (Table 8.8).

Primary Production in Estuaries

Nitrogen has been implicated as the nutrient responsible for eutrophication in the Chesapeake Bay (Cooper and Brush 1991, Bronk et al. 1998, Boesch et al. 2001), the Gulf of Mexico (Turner and Rabalais 1994, Rabalais et al. 2002), Narragansett Bay (Nixon et al. 1995, Howarth and Marino 2006), the Baltic Sea (Conley et al. 2007, Conley et al. 2009a), and many other estuaries in the developing world (Figure 8.34). Nitrogen fixation is often limited in estuarine systems because of the low availability of molybdenum (a critical cofactor in the nitrogenase enzyme) as well as sulfate interference with Mo uptake (Howarth and Cole 1985, Cole et al. 1993, Marino et al. 2003).

In addition, the higher turbulence of estuarine waters (Howarth et al. 1995a, Paerl 1996) and the abundance of zooplankton grazers (Marino et al. 2006) may together constrain the growth of filamentous cyanobacteria that are the common N fixers in freshwater lakes. At the same time that N fixation is hampered, the abundance of SO_4 found in saline waters limits Fe-P binding in estuarine sediments, such that organic P, once mineralized, is likely to be released to the water column (Figure 8.35; Caraco et al. 1990, Blomqvist et al. 2004, Jordan et al. 2008).

Many estuaries show a peak in net primary productivity at intermediate salinities, reflecting the zone of maximum nutrient availability and phytoplankton abundance (Anderson

¹² By convention, a positive FCO_2 indicates the ecosystem is a net sink for atmospheric CO_2 while a negative FCO_2 value indicates that the system is a net source of CO_2 to the atmosphere.

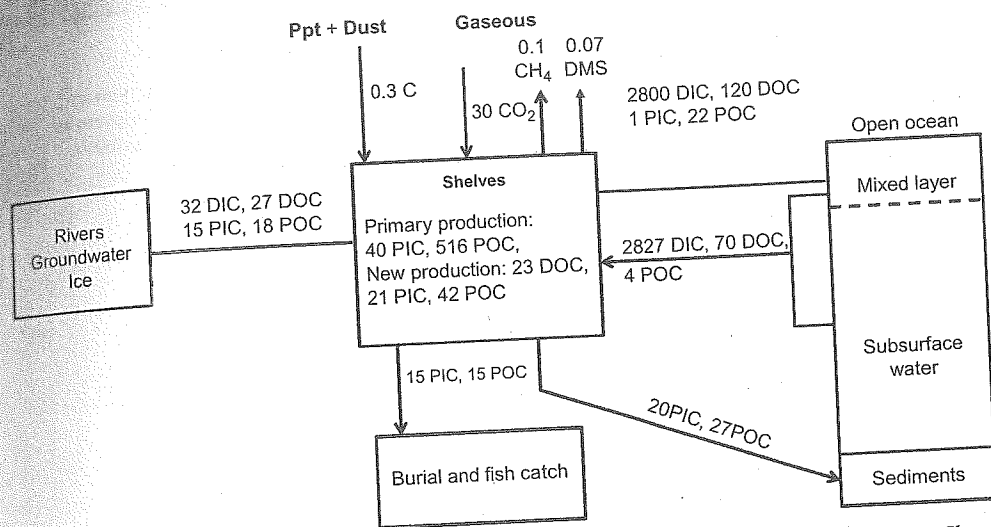


FIGURE 8.33 Mass balance of carbon in continental shelves (flows are in 10^{12} mol C yr⁻¹). Source: From Chen-Tung and Borges 2009.

TABLE 8.8 Air-Water CO₂ Flux in Open Oceanic Waters and Major Coastal Ecosystems (including inner estuaries and salt marshes)

	Surface (10 ⁶ km ²)	Air-Water CO ₂ flux (mol C m ⁻² yr ⁻¹)	Air-Water CO ₂ flux (Pg C yr ⁻¹)
60°-90°			-0.28
Open oceanic waters	30.77	-0.75	0.22
Inner estuaries	0.4	46	-0.15
Open shelf	6.79	-1.88	
Subtotal	37.96	-0.46	-0.21
30°-60°			-2.05
Open oceanic waters	122.44	-1.4	0.16
Inner estuaries	0.29	46	0.04
Non-estuarine salt marshes	0.14	23.45	0.003
Coastal upwelling systems	0.24	1.09	-0.3
Open shelf	14.47	-1.74	
Subtotal	137.58	-1.3	-2.15
30°N-30°S			0.77
Open oceanic waters	182.77	0.35	0.05
Inner estuaries	0.25	16.83	0.02
Coastal upwelling systems	1.25	1.09	0.01
Coral reefs	0.62	1.52	0.04
Mangroves	0.2	18.66	0.03
Open shelf	1.35	1.74	
Subtotal	186.44	0.41	0.92
Coastal ocean	26	0.381	0.12
Open ocean	336	-0.388	-1.56
Global ocean	362	-0.331	-1.44

Source: Compiled by Borges 2005 (Table 3). Used with permission of Springer.

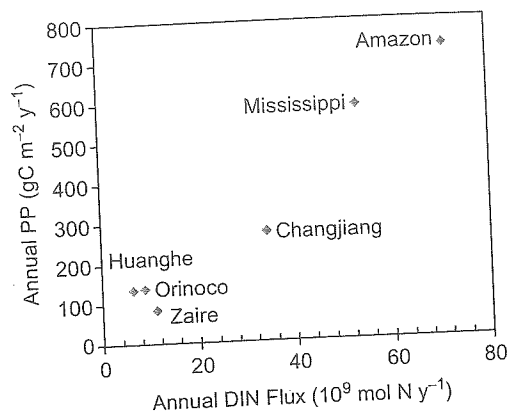


FIGURE 8.34 Relationship between primary production in coastal shelf waters impacted by major rivers and riverine DIN flux. Source: Adapted from Dagg et al. 2004.

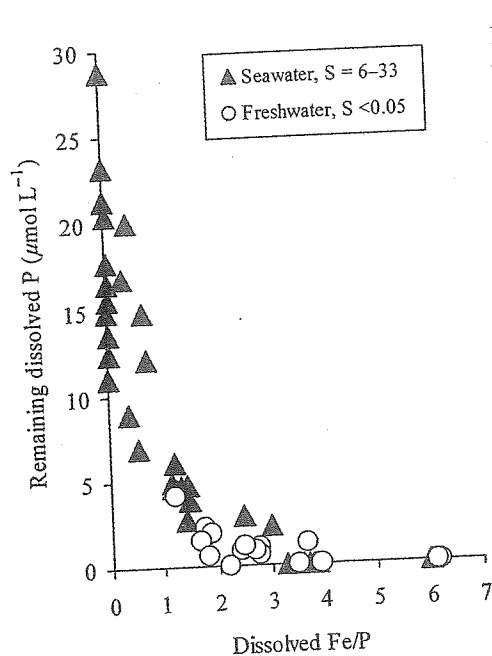


FIGURE 8.35 In experimental oxygenation of anoxic waters collected from the brackish northwestern Baltic Sea and adjoining freshwater Lake Malaren of Sweden, the amount of P remaining in solution following oxygenation was dependent on the dissolved molar Fe:P ratio, irrespective of salinity. Very little P remained in solution at Fe:P ratios > 2 , while below this ratio, dissolved phosphate removal was related to the proportion of Fe(II) present. Source: From Blomqvist et al. 2004. Used with permission of the Association for the Sciences of Limnology and Oceanography. All Rights Reserved.

1986, Lohrenz et al. 1999, Dagg et al. 2004, Benner and Opsahl, 2001). In other cases, hydrologic mixing obscures any obvious relationship between net primary production and conservative properties, such as salinity, in the estuary (Powell et al. 1989).

Phytoplankton productivity and organic matter derived from the surrounding salt marshes fuel the high productivity of fish and shellfish in estuarine waters. For many years the large production of fish and shellfish in estuaries was attributed to an abundance of organic carbon flushing from salt marshes to the open water. Indeed, the losses of organic carbon from salt

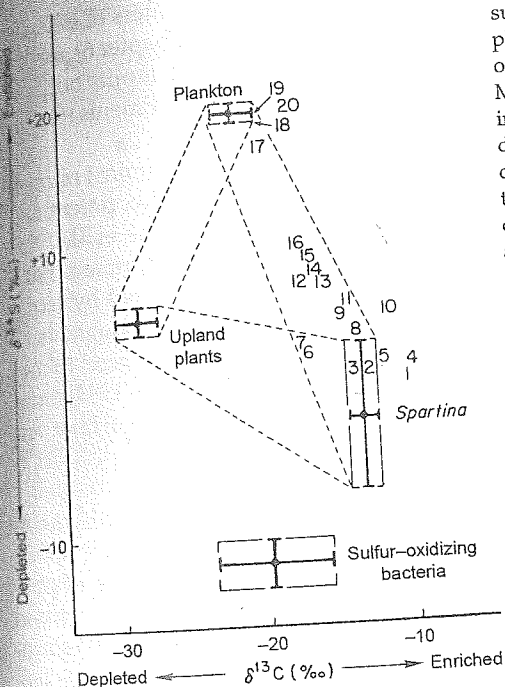


FIGURE 8.36 The isotope ratio for C and S in consumers is shown in relation to their ratios in upland plants, plankton, the salt marsh grass *Spartina*, and sulfur-oxidizing bacteria for Cape Cod's Great Sippewissett Salt Marsh in Massachusetts. The isotope ratios in sulfur-oxidizing bacteria are very different from those of consumers, indicating that sulfur oxidizers are not a major source of carbon for higher trophic levels in the estuary. Similarly, the C isotope ratio for terrestrial plants is considerably more depleted than in consumer biomass, suggesting that allochthonous C is less important than autochthonous C in this marsh. Consumers include shellfish, snails, shrimp, crabs, and fish. The values for each consumer represent pooled samples of 10 to 200 individuals except in the case of the flounder (9) and swordfish (19) Source: From Peterson et al. 1986. Used with permission of the Ecological Society of America.

marshes are usually $>100 \text{ g C m}^{-2} \text{ yr}^{-1}$, compared to values of 1 to $5 \text{ g C m}^{-2} \text{ yr}^{-1}$ from uplands (Nixon 1980, Schlesinger and Melack 1981). Haines (1977), however, suggested that this paradigm was questionable, because the isotopic ratio of carbon in estuarine animals did not match that of *Spartina*.

Using the natural abundance of stable isotopes of both sulfur and carbon, Peterson et al. (Peterson et al. 1985, 1986; Peterson and Howarth 1987) showed that the organic carbon in primary consumers within the Great Sippewissett Marsh in Massachusetts and the Sapelo Island marsh in Georgia was about equally derived from *Spartina* and from phytoplankton production in the open water (Figure 8.36). The shellfish, crabs, fish, and shrimp at the base of the marsh food web show isotopic ratios for C and S that are midway between these sources. Carbon from upland, terrestrial vegetation and carbon fixed by sulfur-oxidizing bacteria in salt marsh soils both play a minor role in supporting the abundant marine life of estuaries.

Nutrient Cycling in Estuaries

A great deal of effort has been directed toward understanding the nitrogen budget of estuaries. Most river waters do not contain large concentrations of available nitrogen (NO_3 and NH_4), and these forms are removed when the waters pass over coastal salt marshes. Indeed, the filtering action of land and marsh vegetation is so effective that inputs of nitrogen in rain

can make a substantial contribution to the nitrogen budget of the central waters of estuaries (Correll and Ford 1982). However, as is the case for terrestrial ecosystems (Chapter 6), most of the nitrogen that supports estuarine productivity is not derived from new inputs but from mineralization and recycling of organic nitrogen within the estuary and its sediments (Stanley and Hobbie 1981).

As discussed previously, rates of N fixation in estuaries tend to be low and most nitrogen is supplied via atmospheric deposition and river runoff. At the pH and redox potential of seawater, nitrification occurs rapidly in estuarine waters (Billen 1975, Capone et al. 1990). Nitrification also occurs in the upper layers of sediment (Admiraal and Botermans 1989). Denitrification in the lower, anaerobic layers of sediment is primarily supported by nitrate diffusing down from the upper sediment (Seitzinger 1988, Kemp et al. 1990), although nitrate in the water column may also diffuse back into the sediments, where it is reduced (Simon 1988, Law et al. 1991b). In Narragansett Bay, Rhode Island, Seitzinger et al. (1980, 1984) found that denitrification removed about 50% of the available NO_3^- entering in riverflow and about 35% of that derived from mineralization within the estuary. The major product of denitrification was N_2 .

In Chesapeake Bay, denitrification leaves the nitrate in the lower water column enriched in $\delta^{15}\text{N}$ (Horrigan et al. 1990). When the nitrification rate in the sediments is low, available NO_3^- may limit the rate of denitrification, and more NH_4^+ remains to support the growth of phytoplankton in the estuary (Kemp et al. 1990). Storms and tidal currents stir up the sediments in an estuary, releasing large quantities of NH_4^+ to the water column (Simon 1989). In oligotrophic estuaries where little carbon accumulates in the sediments, denitrification may be far less important. For example, Fulweiler et al. (2007) found that during periods of low productivity (and low organic matter deposition) the sediments of Narragansett Bay became N sources (through N fixation) rather than N sinks (through denitrification) to the water column.

Estuarine Phosphorus Cycling

Most river waters are supersaturated with dissolved CO_2 , which is derived from the degradation of organic materials during downstream transport. High concentrations of dissolved CO_2 and humic materials cause river waters to be slightly acid. Under these conditions, phosphorus is bound within Fe-hydroxide minerals and is transported in the load of suspended sediment (Figure 4.4, Table 4.8; Eyre 1994). After mixing with the higher pH of seawater, phosphorus desorbs from these minerals and contributes to dissolved phosphorus in the estuary (Lebo 1991, Lebo and Sharp 1993, Berner and Rao 1994, Conley et al. 1995, Lin et al. 2012). Seitzinger (1991) found that an increase in pH in the Potomac River estuary caused a release of P from sediments, stimulating a bloom of N-fixing blue-green algae, a scenario that is analogous to the shifts in species dominance that are seen in P-polluted lakes (Chapter 7). Once phosphorus is released, it is less efficiently adsorbed in saltwater sediments. The iron trap that so effectively sequesters PO_4^{3-} in freshwater sediments is ineffective in saltwaters where Fe is rapidly bound to FeS_2 (Figure 8.35; Blomqvist et al. 2004). For both reasons, phosphorus is often more available in the waters of estuaries than in either freshwater or seawater. De Jonge and Villerius (1989) additionally suggest that the phosphorus bound to carbonate particles delivered to estuaries from the open ocean is released as seawater mixes with freshwater and the carbonates dissolve under the acidic conditions of the estuary.

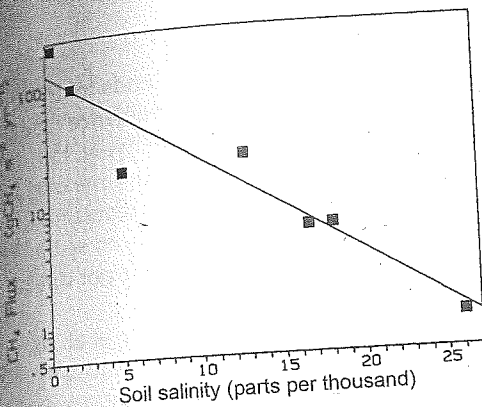


FIGURE 8.37 Annual methane flux as a function of average soil salinity across three southeastern United States salt marshes. Source: From Bartlett et al. 1987. Used with permission of Springer.

Anaerobic Metabolism in Estuarine Sediments

Estuarine sediments show high rates of sulfate reduction (Chapter 7), since they are rich in organic matter, flushed with high concentrations of SO_4^{2-} from seawater, and are frequently anaerobic. Although the exact magnitude of sulfate reduction is the subject of some controversy (Howes et al. 1984), various investigators have suggested that more than half of the CO_2 released during decomposition of organic matter in salt marshes and coastal marine sediments is associated with sulfate reduction (Jorgensen 1982, Howarth 1984, Henrichs and Reeburgh 1987, Skyring 1987, King 1988; see Chapter 7). Very little of the sulfide produced escapes to the atmosphere, so sulfide oxidation presumably contributes energy to sediment microbes. The importance of sulfate reduction depends on the concentration, and the rate of oxidation, of iron in estuarine sediments. When Fe(III) is abundant or when Fe(III) is continuously resupplied in oxidized rhizospheres or animal burrows, Fe reduction is often the most prevalent form of anaerobic metabolism (Gribsholt et al. 2003, Hyun et al. 2009, Attri et al. 2011, Kostka et al. 2012).

At a series of sites along the York River in the Chesapeake Bay estuary, Bartlett et al. (1987) found a gradient of decreasing methanogenesis with increasing salinity, as the SO_4^{2-} from seawater progressively inhibits methanogenesis (see Figure 8.37 above; see also Kelley et al. 1990). Howes et al. (1984) found that only about 0.3% of total carbon input to the sediments of Sippewissett Marsh in Massachusetts was lost through methanogenesis. Slightly higher rates have been reported for the Sapelo Island estuary in Georgia (King and Wiebe 1978), but globally the methane emission from saltwater marshes contributes little to the flux of CH_4 to the atmosphere (Chapter 11). Some salt marsh soils also appear to be a small source of phosphine (PH_3) gas to the atmosphere (Hou et al. 2011).

HUMAN IMPACTS ON INLAND WATERS

Through the creation of water infrastructure (e.g., levees, dams) and our dramatic alteration of the land surface (e.g., drainage of wetlands, stormwater pipes, pavements), humans have fundamentally changed the routing and the timing of hydrologic connections between terrestrial and aquatic ecosystems.

Water Infrastructure

Intensive land use by humans, whether for agriculture or for settlement, tends to dramatically reduce water residence time in upland soils while increasing water residence time in impoundments (e.g., Changnon and Demissie 1996, Walsh et al. 2005). Collectively, the vast increase in water control structures globally has tripled the average residence time of river water (Vörösmarty et al. 1997). Coinciding with this hydrologic rerouting, human activities have greatly increased nutrient and sediment loading to rivers and greatly reduced sediment export to coastal seas. There are no large rivers remaining in the world that are not directly impacted by human infrastructure and human wastes.

Humans now appropriate 17% of the global river volume (Postel 2000, Jackson et al. 2001). In many arid regions this proportion is much higher: In the American Southwest humans appropriate 76% of annual river flows (Sabo et al. 2010). Where annual water extraction exceeds annual runoff, groundwaters are depleted, small streams dry more frequently, river flows decline, and lakes are dewatered (Chapter 10). The most dramatic effect of human water extraction can be seen in the rapid dewatering of once large water bodies. Both the Aral Sea in Siberia and Lake Chad in northern Africa are examples of once great lakes that have shrunk to <20% of their former surface area as a result of water extraction for irrigation: these lakes have also become increasingly saline through evaporative concentration (Figure 8.38). The same process is occurring globally, as water extraction and catchment evapotranspiration increases and water inputs to rivers and lakes decline.

For thousands of years humans have constructed dams to support irrigation to grow crops and to ensure long-term water supply. Both the number and size of manmade dams have increased markedly since 1950, with more than 50,000 large dams (>15 m height) in operation worldwide (Figure 8.39; Berga et al. 2006, Lehner et al. 2011). Collectively the river segments converted to reservoirs by these dams are estimated to store 7000 to 8300 km³ of water (Vörösmarty et al. 2003, Chao et al. 2008), a volume equivalent to 10% of the water stored

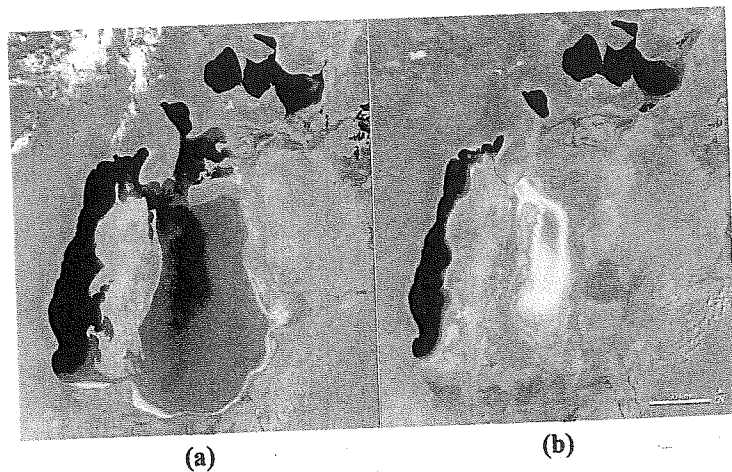


FIGURE 8.38 NASA satellite imagery shows the boundaries of the Aral Sea in 2000 (a) and in 2009 (b). Once the fourth largest lake in the world, the Aral Sea today is an example of a terminal lake that is both shrinking and becoming saltier as irrigation in the lake basin reduces annual river inflows below annual evaporative losses.

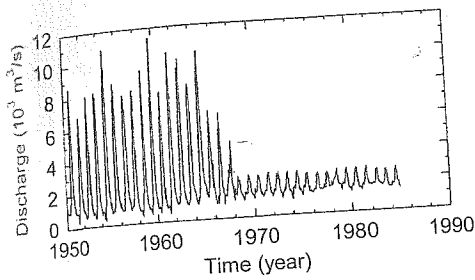


FIGURE 8.39 The effect of dam construction on river flows for the Nile River before and after construction of Aswan High Dam. Discharge is recorded just below the dam. The stabilization of flow is apparent, and it is not difficult to identify the time at which the dam was constructed and the Lake Nasser reservoir filled. The post-impoundment Nile shows reduced overall discharge, substantially truncated peak flows, higher low flows, and a many-month shift in the timing of the natural hydrograph. Source: From Vörösmarty et al. 2004. Used with permission of the American Geophysical Union.

in all natural freshwater lakes on Earth (Gleick 2000). Downing et al. (2006) estimate the current area of impounded surface waters at 258,570 km² (Table 8.9).

The magnitude of this large number of reservoirs on global C cycling is not yet certain, but qualitatively it is clear that reservoirs are C sources that are typically replacing terrestrial ecosystems that were likely carbon sinks. New reservoirs lead to the inundation of terrestrial vegetation and can have high rates of CO₂ and CH₄ emissions as large quantities of flooded organic matter are decomposed (St Louis et al. 2000, Downing et al. 2008). In contrast, reservoir construction appears to confer significant benefits with respect to the amelioration of nitrogen pollution as reservoirs have very high rates of N removal and provide conditions conducive to denitrification (anoxic, carbon-rich sediments receiving high concentrations of nitrogen in surface runoff (Harrison et al. 2005).

Reservoirs intercept more than 40% of global river discharge (Vörösmarty et al. 2003), and more than 50% of large river systems are affected by dams (Nilsson et al. 2005, Lehner et al. 2011). Dams lead to dramatic alterations in the timing and magnitude of riverflows. In many cases dam construction leads to reduced flows over the entire year (e.g., Figure 8.39), leading to less frequent and extensive hydrologic exchange between rivers and their

TABLE 8.9 Estimated Total Global Area of Small and Large Water Impoundments

A_{\min} (km ²)	A_{\max} (km ²)	Number of impoundments	Average impoundment area (km ²)	Total impoundment area (km ²)	d_L (impoundments per 10 ⁶ km ²)
0.01	0.1	444,800	0.027	12,040	2965
0.1	1	60,740	0.271	16,430	405
1	10	8295	2.71	22,440	55.3
10	100	1133	27.1	30,640	7.55
100	1000	157	271	41,850	1.05
1000	10,000	21	2706	57,140	0.14
10,000	100,000	3	27,060	78,030	0.02
All impoundments		515,149	0.502	258,570	

Source: Downing et al. 2008. Used with permission of the American Geophysical Union.

surrounding floodplains. In the case of hydropower dams, dams may be operated to release peak flows several times per day during the hottest days of the summer in a practice known as "hydro-peaking"—with frequent, scouring flows reducing biological activity downstream.

Sediment delivery to many river deltas has been dramatically reduced as a result of flow regulation of rivers (Syvitski et al. 2005, Day et al. 2007, Syvitski and Saito 2007). Many of the major river deltas on Earth are now sinking at rates many times faster than global sea level is rising (Syvitski et al. 2009). Sinking deltas and rising seas are a bad combination because even in the absence of rising sea levels, storm surges can inundate increasingly large fractions of low deltas. Within estuaries, fringing salt marsh vegetation exists in a dynamic equilibrium between the rate of sediment accumulation and the rate of coastal subsidence or change in sea level (Kirwan and Murray 2007, Langley et al. 2009b, Kirwan and Blum 2011). As deposits accumulate, the rate of erosion and the oxidation of organic materials increase, slowing the rate of further accumulation.

Conversely, as sea level rises, deposits are inundated more frequently, leading to greater rates of sediment deposition and peat accumulation. Along the Gulf Coast of the United States, the rate of sedimentation has not kept pace with coastal subsidence, and substantial areas of marshland have been lost (DeLaune et al. 1983, Baumann et al. 1984). This loss of protective fringing wetlands is considered to be a critical factor in the extensive flooding caused by Hurricane Katrina in 2005 (Tornqvist et al. 2008). Current models suggest that from 5 to 20% of coastal wetlands will be lost by the 2080s as a result of coastal subsidence and sea level rise (Nicholls 2004).

Reservoirs, because they trap and retain a large portion of the sediments transported by their contributing rivers, are very effective at retaining mineral elements. The construction of dams can significantly reduce the export of Fe, P, and Si from the continents. When the High Aswan Dam on the Nile River was built, for example, N and P exports to the Nile River estuary dropped precipitously (Table 8.10) and an 80% decline in fish and shrimp abundance was observed (Nixon 2003). The fisheries began to recover ~15 years later as the cities of Cairo and Alexandria grew and released larger fluxes of sewage N and P into the Nile (Table 8.10). Productivity in upstream reservoirs can sequester and trap silica in reservoir sediments, reducing Si inputs to coastal waters (Teodoru and Wehrli 2005, Humborg et al. 2006). In the post-dam period, diatoms were far less dominant in the Nile estuary, probably because urban wastewaters failed to replace the riverine Si flux. Across many coastal waters, reductions in Si coupled with coastal city pollutant inputs are leading to increases in N:Si or P:Si element ratios that favor the growth of nuisance algae over siliceous diatoms (Howarth et al. 2011).

Eutrophication

Humans are causing rapid "cultural eutrophication" of many inland and coastal waters by increasing the amount of nitrogen and phosphorus in the biosphere (Vitousek et al. 1997, Diaz and Rosenberg 2008, Galloway et al. 2008, Rabalais et al. 2009, Childers et al. 2011, Schipanski and Bennett 2012). While better sewage treatment and a ban on detergent phosphates have reduced P loading to many freshwaters, there is mixed evidence to suggest that cultural eutrophication can be reversed when pollution controls are implemented. Some lakes show rapid declines in algal productivity following reductions in nutrient loading (Edmondson and Lehman 1981, Jeppesen et al. 2005, Kronvang et al. 2005) while in other systems only limited responses are seen (Jeppesen et al. 2005, Kemp et al. 2009).

TABLE 8.10 Potential Release of P and N by the Urban Populations of Greater Cairo and Alexandria and the Total Urban Population of Egypt Compared with the Estimated Flux of Nutrients from the Nile

	10 ³ tonnes yr ⁻¹	
	P	N
The Nile		
Pre-Aswan High Dam	3.2	6.7
Dissolved	4-8	?
On sediments		6.7
Total	7-11	
Post-High Dam		
Dissolved	0.03	0.2
On sediment	0	0
Total	0.03	0.2
Human Waste		
Total generated in Cairo and Alexandria		
1965	4.4	21
1985	8.9	55
1995	12.6	87
Potential N and P in wastewater discharge Cairo and Alexandria^a		
1965	1.1	5
1985	3.6	22
1995	9.5	65
Potential N and P in wastewater discharge Total urban population^b		
1965	2.4	12
1985	6.7	41
1995	15.8	108

^a Assuming that the population connected to the sewers was 25% in 1965, 40% in 1985, and 75% in 1995. The 1965 estimate is very uncertain.

^b Extrapolated from Cairo and Alexandria assuming that it accounted for 45% of the total urban population in 1965, 54% in 1985, and 65% in 1995 (see text).

Source: From Nixon 2003. Used with permission of Springer.

Many culturally eutrophied lakes contain large quantities of "legacy P" in their sediments, and the extent to which this P is susceptible to mineralization and mixing into the epilimnion appears to be a major constraint on reversing eutrophication (Martin et al. 2011). In addition, continued sulfate loading to lakes from acid rain or saltwater intrusion can counteract reductions in P loading through internal eutrophication (Caraco et al. 1989, Smolders et al. 2006). Under sulfur-rich reducing conditions, most Fe is present as FeS_x, leaving little oxidized Fe available to bind P in lake sediments; thus the "iron trap" for phosphorus becomes much less effective (Blomqvist et al. 2004).

Perhaps because primary productivity in streams and rivers is less likely to be nutrient limited (Dodds et al. 2002), the subject of river eutrophication is less well represented in the literature than lake or coastal eutrophication (Hilton et al. 2006). The well-recognized increases

in nutrient loading to rivers (Green et al. 2004, Boyer et al. 2006, Alexander et al. 2008, Howarth et al. 2012) are typically linked to issues of coastal eutrophication. Yet the supply of anthropogenic nutrients to rivers can lead to algal blooms where there is sufficient light and limited flow disturbance (Peterson 1985, Hilton et al. 2006). In shaded streams, nutrient loading may speed the decomposition coarse particulate organic matter (Benstead et al. 2009, Woodward et al. 2012), and by lowering CPOM C:N and C:P ratios it may enhance C consumption by invertebrate consumers (Cross et al. 2007). Where allochthonous DOC concentrations are very high, nutrient loading is likely to directly stimulate heterotrophic activity which may exacerbate and expand problems of river hypoxia (Mallin et al. 2006).

The management of polluted estuaries is the subject of much controversy. Some workers argue that an improvement in estuarine conditions will be directly related to efforts to reduce nutrients in inflowing waters (Boesch 2002, Howarth and Marino 2006, Smith and Schindler 2009). Others suggest that the retention of prior inputs and the recirculation of nitrogen within the system mean that efforts to reduce new inputs will not necessarily produce immediate improvements in water quality (Kunishi 1988, Van Cappellen and Ingall 1994). Some have argued that the prevalence of nitrogen limitation in estuaries with long histories of human impacts occurs simply because of historic phosphorus loading.

This controversy over which element is most limiting, and thus what sorts of nutrient controls should be implemented, is similar to the ongoing debates about the relative importance of regulating N versus P inputs to lakes (Schindler et al. 2008, Conley et al. 2009b, Lewis et al. 2011). In fact, both elements can enhance eutrophication and exacerbate the duration and extent of anoxia. Anoxic conditions in turn, can enhance rates of phosphorus regeneration from sediments and provide a positive feedback to eutrophication (Van Cappellen and Ingall 1994, Vahtera et al. 2007). Phosphorus loading, because it cannot be easily removed, will likely have longer-term impacts than nitrogen loading—however, the impacts of enhanced N loads have more immediate effects on phytoplankton growth in estuaries (Conley et al. 2009b).

Global Climate Change

The extensive direct manipulation of inland waters by human activities makes it difficult to detect and predict the effects of climate change on freshwaters (Vörösmarty et al. 2000, Barnett et al. 2008, Milly et al. 2008, Arrigoni et al. 2010, Wang and Hejazi 2011). In the rare freshwaters where CO₂ concentrations are low and nutrients are abundant, rising atmospheric CO₂ may increase DIC and stimulate enhanced productivity (Schippers et al. 2004). The majority of lakes, rivers, and estuaries, however, are already supersaturated with CO₂. In these ecosystems rising atmospheric CO₂ is likely to enhance CO₂ evasion rates but is unlikely to fundamentally alter aquatic biogeochemistry. The global warming caused by rising atmospheric CO₂ is having much greater impacts on the water and nutrient budgets of freshwaters.

A warmer climate is predicted to generate a more rapid hydrologic cycle with higher evapotranspiration and rainfall across much of the planet but less certain consequences for soil moisture and surface runoff (see Chapter 10). Climate models suggest that climate warming will lead to a 10 to 40% increase in surface runoff by mid-century (Milly et al. 2005) and that in many regions a significant proportion of this increase will occur during extreme seasonal precipitation events (Milly et al. 2002, Palmer and Ralsanen 2002). Thus, somewhat paradoxically, climate change is expected to increase the severity of both droughts and floods in many regions because increases in stormflows will be rapidly transported off landscapes and

toward terminal lakes and estuaries. In the equatorial to subtropical latitudes, intensification of Hadley cell circulation (Chapter 3) is expected to lead to a poleward expansion of the latitudinal bands of aridity (Held and Soden 2006, Lu et al. 2007), which will exacerbate water shortages for people in North America's desert southwest and throughout Europe's Mediterranean (Beniston et al. 2007, Seager et al. 2007).

Across the coterminous United States, a long-term increase in precipitation throughout the twentieth century and in stream flow since at least 1940 has been observed (Karl and Knight 1998, Lins and Slack 1999, McCabe and Wolock 2002, Groisman et al. 2004, Krakauer and Fung 2008). These patterns are primarily driven by data from the eastern United States, with evidence of declines or no change predominating for gauged streams of the Pacific Northwest (Luce and Holden 2009). These trends cannot be attributed solely to climate change; in some regions irrigation, damming, and urbanization are having much greater effects on runoff patterns than climate change (Arrigoni et al. 2010, Schilling et al. 2010). Generally, stream flows have increased in watersheds in proportion to their population density and the percent of land converted to urban areas or cropland. Streamflows have declined in proportion to reservoir volume and the area of irrigated land (Wang and Hejazi 2011). After accounting for these direct influences, the predominant effect of climate change on historical stream flows appears to be increases in annual stream flow (Figure 8.40; Wang and Hejazi 2011).

More frequent storm events are likely to contribute larger pollutant loads to rivers during peak flows when river biota have a limited capacity to assimilate excess nutrients (Kaushal et al. 2008). Increasing storm pulses of nutrients are thus likely to exacerbate problems of freshwater and coastal eutrophication (e.g., Paerl et al. 2001). Hotter temperatures combined with higher nutrient loading will likely contribute to already widespread problems with summer anoxia in rivers and estuaries.

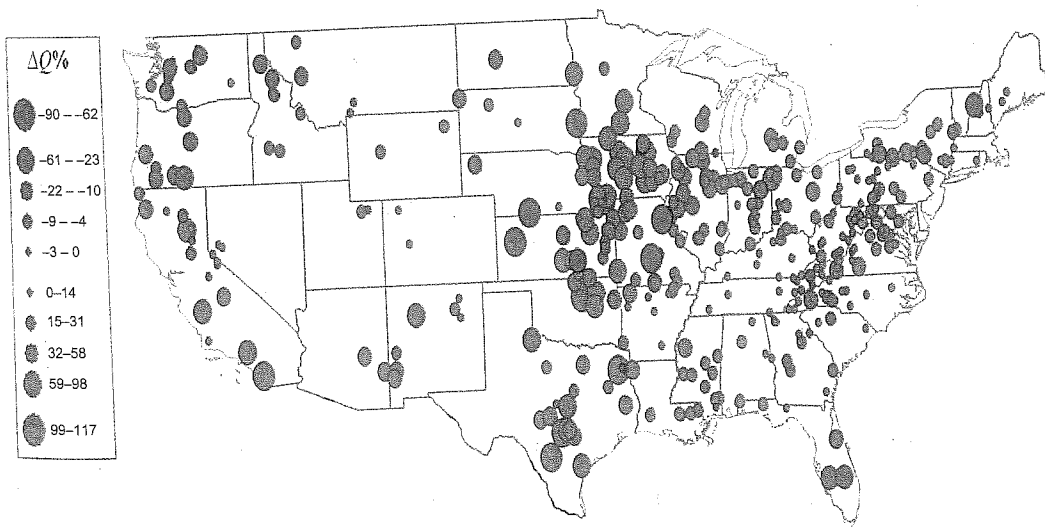


FIGURE 8.40 Spatial distribution of the change in stream flow (Q) recorded for 413 U.S. watersheds between the periods 1948–1970 and 1971–2003. Source: From Wang and Hejazi 2011. Used with permission of the American Geophysical Union.

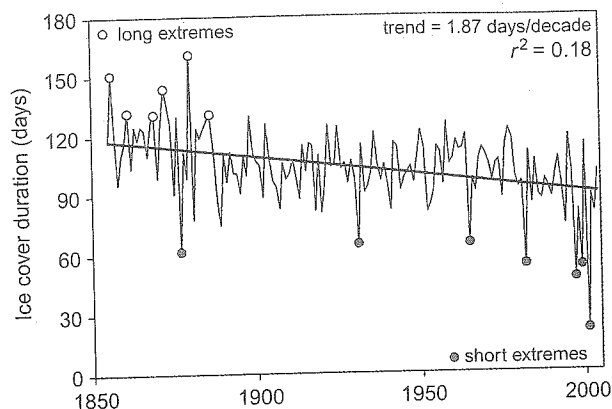


FIGURE 8.41 Graphic of the ice cover duration and extremes for the winters of 1855–1856 through 2004–2005 for Lake Mendota, Wisconsin. Over the 150-year record the six most extreme short and long ice duration winters (25-year events) are marked as closed or open circles. Source: From Benson et al. 2012. Used with permission of Springer.

Rising air temperatures are leading to later freeze dates and earlier thaw dates for ice-covered lakes and rivers, earlier dates for snowmelt flows in rivers, and increasing contributions of glacial and permafrost meltwater to rivers (Magnuson et al. 1997, Peterson et al. 2002, Barnett et al. 2005). For many northern temperate lakes the period of ice cover has declined over the last 50 years (Figure 8.41; Magnuson et al. 2000, Benson et al. 2012). The longer ice-free period and rising air temperatures are lengthening the period of thermal stratification in northern temperate lakes, a change that is expected to lead to accompanying increases in lake productivity (Carpenter et al. 1992).

A major uncertainty in this prediction is how DOC loading to freshwaters may also change in response to climate change or other anthropogenic forcing (Freeman et al. 2004) potentially constraining productivity responses to increased growing season length. For the many arid-land rivers that are fed primarily by snowmelt, earlier and smaller snowmelt flows may lead to substantial declines in annual flows and the spatial extent of river networks. Finally, sea level rise, declining coastal sediment accumulation, and drought-induced saltwater intrusion are moving the saltwater–freshwater interface further inland (see Chapter 7).

SUMMARY

Freshwater ecosystems are intimately tied to biogeochemical reactions in the surrounding terrestrial ecosystems. The rate of water delivery and the chemical properties of freshwater are largely determined by the soil properties, vegetation, and hydrology of the contributing watershed. Most inland water ecosystems are heterotrophic, showing an excess of respiration over net primary production. During transport through freshwater, nutrients are removed from the water column and sequestered in organic and inorganic forms in sediments or, in the case of N, exported as gaseous products.

Because most inland waters are hydrologically connected, from the smallest headwater streams, through rivers and lakes, all the way to estuaries or terminal lakes, their global importance really must be considered collectively. Although inland waters occupy only a small portion of the terrestrial land surface and a small fraction of the total liquid water volume on Earth, the relatively high rates of carbon and nutrient transformations in freshwater

I. PROCESSES AND REACTIONS

SUMMARY

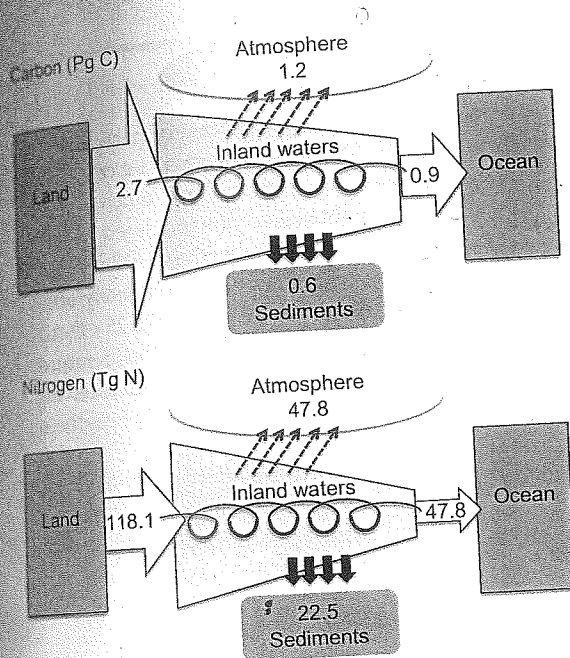


FIGURE 8.42 The cumulative effect of inland waters on global C and N cycling. Note that rivers and lakes deliver as much C and N to the atmosphere as to the ocean, indicating that biological processing of these elements within freshwaters is as important as their physical transport. Source: Numbers for the C cycle from Cole et al. 2007 with modifications from Aufdenkampe et al. 2011. Numbers for the N cycle from Galloway et al. 2004.

ecosystems makes them more important in global nutrient cycles than surface area alone would suggest. Collectively the biota of inland waters respire $\sim 40\%$ and store $\sim 20\%$ of the 2.7 Tg of allochthonous carbon, and denitrify or store $\sim 60\%$ of the 118 Tg of nitrogen they receive each year from terrestrial ecosystems (Cole et al. 2007, Galloway et al. 2004, Aufdenkampe et al. 2011; Figure 8.42). The construction of reservoirs has likely enhanced the storage and removal of both elements (St Louis et al. 2000, Downing et al. 2008, Harrison et al. 2009, Heathcote and Downing 2012).

Humans have had a dramatic impact on inland waters throughout the world, regulating the flow of water and altering the load of dissolved and suspended materials. The mixing of freshwater and seawater occurs in estuaries, located at the mouth of major rivers. In response to changes in pH, redox potential, and salinity, river waters feed estuaries with a rich solution of available N and P, and high rates of net primary production fuel a productive coastal marine ecosystem. Despite a temporary storage of nutrients in salt marshes and estuarine sediments, river waters are always a net source of nutrients to their estuary and the coastal ocean. As we shall see, rivers are a major source of nutrients in the global budgets of biogeochemical elements in the ocean.

Recommended Readings

- Allan, J. D., and M. M. Castillo. 2007. *Stream Ecology* (second ed.). Springer.
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- Stumm, W., and J. J. Morgan. 1996. *Aquatic Chemistry Chemical Equilibria and Rates in Natural Waters* (third ed.). Wiley.
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