

Inland Waters

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INTRODUCTION

At any given time surface freshwater ecosystems (lakes and rivers) hold less than 0.02% of all water on Earth and occupy less than 3% of the land surface area (Figure 10.1; Wetzel 2001, Lehner and Doll 2004). The small footprint of surface waters on the terrestrial land surface belies their importance to human civilization and to global biogeochemistry. Because surface waters are constantly replenished and easily accessed, rivers and lakes provide the water supply for the vast majority of humans on Earth. In addition to providing the water necessary to grow most crops, inland waters support freshwater fisheries that currently provide around one-third of global annual fish production.¹ At the same time, surface waters are highly managed for the disposal of wastes, the transport of cargo, and the generation of electricity.

¹ From the Food and Agriculture Organization's "The State of World Fisheries and Aquaculture 2010" report, available from www.fao.org/docrep/013/i1820e/i1820e.pdf.

In Chapter 4 the role of rivers in moving elements from the continents to the oceans was discussed at length. Over geologic time the movement of water across the land surface has weathered igneous rock, producing sedimentary rocks and salty seas. However, the biota of freshwater aquatic ecosystems assimilate and transform elements many times during downstream transport, and large amounts of weathered material and terrestrially derived organic matter are stored for millennia in the sediments of lakes. In this chapter we describe the biogeochemistry within aquatic ecosystems, focusing particularly on their capacity to change the form, timing, and magnitude of downstream biogeochemical export from the terrestrial surface to the oceans.

Much of this chapter is devoted to the distinguishing features of lakes, rivers, and estuaries. Although traditional biogeochemical studies have focused on these as discrete systems, in reality streams, ponds, lakes, rivers, and estuaries exist along a continuum of freshwater habitats that stretch from the smallest headwaters to their confluence with the oceans or terminal lakes. Even water bodies that have no apparent surface water connection to rivers are hydrologically connected to a major river or its tributaries via groundwater or floodwaters at sufficiently long time scales. Examining satellite imagery of any landscape effectively demonstrates the network structure of rivers and the intersections between lotic (*~flowing water*) and lentic (*~standing water*) water habitats (Figure 8.1).

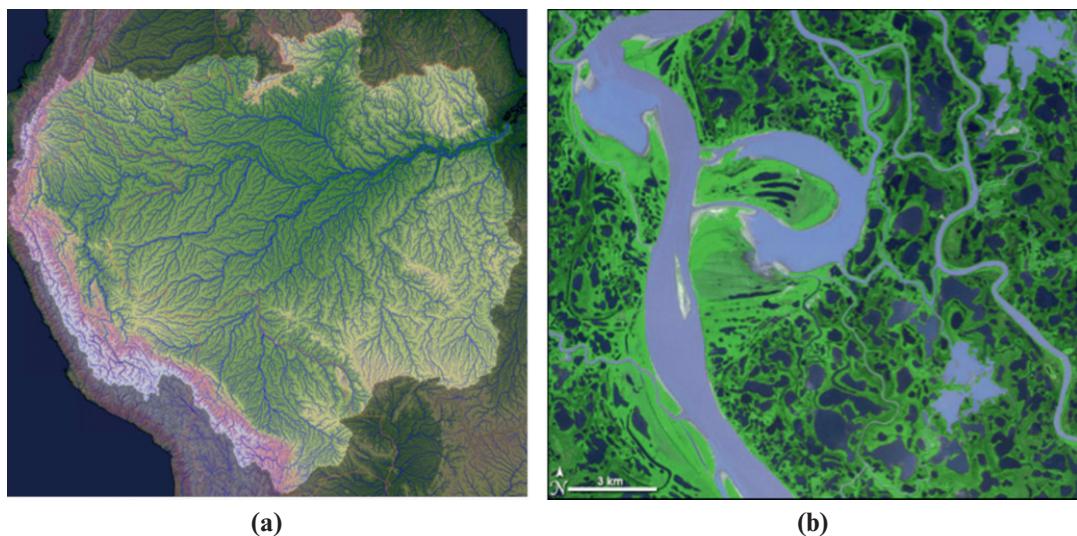


FIGURE 8.1 Two views of river networks: (a) the Amazon River Basin, which is currently estimated to be 6800 km long and drains a landscape that ranges in elevation from 4500 m (in white) to sea level (in dark green); (b) a segment of Canada's Mackenzie River Delta from August 4, 2005, when lakes throughout the Mackenzie's floodplain had thawed. Source: Both images from NASA's Earth Observatory. (a) Created using Shuttle Radar Topography Mission (SRTM) data together with river data developed by the World Wildlife Fund's HydroSHEDS program (Lehner et al. 2008). (b) from NASA's Terra Satellite Advanced Spaceborne Thermal Emission and Reflection Radiometer (ASTER).

Special Properties of Water

The unique physical and chemical properties of water exert significant control over the biogeochemistry of aquatic ecosystems. Light is attenuated as it passes through water so that the proportion of solar energy delivered to a freshwater ecosystem diminishes with depth. Typically surface waters are warmer and better lit than deep waters. In contrast to terrestrial ecosystems where the atmosphere is warmed from below (see [Chapter 2](#)), surface waters are warmed by light absorption at the surface. The density of liquid water varies with temperature, with freshwaters having their highest density at 4°C. The surface delivery of solar energy can thus generate density gradients that physically separate surface and deepwater habitats with important consequences for the biogeochemistry of lakes, reservoirs, and large rivers.

Gas Diffusion and Solubility

In [Chapter 7](#) we discussed how the slow diffusion of oxygen through water explains much of the difference between wetland and upland soil biogeochemistry. Surface waters readily exchange oxygen with the overlying atmosphere, but the oxygen content of deeper waters can become depleted when respiration exceeds the rate of O₂ diffusion. Therefore the sediments of aquatic ecosystems are often anoxic, and anaerobic metabolism dominates their biogeochemistry.

In contrast to terrestrial systems, aquatic biota are not bathed in an atmosphere of carbon dioxide. Instead, carbon dioxide dissolved in water is partitioned between dissolved CO₂ and bicarbonate and carbonate ions. Collectively these three forms are referred to as dissolved inorganic carbon, or DIC, and are often abbreviated as ΣCO₂. The relative proportion of forms depends on pH:



At pH < 4.3 most carbon dioxide is found as a dissolved gas; between 4.3 and 8.3 bicarbonate (HCO₃⁻) is the dominant form of dissolved inorganic carbon (DIC); and at pH > 8.3 carbonate (CO₃²⁻) dominates. The majority of freshwater ecosystems have pHs between 5 and 8; thus bicarbonate dominates the inorganic C content of most freshwaters.

Terrestrial–Aquatic Linkages

Hydrologic Flowpaths

Precipitation exceeds evapotranspiration across most of the land surface, and surface waters flow downhill as a result of gravity acting on the excess water. When water is supplied to the land surface in excess of evapotranspiration, excess water may leach vertically into groundwater, may be transported laterally downslope through subsurface flowpaths, or, in cases where the rate of precipitation is higher than the rate of soil infiltration (or when soils have been compacted or replaced by pavements), water may flow over the land surface downslope. Water that makes its way to a receiving water body may thus enter as *groundwater flow*, *subsurface flow*, or *overland flow* ([Figure 8.2](#)). Permanent surface waters are found wherever the land surface is below the water table ([Chapter 7](#)). When water flow from the surrounding landscape is sufficient to erode

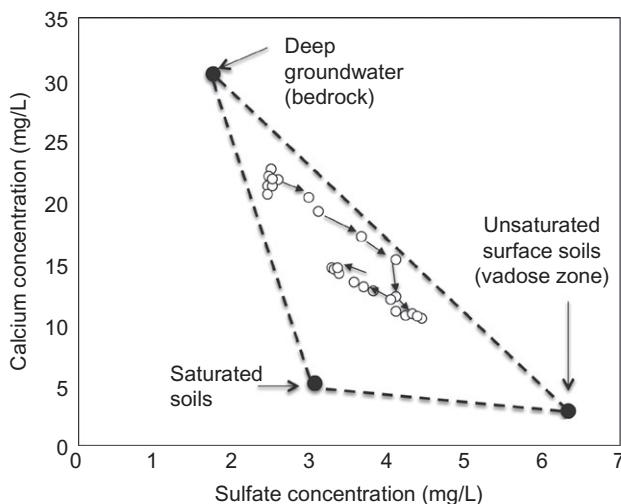


FIGURE 8.2 Using a three component model of hydrologic flowpaths in Walker Branch Watershed, changes in stream-water calcium and sulfate concentrations over the course of a March 1991 storm (open symbols) are shown relative to the average $[Ca^{2+}]$ and $[SO_4^{2-}]$ of the three contributing flowpaths. Note that as the storm progresses, stream water quickly becomes dominated by shallow vadose zone flowpaths and later by saturated soil flowpaths. Source: Modified from Mulholland 1993.

sediments and materials from the land surface, channels are formed (Montgomery and Dietrich 1988).

The route and the rate at which water moves along flowpaths will determine its chemical properties. For example, the subsurface flowpaths feeding a small stream in eastern Tennessee during summer low flow have high concentrations of Ca^{2+} because of their long residence time in carbonate bedrock, while stormwaters passing through the vadose zone² accumulate high concentrations of SO_4^{2-} deposited by acid deposition (Mulholland 1993). In contrast, water that flows through permanently saturated soils enters the stream with relatively low concentrations of both ions (Figure 8.2). Because each flowpath has a characteristic $Ca^{2+}:SO_4^{2-}$ ratio, it is possible to determine the relative contribution of each source to stream flow by measuring stream water $Ca^{2+}:SO_4^{2-}$ ratios over time.

Similar comparisons can distinguish the dominant sources of water for different aquatic ecosystems. In a comparison of stream and lake water chemistry across the Northern Highland Lake District of Wisconsin, Lottig et al. (2011) found that streams tended to have Ca^{2+} concentrations $\sim 4\times$ higher than lakes in the region, and suggested that stream flows in this region were primarily derived from groundwaters with long mineral–water contact times while lake inflows were dominated by precipitation and groundwater from short flowpaths with minimal water–mineral contact time.

As this example shows, for the majority of rivers the predominant source of water is delivery from the surrounding terrestrial landscape via groundwater and upstream headwaters, while precipitation is an important source of water to lakes, with its relative contribution increasing with lake size. At any given time, the volume of water (V) in a river or lake reflects the balance between inputs in precipitation, surface inflows, and subsurface exchange with soil waters and groundwater (as in Eq. 7.1). The residence time of water within an aquatic

² Unsaturated surface soils.

ecosystem (MRT) determines the extent to which organisms can affect the form, magnitude, and timing of element exports:

$$\text{MRT} = V / \Sigma \text{ Inputs.}$$

River inflows and precipitation are relatively easy inputs to measure; however, an accurate characterization of groundwater inputs is often difficult. Net groundwater inputs or exports are typically calculated by difference. The *benthos*, or bottom sediments, of many lakes and rivers are sites of active exchange between surface waters and groundwaters such that these net flux estimates may considerably underestimate the gross flux of groundwater exchange (Covino and McGlynn 2007, Poole et al. 2008).

The water delivered to surface waters and groundwaters from the surrounding terrestrial landscape carries with it the soluble and erodible elements characteristic of the watershed flowpaths through which it is routed. Because of this stream element fluxes have been used effectively to understand the biogeochemistry of terrestrial ecosystems (Chapters 4 and 6; Likens and Bormann 1995). For example, seasonal variation in stream NO_3^- concentrations, with high concentrations outside of and very low concentrations during the growing season, is commonly used as an indicator that nitrogen uptake by vegetation drives watershed export (e.g., Bear Brook, NH; Bernhardt et al. 2005) (Figure 8.3). Yet this effect of terrestrial vegetation on stream nutrient concentrations will only be observed in watersheds where water residence times are relatively short (<1 year; Lutz et al. 2012).

In watersheds with deep soils and long groundwater residence times, seasonal variation in N uptake by terrestrial vegetation will be insufficient to change the concentration of the large groundwater volume, and patterns of N loading to streams may be relatively constant over time. In such watersheds stream nutrient concentrations will be reduced during periods of peak biological demand within the stream. Such is the case for Walker Branch, where NO_3^- concentrations in groundwater seeps are constant year-round and the lowest annual NO_3^- concentrations are observed during spring algal blooms and following autumn litterfall (Figure 8.3; Mulholland 2004, Roberts et al. 2007). Despite draining mature deciduous forests

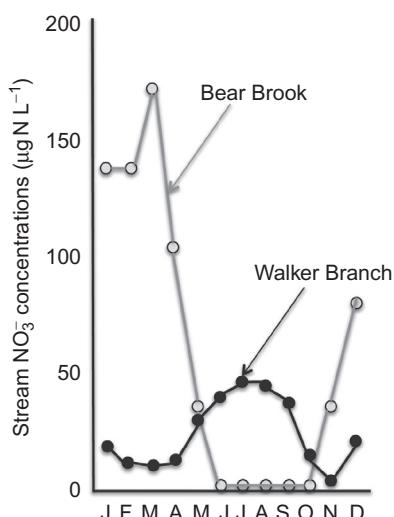


FIGURE 8.3 A comparison of average monthly stream NO_3^- concentrations for Walker Branch, Tennessee (black circles) in the Oak Ridge National Lab and for Bear Brook, New Hampshire (gray circles) in the Hubbard Brook Experimental Forest. Source: Drawn with data from Mulholland 2004 and Bernhardt et al. 2005.

and having similarly steep, rocky channels, the difference in the annual pattern of NO_3^- export from these two watersheds can be attributed primarily to differences in their hydrology.

Ion Chemistry

The ionic composition of surface waters is typically dominated by four major cations (Ca^{2+} , Mg^{2+} , Na^+ , and K^+) and four major anions (HCO_3^- , CO_3^- , SO_4^{2-} , and Cl^-) with ionic forms of N, P, Fe, and other trace elements at lower concentrations (Livingstone 1963, Meybeck 1979) (Table 4.7). The concentration and composition of these ions within surface waters can vary considerably as a function of catchment geology, the chemistry of precipitation, and the extent of evaporative concentration (Gibbs 1970). Atmospheric deposition of marine salts and acid volatiles contributes substantial amounts of base cations (Na^+ , Ca^{2+} , Mg^{2+}) or acid anions (SO_4^{2-} , NO_3^-) to catchments, many of which are transported to surface waters.

About two-thirds of the HCO_3^- in rivers is derived from the atmosphere, either directly from CO_2 or indirectly via organic decomposition and root respiration in contributing terrestrial ecosystems (Meybeck 1987, Jones and Mulholland 1998, Raymond and Cole 2003). River and lake waters are typically supersaturated with CO_2 and are a net source of CO_2 to the atmosphere (Table 8.1) (Cole et al. 1994, Quay et al. 1995, Richey et al. 2002, Mayorga

TABLE 8.1 Estimates of CO_2 Outgassing from Inland Waters

Zone-class	Area of inland waters (1000s km ²)	pCO ₂ (ppm)	Gas exchange velocity (k_{600} cm hr ⁻¹)	Areal outgassing (g C m ⁻² yr ⁻¹)	Zonal outgassing (Pg C yr ⁻¹)
	min-max	median	median	median	median
Tropical (0°–25°)					
Lakes and reservoirs	1840–1840	1900	4.0	240	0.45
Rivers (>60–100 m wide)	146–146	3600	12.3	1600	0.23
Streams (>60–100 m wide)	60–60	4300	17.2	2720	0.16
Wetlands	3080–6170	2900	2.4	240	1.12
Temperate (25°–50°)					
Lakes and reservoirs	880–1050	900	4.0	80	0.08
Rivers (>60–100 m wide)	70–84	3200	6.0	720	0.05
Streams (<60–100 m wide)	29–34	3500	20.2	2630	0.08
Wetlands	880–3530	2500	2.4	210	0.47
Boreal and Arctic (50°–90°)					
Lakes and reservoirs	80–1650	1100	4.0	130	0.11
Rivers (>60–100 m wide)	7–131	1300	6.0	260	0.02
Streams (<60–100 m wide)	3–54	1300	13.1	560	0.02
Wetlands	280–5520	2000	2.4	170	0.49
Global					
<i>Global land area</i>					
Lakes and reservoirs	2800–4540	2.1–3.4%			0.64
Rivers (>60–100 m wide)	220–360	0.2–0.3%			0.30
Streams (<60–100 m wide)	90–150	0.1–0.1%			0.26
Wetlands	4240–15 220	3.2–11.4%			2.08
All inland waters	7350–20 260	5.5–15.2%			3.28

Source: Aufdenkampe et al. 2011. Used with permission of the Ecological Society of America.

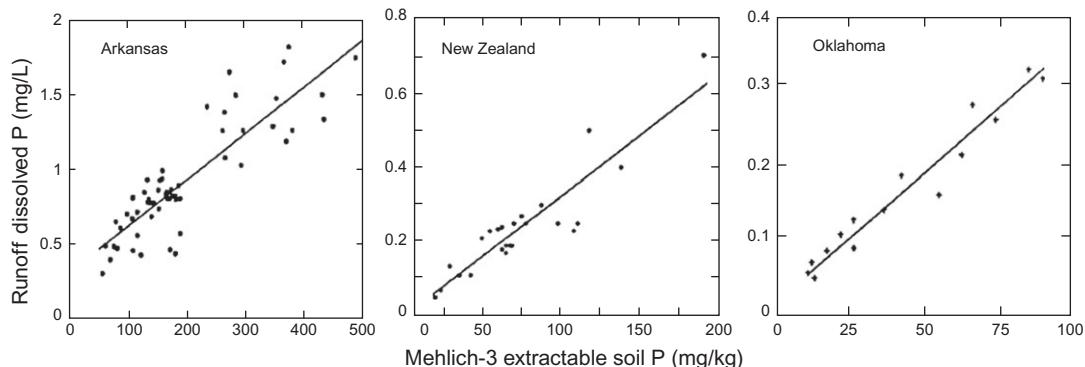


FIGURE 8.4 The nutrient content of surface waters reflect nutrient loading to their catchments. In A–C, the extractable soil phosphorus in agricultural watersheds is a good predictor of the concentrations of dissolved P in receiving streams. Source: Sharpley et al. 1996. Used with permission of the Soil and Water Conservation Society.

et al. 2005, Cole et al. 2007, Aufdenkampe et al. 2011). This is in part because of the decomposition of terrestrial organic matter within aquatic systems, but it is also due to the hydrologic transfer of terrestrially respiration CO₂ through subsurface flowpaths into aquatic ecosystems. This displaced soil respiration represents a substantial fraction of CO₂ outgassing from many freshwater ecosystems.

Inorganic nutrients leached from terrestrial ecosystems become the nutrient supply to receiving waters. Just as water in excess of evapotranspiration results in surface runoff, nutrients supplied to the land surface in excess of biological demand and soil sorption capacity result in increasing nutrient loading to receiving surface waters. The concentrations of surface water N and P rise predictably with rates of watershed nutrient loading (Figures 8.4 and 8.5; Vollenweider 1976, Meybeck 1982, Peierls et al. 1991, Sharpley et al. 1996, Boyer et al. 2002, Howarth et al. 2012). The positive correlation between watershed nutrient loading and nutrient concentrations in receiving waters is enhanced by common watershed alterations (e.g., tile drains, stormwater pipes, soil compaction, and pavement) that reduce the residence time of water in terrestrial soils and the proportion of rainfall that is transmitted to groundwater.

Aquatic algae have body mass N:P ratios³ of ~7.2 on average (although this varies between 3 and 20; Klausmeier et al. 2004), but runoff sources can vary much more widely. Runoff from unfertilized forests and fields typically has N:P mass ratios of 20 to 200 while many pollutant sources are enriched in both N and P—with raw sewage, urban stormwaters, and feedlot runoff each having N:P ratios between 1 and 10 (Downing and McCauley 1992). Both the absolute amount of N and P and their relative proportions are important drivers of freshwater biogeochemistry.

The total mass of dissolved ions in solution is its ionic strength. Ionic strength is typically reported in units of milliequivalents (mEq) of charge (Chapter 4) and is often measured in the

³ Convert N:P mass ratios to N:P molar ratios by multiplying by 2.21. The mass ratio of 7.2 is equivalent to a molar N:P ratio of 16, and the range of molar N:P ratios reported by Klausmeier et al. 2004 is 6.6 to 44.2.

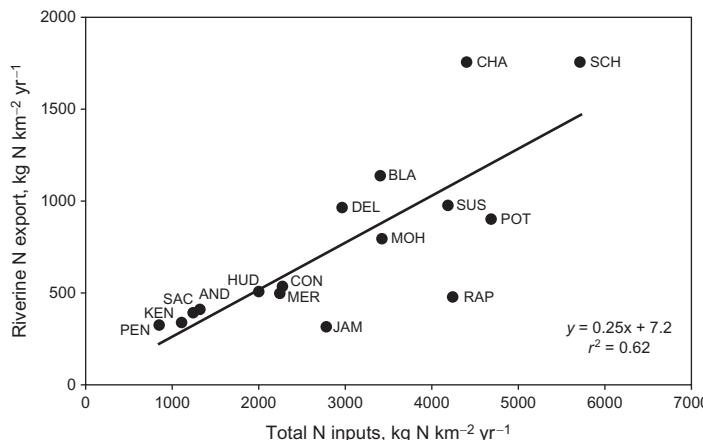


FIGURE 8.5 In an analysis of 16 large rivers in the northeastern U.S. nitrogen exports in streamflow were strongly related to the total new inputs of nitrogen to each catchment measured. From north to south, the catchments are: Penobscot (PEN), Kennebec (KEN), Androscoggin (AND), Saco (SAC), Merrimack (MER), Charles (CHA), Blackstone (BLA), Connecticut (CON), Hudson (HUD), Mohawk (MOH), Delaware (DEL), Schuylkill (SCH), Susquehanna (SUS), Potomac (POT), Rappahannock (RAP), and James (JAM). Source: From Boyer et al. 2002. Used with permission of the Ecological Society of America.

field as electrical conductivity.⁴ The ionic composition of surface waters determines their alkalinity, which is a measure of the buffering capacity of the carbonate system in water. Alkalinity is defined as

$$\text{Alkalinity} = [2\text{CO}_3^{2-} + \text{HCO}_3^- + \text{OH}^-] - \text{H}^+, \quad (8.1)$$

which is roughly equivalent to the balance of cations and anions in water, where

$$\text{Alkalinity} = [2\text{Ca}^{2+} + 2\text{Mg}^{2+} + \text{Na}^+ + \text{K}^+ + \text{NH}_4^+] - [\text{SO}_4^{2-} + \text{NO}_3^- + \text{Cl}^-]. \quad (8.2)$$

Generally, alkalinity is measured in milliequivalents per liter by titration of a water sample to a pH of 4.3. In addition to base cation exchange (as in Chapter 4), hydrogen ions (H^+) can be consumed through the protonation of organic acids (A^-) (Hedin et al. 1990) or through release of the acid cation Al^{3+} through dissolution or exchange processes (Eqs. 4.10–4.12). Thus, the titration of a water sample to a pH of 4.3 is often said to represent its *acid-neutralizing capacity* (ANC), a term used to denote the total suite of inorganic and organic constituents that allow a surface water to resist acidification (*sensu* Schindler 1988). Alkalinity and ANC are used interchangeably.

The easiest way to understand the acid-neutralizing capacity of a system is to examine its charge balance. Negatively and positively charged ions in solution must balance; thus as more acid anions (SO_4^{2-} and NO_3^-) are added to watersheds in acid rain or to surface waters as acid mine drainage, this charge must be balanced either by the accompanying protons (H^+) or by positively charged cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Al^{n+}) released through dissolution or ion exchange processes. In a well-buffered catchment receiving increasing deposition of H_2SO_4 and HNO_3 , Hinderer et al. (1998) documented no changes in H^+ in a receiving lake. Acid rain derived increases in SO_4^{2-} and NO_3^- deposition were instead accompanied by large increases in base cation concentrations in lake inflows (Figure 8.6). It is by this mechanism that acid rain can

⁴ The capacity of water to conduct electricity, typically reported in $\mu\text{S}\text{cm}^{-1}$; conductivity increases with ionic strength.

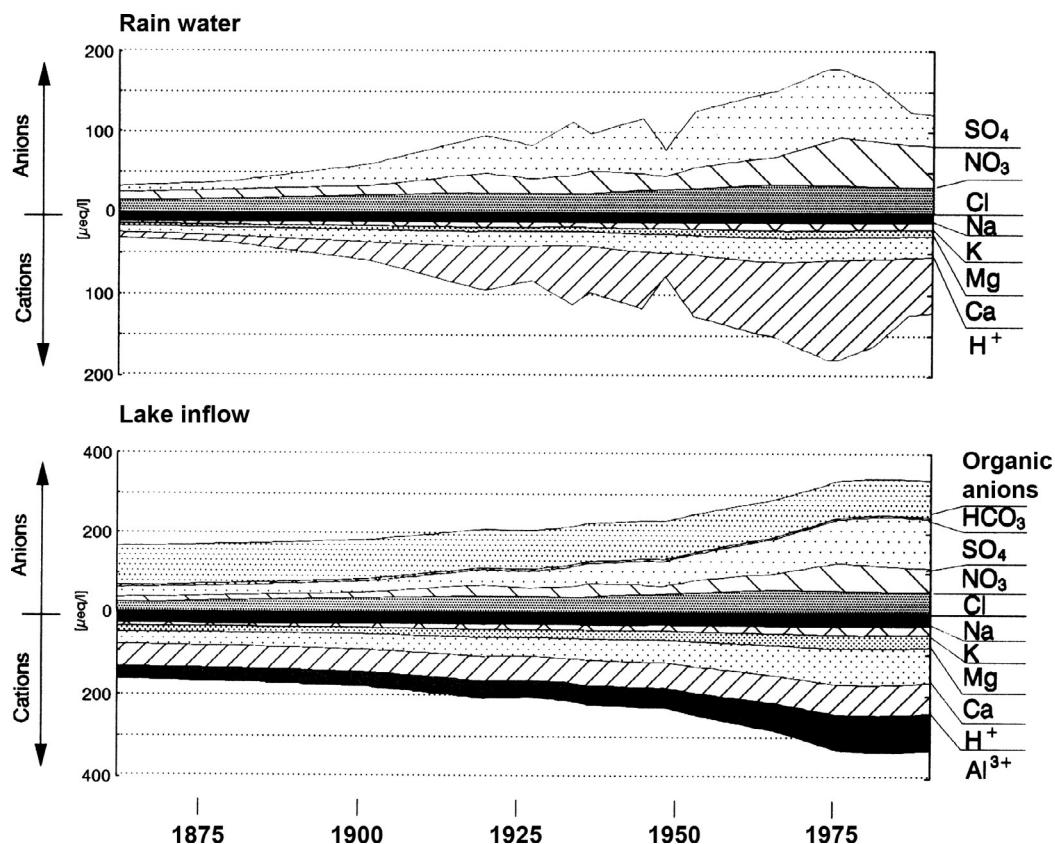


FIGURE 8.6 A paleolimnological reconstruction of changes in the charge balance of rain and lake inflow over the period of the Industrial Revolution. Note that while rainwater became more acidic over the record (increasing contribution of H⁺ and the acid anions SO₄²⁻ and NO₃⁻ through time) the interflow waters have seen little change in pH (H⁺). Instead, large increases in the concentrations of sulfate and nitrate over time have been accompanied by increases in the base cations (K⁺, Mg²⁺, Ca²⁺) and in soluble Al³⁺. Source: Hinderer *et al.* 1998.

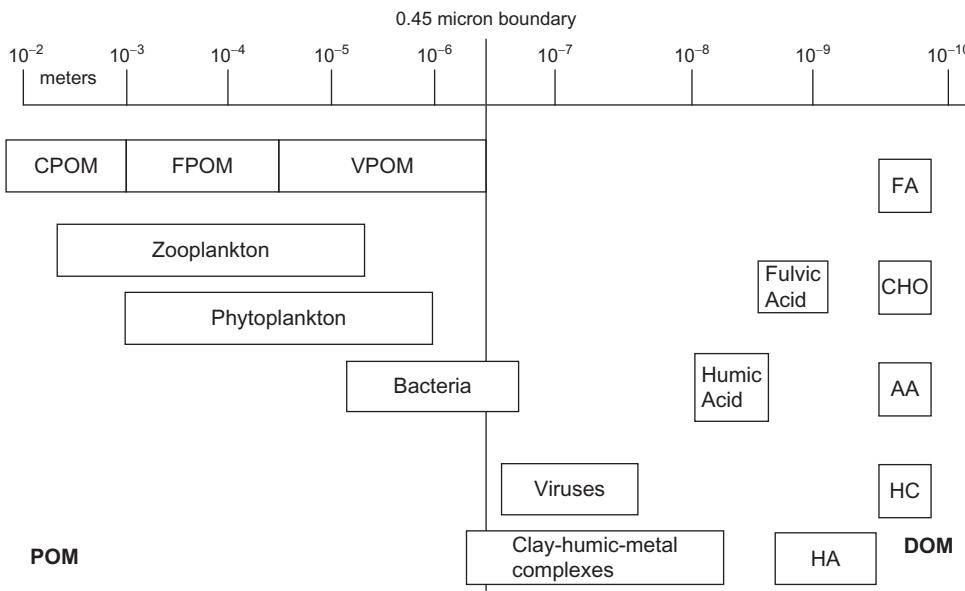
raise the alkalinity of receiving surface waters for watersheds dominated by carbonate rock (Kilham 1982, Lajewski *et al.* 2003).

In most freshwaters, ions delivered from the drainage basin are the dominant source of ANC, because the runoff of cations is usually balanced by HCO₃⁻ (Stoddard 1999). Land use change can contribute additional alkalinity through enhanced erosion of base cations from soils and enhanced weathering associated with cultivation (Edmondson and Lehman 1981, Renberg *et al.* 1993, Raymond and Cole 2003). In contrast, surface waters draining poorly buffered watersheds, where precipitation passes through soils of low cation exchange capacity and does not encounter carbonate rock, are more likely to become acidified in response to acid rain. Generally, the ANC of lakes is much lower than that of streams in the same landscape (Lottig *et al.* 2011), so lakes are more susceptible to acidification than streams.

Internal generation of alkalinity within lakes can become increasingly important as acidification progresses (Schindler 1986). Lake alkalinity increases as a result of processes that remove SO_4^{2-} or NO_3^- from the water column, including sulfate reduction, sulfate adsorption on minerals, and denitrification (Schindler 1986, Kelly et al. 1987). It is because of this that, paradoxically, both nitrate and sulfate loading to lakes can enhance their ANC (Cook and Schindler 1983). In contrast, the production of organic carbon in photosynthesis and the deposition of calcite by phytoplankton reduce alkalinity internally by consuming HCO_3^- , converting it into biomass or sediment minerals.

Organic Subsidies

Organic C that is not stored within or respiration from terrestrial ecosystems is exported hydrologically as soluble organic molecules (collectively DOM), OM attached to eroded soil minerals, or plant litter. These terrestrial carbon inputs subsidize, and often dominate, aquatic ecosystem metabolism. Allochthonous carbon inputs occur along a continuous gradient of particle sizes, with OM fractions often described by their particle size (Figure 8.7). For aquatic habitats with high edge:volume ratios (e.g., small streams, braided rivers, ponds), direct litterfall represents a substantial annual input of particulate organic material (POM), which varies greatly in particle size and availability to heterotrophs (Figure 8.7). Generally, POM is



AA = amino acids; CHO = carbohydrates; CPOM = coarse particulate organic matter;
FA = fatty acids; FPOM = fine particulate organic matter; HA = hydrophilic acids;
HC = hydrocarbons; VPOM = very fine particulate organic matter

FIGURE 8.7 Size range of particulate and dissolved organic matter and carbon compounds in natural waters. The distinction between dissolved and particulate organic carbon is operationally defined, with investigators typically considering organic molecules that pass through a 0.45-mm filter dissolved. *Source: Reproduced from Hope et al. 1994.*

subdivided into two size classes of >1 mm coarse (CPOM) and 1 mm to 53 μm fine (FPOM) particulate organic matter (Hope et al. 1994). Particulate carbon inputs to freshwaters typically represent a small fraction (about 10%) of total allochthonous carbon exports from terrestrial watersheds (Schlesinger and Melack 1981) but can represent important seasonal or pulsed inputs to small forested streams (Fisher and Likens 1972, Wallace et al. 1997, Meyer and Eggert 1998).

In larger aquatic ecosystems, dissolved organic matter (DOM) and FPOM are the dominant forms of terrestrial carbon inputs. Riverine DOM is composed of a diverse and complex array of organic molecules, much of which is derived from the surrounding terrestrial watershed (Hope et al. 1994, Findlay and Sinsabaugh 1999, Kujawinski et al. 2004, Seitzinger et al. 2005). In general, the amount of DOM delivered to rivers increases with riverflow (Figure 8.8; Schlesinger and Melack 1981) and with catchment soil C:N ratios (Aitkenhead and McDowell 2000). As for POC, this DOM represents a small loss term for C and organic nutrients from terrestrial ecosystems (Hedin et al. 1995, Neff and Asner 2001) but is a primary energy source for receiving aquatic ecosystems (Wetzel 1992, Cole et al. 2007). The majority of freshwater DOM (50–75%) is comprised of fulvic and humic acids derived from terrestrial soils and upstream wetlands (Wetzel 1992, Hope et al. 1994). It is generally assumed that this terrestrial DOC (the C contained in DOM) is only exported because it is recalcitrant, yet

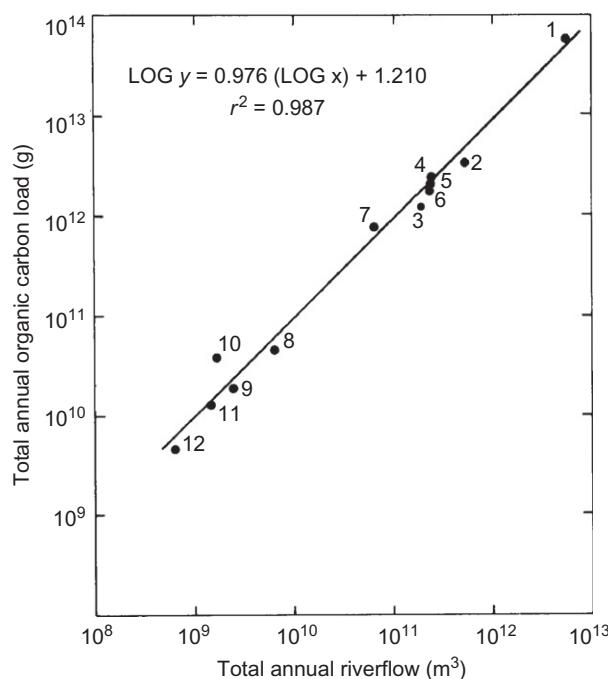


FIGURE 8.8 Total annual load of organic carbon shown as a logarithmic function of total annual riverflow for major rivers of the world. Source: From Schlesinger and Melack 1981 with a revision of the data for the St. Lawrence derived from Pocklington and Tan (1987). Used with permission of the Ecological Society of America.

Rivers 1–7 are among the 50 largest.
 1 = Amazon; 2 = Mississippi; 3 = St. Lawrence;
 4 = MacKenzie; 5 = Danube; 6 = Volga; 7 = Rhine

DOM is rapidly assimilated by freshwater biota (Brookshire et al. 2005, Kaushal and Lewis 2005, Bernhardt and McDowell 2008, Lutz et al. 2012).

There are several explanations for this seeming paradox. First, the proportion of the contributing watershed occupied by wetlands explains much of the variation in DOM across freshwater ecosystems (Chapter 7). The darkly stained organic rich waters of blackwater rivers contain high concentrations of humic and tannic acids. Recall, however, that the primary constraint on the decomposition of organic matter in wetlands is the absence of electron acceptors and the slow speed of fermentation (Chapter 7). Thus DOM that is unavailable to microbes in anoxic sediments becomes more available to freshwater microbes in the presence of oxygen, because aerobic respiration does not require these fermentation steps.

Second, freshwater ecosystems differ from terrestrial soils and wetland sediments in the availability of sunlight. Complex organic molecules within DOM can be degraded by UV exposure into a wide variety of photoproducts with enhanced lability (Wetzel 1992, Moran and Zepp 1997, Bertilsson and Tranvik 2000). Exposing field DOM samples to sunlight can substantially enhance their lability. For example, by simply exposing lake water DOM to natural sunlight prior to incubation studies, Lindell et al. (1996) were able to increase bacterial biomass growth by 83 to 175% above assays without prior sunlight exposure.

In many aquatic ecosystems the annual input of terrestrially derived C exceeds C fixation by aquatic algae and plants. In these “donor-controlled” aquatic systems, the annual rates of respiration, export, and storage of carbon may each be significantly larger than GPP, a condition that is rarely observed in terrestrial ecosystems (Delgorgio and Peters 1994, Duarte and Agusti 1998, Cole et al. 2007, Battin et al. 2009). In addition to providing organic matter to aquatic heterotrophs, terrestrial DOM released to surface waters reduces the depth of light penetration and can substantially limit freshwater ecosystem GPP (Carpenter et al. 1998, Karlsson et al. 2009). Thus, increases in DOM loading drive aquatic ecosystems toward greater heterotrophy.

In remote watersheds with little direct human influence, organic matter not only is an important source of energy, but is also the dominant form of nutrient input. Dissolved organic nitrogen (DON) dominates annual nitrogen losses from unpolluted terrestrial ecosystems (Meybeck 1982, Hedin et al. 1995, Campbell et al. 2000, Perakis and Hedin 2002, Scott et al. 2007).

Unique Features of Aquatic Food Webs

On an annual basis, most freshwater ecosystems are net heterotrophic ($NEP < 1$), and they may be classified along a gradient of heterotrophy by their P:R ratio.⁵ Generally, we expect the P:R ratio to increase as the size of lakes or rivers increases (Vannote 1980), because an aquatic ecosystem’s receipt of solar energy is a function of its surface area and because the relative importance of terrestrial carbon inputs should decline with decreasing edge:volume ratios (Figure 8.9; Finlay 2001, Alin and Johnson 2007, Staehr et al. 2012a). There are many exceptions to this general rule because aquatic ecosystems vary in light attenuation with depth and because autochthonous production may become increasingly nutrient-limited in larger aquatic ecosystems with lower terrestrial subsidies (Figure 8.9).

⁵ A widely used abbreviation for the ratio of GPP:R.

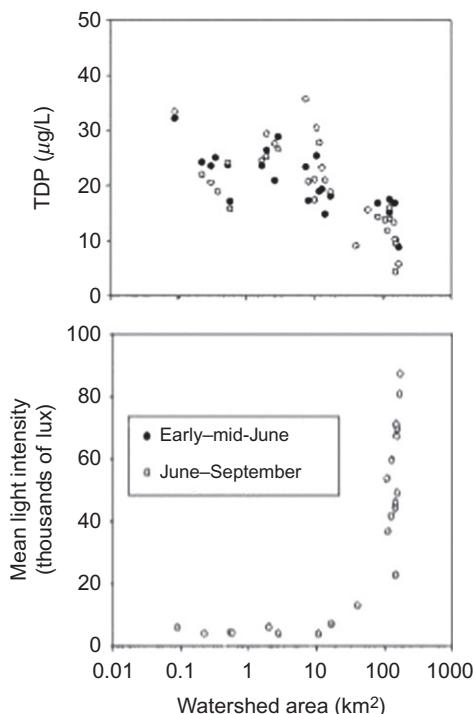


FIGURE 8.9 As the contributing watershed area increases, rivers grow wider and deeper. In a survey of streams in the Coast Range of northern California, Finlay et al. (2011) found that phosphorus availability declines and light availability increases with watershed (~stream) size. Used with permission of the Ecological Society of America.

In contrast to terrestrial food webs where autotrophs are large and the majority of grazers are small, the dominant autotrophs in most inland waters are algae, which are consumed by much larger zooplankton, grazing insects, and fish. Unlike woody plants, algae do not invest heavily in structural tissues and often the entire autotroph is consumed by herbivores. Because of this, and because terrestrial carbon inputs are a dominant energy source, the standing biomass of autotrophs in aquatic ecosystems often does not provide an effective index of ecosystem productivity as it does in terrestrial ecosystems. Rivers and lakes with low P:R ratios can still produce large numbers of insects and fish (Webster and Meyer 1997). Therefore, aquatic carbon budgets often focus instead on carbon fluxes into the biomass of higher trophic levels or may include estimates of ecosystem *secondary production*.⁶

The effort to calculate complete secondary production estimates for all heterotrophs within a system is usually cost and labor prohibitive; thus most secondary production estimates focus on the productivity of a limited subset of heterotrophs (e.g., bacterial, insect, or fish productivity). Stable isotope ratios (i.e., $\delta^{13}\text{C}$) are often used to estimate the relative contribution of autochthonous algae ($\delta^{13}\text{C} \sim$ atmospheric CO_2) compared to allochthonous inputs from land vegetation ($\delta^{13}\text{C}$ depleted relative to atmospheric CO_2) (Finlay 2001, Cole et al. 2002, McCutchan and Lewis 2002, Pace et al. 2004). Such studies have demonstrated that as aquatic ecosystems increase in P:R ratios, the $\delta^{13}\text{C}$ of herbivores becomes more similar to atmospheric CO_2 (indicative of autochthonous sources). These studies also show that allochthonous C

⁶ The formation of a living mass of heterotrophs within an ecosystem (Benke and Huryn 2006).

remains an important energy source for the aquatic food webs of well-lit rivers and lakes (Bade et al. 2007, Pace et al. 2007).

LAKES

A lake is defined simply as a permanent body of water surrounded by land. Lakes can vary in size from small permanent ponds to the world's largest lake, Lake Baikal in southeastern Siberia, which is also the oldest (25 million years) and deepest (1700 m) lake in the world. Lake Baikal alone holds 20% of the total global surface freshwater on Earth ($\sim 23,000 \text{ km}^3$; Wetzel 2001). The vast majority of natural lakes are located in the northern temperate zone in formerly glaciated landscapes. Humans are increasing global lake area through the creation of manmade lakes. According to the international commission on large dams,⁷ the global surface area of the impoundments created by 37,641 registered large reservoirs is $\sim 400,000 \text{ km}^2$. When smaller lakes and ponds are included, the estimate of the total global surface area of impoundments expands to $\sim 1,500,000 \text{ km}^2$ (St Louis et al. 2000). Lehner and Doll (2004) estimate the current global area of lakes and reservoirs at 3.2 million km^2 , or 2.4% of the total global land surface.

Lake Water Budgets and Mixing

Lakes receive water from precipitation, surface inflows, and subsurface inputs, and they export water through evaporation, surface outflows, and export to groundwaters. The residence time of water within a lake varies as a function of both lake volume and watershed area. River and groundwater inflows increase with increasing catchment size; thus lakes that are small relative to their watersheds have shorter residence times. Small lake basins that are set within large river networks may have large river inputs relative to their total volume. These "open systems" effectively function as slow-moving pools within a network of rivers and the flux of elements through the lake may be much higher than the turnover of elements within the lake itself. Most reservoirs, for example, are typically built on large rivers and are small in size relative to their watersheds and have short MRT. In contrast, some terminal lakes, such as Utah's Great Salt Lake or Siberia's Aral Sea, have nearly closed water budgets, in which inputs from riverflows, and precipitation are balanced by evaporative losses. In these closed systems, elements without a gaseous phase accumulate over time. This is why most terminal lakes are saline.

Physical stratification can occur in water bodies of sufficient depth, where less dense warm waters float above colder bottom waters. In lakes, the warmer (low-density) surface layer is referred to as the *epilimnion*, which floats atop the darker, cooler (high-density) *hypolimnion*. The zone of rapid temperature change between these two water masses is known as the thermocline or *metalimnion* (Figure 8.10). The persistence of this density-driven separation of surface and bottom water masses depends on the extent of mixing by floods and winds, the bathymetry⁸ of the water body, and the variation in external climate drivers. Many lakes

⁷ ICOLD, available from www.icold-cigb.org/.

⁸ The measurement of water depth at various places in a body of water—used to define the underwater topography of a freshwater system.

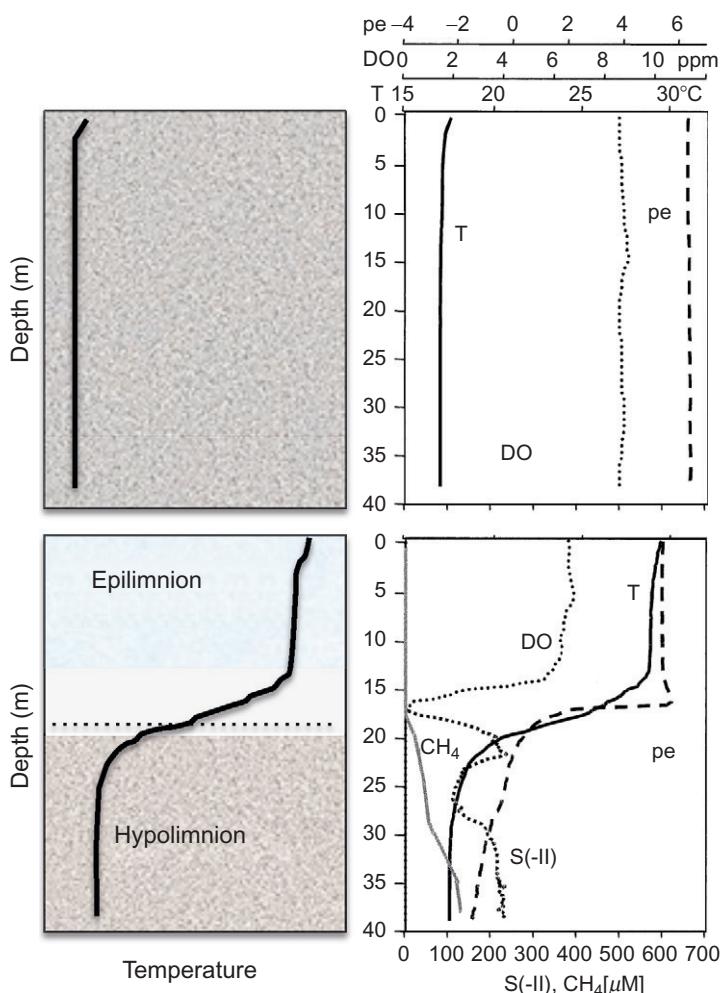


FIGURE 8.10 In the upper panels are shown a hypothetical and an actual lake temperature profile during winter (data from January). The lower panels show profiles during the period of summer stratification (data from July). The dashed line in the lower left panel indicates the lake thermocline. Depth profiles for temperature (T), dissolved oxygen (DO), redox potential (pe), total sulfide (S(-II)) and methane (CH₄) measured in the water column of Lake Kinneret in the Afro-Syrian rift valley during 1999. Source: From Eckert and Conrad 2007. Used with permission of Springer.

are seasonally stratified (Figure 8.10), and shallow lakes worldwide can have periods of stratification punctuated by storm-driven mixing events.

Very deep tropical lakes may be permanently stratified. Lake Nyos in Cameroon is a permanently stratified volcanic crater lake that receives high inputs of carbon dioxide from deep geothermal seeps. In 1986, the concentrations of CO₂ at depth became so high (~1–5 L of CO₂ per L of hypolimnetic water) that the lake explosively outgassed CO₂. As if the lake had been carbonated, the hypolimnetic and epilimnetic waters were rapidly mixed and a gas cloud was released from the lake surface. Because the nearly pure CO₂ was denser than air, the gas cloud flowed down the slopes of the ancient volcano, killing 1700 people and many livestock (Kling et al. 2005).

The depth of the epilimnion depends on air temperature, lake surface area (which determines the total capacity to absorb heat), and the extent of wind mixing (which acts to mix

surface and deep waters and reduces the density gradient). The depth of the thermocline (h) for lakes less than 5000 meters in diameter can be predicted from

$$h \cong 2.0 [\tau / (g\Delta\rho)]^{1/2} L^{1/2}, \quad (8.3)$$

where τ is the wind stress associated with late summer storms, $\Delta\rho$ is the density contrast between the epilimnion and hypolimnion typical for lakes in the region of interest at the time of maximum heat content, g is gravity, and L is the square root of the surface area of the lake (Gorham and Boyce 1989). The mixing depth of the surface layer is an important determinant of lake productivity.

Trophic Status of Lakes

Lakes are often classified into trophic categories by the level of nutrient inputs relative to lake volume (Table 8.2). Trophic status is useful in distinguishing low-productivity *oligotrophic* lakes from high-productivity *eutrophic* lakes. Oligotrophic lakes are nutrient-poor and classified as having productivity $<300 \text{ mg C m}^{-2} \text{ day}^{-1}$ (Likens 1975). Oligotrophic lakes are often of relatively recent geologic origin (e.g., postglacial) and deep, with cold hypolimnetic waters. Such lakes often show a relatively large ratio between lake area and drainage area, and a long mean residence time for water (Dingman and Johnson 1971). In large lakes within small catchments, nutrient inputs are dominated by precipitation and terrestrial organic matter with a low nutrient content and a high N:P ratio.

Eutrophic lakes are dominated by inorganic nutrient inputs from the surrounding watershed, and they typically have lower N:P ratios as a result of higher P inputs from runoff, with the most eutrophic lakes having a TN:TP ratio less than 10. These nutrient-rich lakes are often shallow, with warm, highly productive waters. Sedimentation will eventually convert the physical state of many oligotrophic lakes to shallow, eutrophic conditions, so these concepts have also been used to describe lake age. However, in most cases, nutrient status remains the most useful criterion to distinguish between oligotrophic and eutrophic conditions (Table 8.2). Highly colored lakes are sometimes classified separately as dystrophic lakes, since as DOM increases, light penetration is reduced (Thienemann 1921), and algae in such lakes are likely to be light rather than nutrient limited (Karlsson et al. 2009).

Carbon Cycling in Lakes

The earliest efforts to understand carbon cycling in lakes involved carbon mass-balance studies in which investigators attempted to quantify all inputs and outputs of carbon over the course of a year (e.g., Richey et al. 1978). The idealized organic carbon budget for a lake can be expressed as

$$\Delta\text{Storage} = [\text{Inputs}] - [\text{Outputs}] \quad (8.4)$$

$$\Delta S = [P_W + P_B + A_I] - [R_W + R_B + B + H_O], \quad (8.5)$$

where ΔS = change in C storage within the lake, P_W = water column photosynthesis, P_B = benthic photosynthesis, A_I = allochthonous input of organic carbon, R_W = water column respiration, R_B = benthic respiration, B = permanent burial in sediments, and H_O = hydrologic loss of organic carbon from outflows.

TABLE 8.2 Lake Classification by Trophic Status

Trophic type	Mean primary productivity (mg C m ⁻² d ⁻¹)	Phytoplankton biomass (mg C m ⁻³)	Chlorophyll a (mg m ⁻³)	Light extinction coefficient (nm ⁻¹)	Total Organic Carbon (mg L ⁻¹)	Total P (µg L ⁻¹)	Total N (µg L ⁻¹)
Ultra-oligotrophic	<50	<50	0.01–0.05	0.03–0.08		<1–5	<1–250
Oligotrophic	50–300	20–100	0.3–3	0.05–1	<1–3		
Oligomesotrophic						5–10	250–600
Mesotrophic	250–1000	100–300	2–15	0.1–2.0	<1–5		
Mesoeutrophic						10–30	500–1100
Eutrophic	>1000	>300	10–500	0.5–4.0	5–30		
Hypereutrophic						30–>5000	500–>15,000
Dystrophic	<50–500	<50–200	0.1–10	1.0–4.0	3–30	<1–10	<1–500

Source: Modified from Wetzel 2001 ([Table 15.13](#), p. 389).

Studies of the production and fate of organic carbon are useful in understanding the overall biogeochemistry of lakes. Rich and Wetzel (1978) present a carbon budget for Lawrence Lake, a small shallow lake in Michigan in which rooted aquatic plants (macrophytes) contribute ~51.3% of annual autochthonous net primary production while phytoplankton contribute only 25.4% (Table 8.3). In contrast, Jordan and Likens (1975) showed that phytoplankton accounted for ~90% of annual NPP in Mirror Lake, a deep oligotrophic lake in New Hampshire. In Lawrence Lake, with its abundant macrophytes, NPP exceeds total ecosystem respiration (R), while in Mirror Lake NPP and R are equivalent. The more productive shallow lake has higher rates of carbon burial in sediments and exports more DOC (the C contained within DOM) in outflow than seen for Mirror Lake.

TABLE 8.3 Organic Matter Budgets for Lawrence Lake in Michigan and Mirror Lake in New Hampshire

Inputs	Lawrence Lake, MI		Mirror Lake, NH	
	g C m ⁻² yr ⁻¹	Inputs	g C m ⁻² yr ⁻¹	Inputs
Net primary production (NPP)	191.4	88%	87.5	83%
POC				
Phytoplankton	43.3	20%	78.5	74%
Epiphytic algae	37.9	18%	2.2	2%
Epipelagic algae	2	1%	—	—
Macrophytes	87.9	41%	2.8	3%
Bacterial CO ₂ fixation	—	—	4	4%
DOC released by macrophytes				
Littoral	5.5	3%	—	—
Pelagic	14.7	7%	—	—
Imports	25.1	12%	17.93	17%
POC	4.1	2%	6.63	6%
DOC	21	10%	11.3	11%
Total available organic inputs	216.5		105.43	
Outputs	g C m ⁻² yr ⁻¹	Outputs	g C m ⁻² yr ⁻¹	Inputs
Respiration	159.7	74%	87.53	83%
Benthic	117.5	55%	43.13	41%
Water column	42.2	20%	44.4	42%
C Storage in Sediments	16.8	8%	7.6	7%
Exports	38.6	18%	10.2	10%
POC	2.8	1%	1.05	1%
DOC	35.8	17%	9.15	9%
Total removal of carbon	215.1		105.33	

Sources: Rich and Wetzel 1978; Jordan and Likens 1975.

Primary Production in Lakes

When air temperatures are cold or surface winds maintain a well-mixed water column (e.g., Figure 8.3a), phytoplankton, the free-floating algae that contribute most of the net production in large lakes, are frequently transported out of the well-lit surface waters (or photic zone). In deeper waters low light limits algal productivity. Light attenuates rapidly through the lake water column; the depth at which light levels are insufficient to support photosynthesis in excess of respiration is known as the *compensation depth*. During periods of stratification, phytoplankton are confined to the epilimnion. If the thermocline is above the compensation depth, phytoplankton will have sufficient light to meet their respiratory demands and productivity is likely to be limited by factors other than light.

During stratification, nutrients often limit productivity. Nutrients incorporated into biomass in the surface layers sink out of the epilimnion in the form of dead organisms and fecal pellets so that during prolonged periods of stratification surface waters become increasingly depleted in nutrients. This sinking organic matter is decomposed by heterotrophs in the hypolimnion, enriching bottom waters with inorganic nutrients and resulting in a depletion of oxygen and lower redox potential (Figure 8.10). Nutrients typically accumulate in the hypolimnion because heterotrophs in the dark, cool bottom waters are ultimately limited by the supply of fixed carbon from the lake surface. Periods of mixing bring these hypolimnetic nutrients back into contact with sunlight where they can stimulate phytoplankton growth. The spring algal blooms characteristic of many temperate lakes occur at the onset of seasonal stratification since at this time, nutrients are mixed throughout the lake water volume and thermal stratification constrains floating algae within the well-lit photic zone.

Measuring Primary Productivity

Rooted and floating aquatic plants in shallow lakes or along the margins of deep lakes contribute to lake productivity (Table 8.3), but their importance diminishes with lake size and depth. In deep lakes, the dominant primary producers are phytoplankton. Historically, methods for assessing net primary production in lakes ignored benthic productivity and used bottle assays to estimate lake NPP. Two different bottle assay approaches are still widely used to measure NPP or to assess algal nutrient limitation in lakes (Wetzel and Likens 2000). In the first method, lake water is placed in gas-tight glass bottles that are either clear or opaque to sunlight. Bottles are incubated (often in the lake itself) and researchers measure changes in oxygen concentration over time in both the light and dark bottles. In the light bottles, photosynthesis, photorespiration, and heterotrophic respiration co-occur. An increase in O₂ concentration over the course of the incubation is taken as the equivalent of net primary production—that is, photosynthesis in excess of respiration by the plankton. Over the same period, the reduction of O₂ in the dark bottles is taken as a measure of autotrophic and heterotrophic respiration. By summing the O₂ consumption of the dark bottles to the O₂ production in the light bottles, researchers can estimate gross primary production.

$$\text{NPP} = ([\text{O}_2]_{t2} - [\text{O}_2]_{t1})_{\text{LIGHT}} \quad (8.6)$$

$$\text{GPP} = ([\text{O}_2]_{t2} - [\text{O}_2]_{t1})_{\text{LIGHT}} - ([\text{O}_2]_{t2} - [\text{O}_2]_{t1})_{\text{DARK}}. \quad (8.7)$$

Although widely used and inexpensive, these bottle assays suffer from a series of experimental artifacts (reviewed by Peterson 1980). The sensitivity of most oxygen measurements

is relatively low, so incubations must be of long duration in order to ensure measurable changes. Confining a small water sample in a bottle for long periods can exacerbate nutrient or CO₂ limitation of algal growth that may not occur in the well-mixed surface waters of a large lake. This method also makes a simplifying assumption that O₂ consumption in the light and dark bottles is equivalent.

A refinement of the classic light versus dark bottle approach uses ¹⁴C-labeled DIC that is added to light bottles to measure the incorporation of ¹⁴C into biomass over the course of short-term incubations (Wetzel and Likens 2000). Because ¹⁴C can be measured with high precision, these assays can be conducted quickly and thus avoid many of the bottle artifacts mentioned earlier. Because the pH of most surface waters is in the range of 4.3 to 8.3, typically these assays add radiolabeled bicarbonate, frequently as NaH¹⁴CO₃, to a plankton sample. After a short incubation period, the sample is filtered and the accumulation of ¹⁴C in the solids collected on the filter is determined with a scintillation counter.

A major shortcoming of the ¹⁴C method is that any DIC fixed and subsequently released from an algal cell as DOC (as exudates or cell contents lysed during zooplankton feeding) is not captured on the filter and thus not counted as part of carbon fixation. Filters may also not effectively capture very small picoplankton that can be an important component of productivity in some surface waters. When the two methods are compared side by side, the oxygen method typically gives higher values for net primary production than does the ¹⁴C method. The ¹⁴C method also provides no estimate of respiration, so it is not possible to use this method to estimate gross primary productivity. Each bottle method provides an instantaneous assessment of net primary production, but in order to determine annual production, or to make comparisons of productivity across lakes, it is necessary to repeat the assays many times over the course of a year.

With the development of field-deployable oxygen sensors, limnologists increasingly use diel variation in dissolved oxygen concentrations to calculate net ecosystem production at the ecosystem-scale (Staehr et al. 2010a, 2012b). In concept, such measurements are similar to estimates of NEP derived from eddy-flux tower measurements of terrestrial ecosystems ([Chapter 5](#)). To estimate lake NEP, an oxygen sensor is suspended from a floating buoy, usually in the center of a lake. Changes in oxygen concentration between measurements (often 5 to 30 minutes apart) are used to calculate instantaneous oxygen production (by photosynthesis) or consumption (by respiration) ([Figure 8.11](#)). At each time step, changes in oxygen concentration must be corrected for the physical processes of oxygen exchange with the overlying atmosphere:

$$\text{NEP}_{\Delta t} = \Delta O_2 - D/Z_{\text{mix}}, \quad (8.8)$$

where ΔO_2 (mmol O₂ m⁻³ time interval⁻¹) is change in oxygen concentration over the time interval, D is the physical exchange with the atmosphere over the time interval, and Z_{mix} is the mixing depth of the lake during the interval.

Atmospheric exchange (D) is calculated as

$$D = k (O_{2\text{obs}} - O_{2\text{sat}}), \quad (8.9)$$

where O_{2obs} is the actual oxygen concentration, O_{2sat} is the oxygen concentration in equilibrium with the atmosphere at the ambient temperature, and k is the oxygen exchange coefficient calculated for each time step. The gas exchange coefficient, k, can be estimated directly by measuring exchange of a gas tracer (e.g., sulfur hexafluoride or propane; Cole and

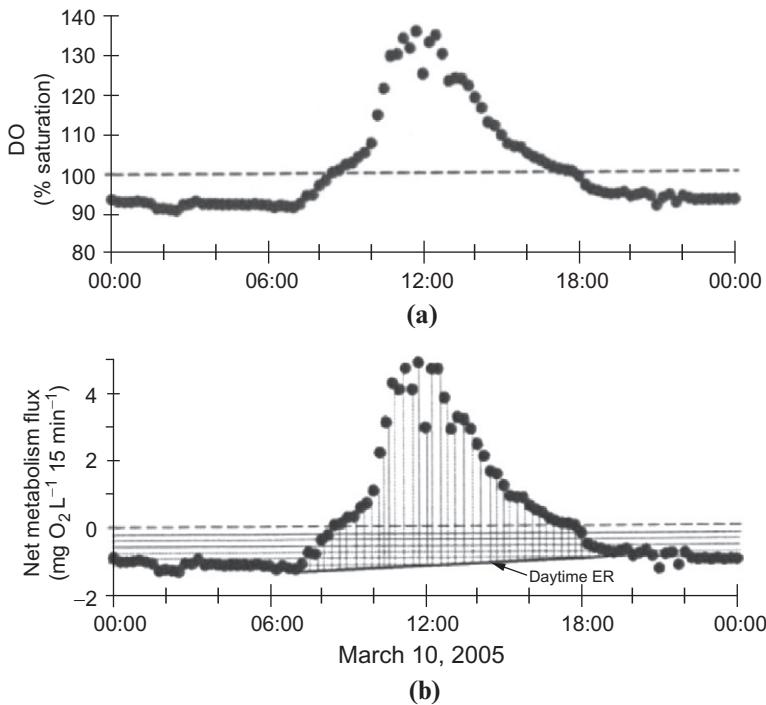


FIGURE 8.11 GPP and ER are typically derived from diel oxygen concentrations like the one shown here for a small stream in Tennessee. Diel profiles of (a) percent saturation of DO and (b) net metabolism flux showing the area representing gross primary production (GPP, vertical lines) and ecosystem respiration (ER, horizontal lines). Dashed lines indicate 100% saturation in (a) and a net metabolism flux of zero in (b). The solid line in (b) indicates the interpolated values of daytime ER. Data are from March 2005 in Walker Branch, Tennessee. Source: From Roberts et al. 2007. Used with permission of Springer.

Caraco 1998) and using the ratio of Schmidt numbers⁹ between the tracer gas and oxygen to predict O_2 diffusion across the air–water interface (Jahne et al. 1987). The sum of oxygen produced over the course of daylight hours is used as an estimate of NEP. Using this method, nighttime oxygen consumption (from 1 hour past sunset to 1 hour prior to sunrise) is used to represent ecosystem respiration:

$$\text{ER} = \text{average nighttime R} \times 24 \text{ hours.} \quad (8.10)$$

The estimate of ER is added to daytime estimates of oxygen production to calculate a cumulative diel estimate of GPP. This technique makes the simplifying assumption that daytime respiration rates are similar to nighttime rates and is thus likely to provide a conservative estimate of GPP (Staehr et al. 2010a). By measuring the isotopic composition of atmospheric and dissolved O_2 and the rate of exchange of O_2 between air and water it is possible to gain more accurate estimates of daytime respiration (Quay et al. 1995) and thus better estimates of

⁹ Each gas can be characterized by its Schmidt number (a ratio of momentum diffusivity to mass diffusivity). Exchange coefficients measured for inert tracer gases can be converted into exchange coefficients for oxygen using the ratio of Schmidt numbers for the two gases.

NPP and NEP. A major constraint on sensor-derived estimates of lake NPP is the difficulty of determining the volume of water from which the diel oxygen signal is derived, and thus the appropriate scaling term for extrapolation. The difficulty in attributing metabolism to the appropriate lake volume is similar to the challenge of attributing eddy-flux measurements to the appropriate area of terrestrial vegetation (Chapter 5).

Nutrient Limitation of Lake NPP

As for terrestrial systems, growing season length is an important constraint on lake NPP. While peak productivity in arctic lakes may reach that of temperate and tropical lakes, arctic lake phytoplankton have a far shorter growing season. In compilations of annual NPP estimates for low nutrient lakes, Wetzel (2001) and Alin and Johnson (2007) each found the lowest annual NPP in arctic, antarctic, and alpine lakes and the highest in tropical lakes (Figure 8.12). Lake size is also an important determinant of productivity since lake area is positively correlated with wind exposure and mixing depth and negatively correlated with nutrient and DOC inputs per water volume (Brylinski and Mann 1973, Duarte and Kalff 1989, Fee et al. 1994). The drainage ratio of a lake (the ratio of catchment area to lake area) is positively related to the external inputs of nutrients, DOC, and CO₂ (Gergel et al. 1999) and thus to increasing primary productivity (Alin and Johnson 2007). Put simply, the greater the edge:volume ratio, the larger the influence of terrestrial vegetation and soils on the biogeochemistry of a lake and thus the greater the supply of nutrients from the landscape. Larger lakes, with longer residence times and low edge:volume ratios, are more dependent on internal mineralization to supply the nutrients for new productivity.

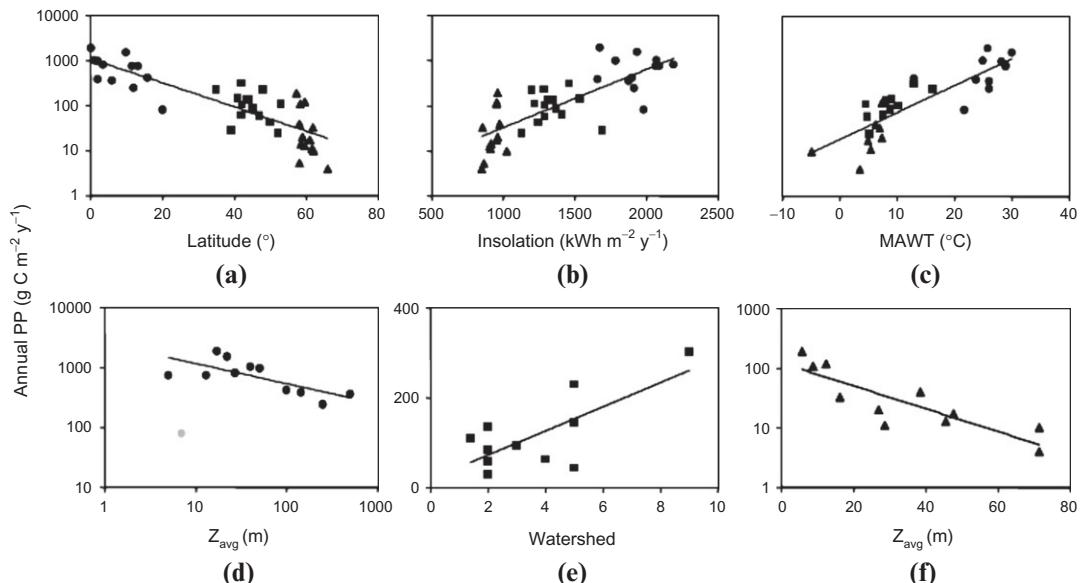


FIGURE 8.12 Global-scale relationships between annual primary production and the environmental variables: (a) latitude, (b) incident solar radiation, (c) mean annual water temperature, (d) depth, (e) watershed to lake area ratio, and (f) average lake depth (z). Source: From Alin and Johnson 2007. Used with permission of the American Geophysical Union.

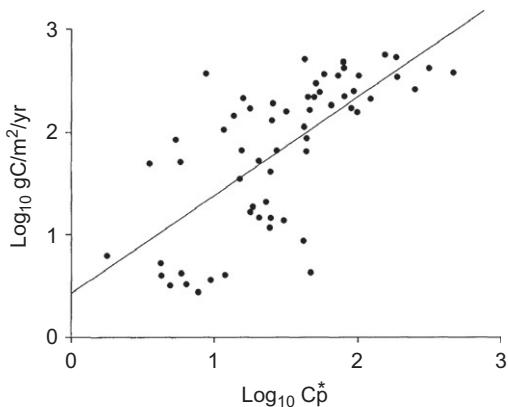


FIGURE 8.13 The relationship between net primary production and the phosphorus concentration of lakes of the world is fit by the line $\log [P] = 0.83 \log \text{NPP} + 0.56$ ($r=0.69$). Schindler excluded lakes with N:P ratios in inputs of <5:1 from this analysis. Source: Adapted with permission from Schindler (1978).

Within biomes, lakes receiving higher supplies of nitrogen and phosphorus (from urban or agricultural pollution) support greater phytoplankton NPP than do lakes with low nutrient loading (Wetzel 2001). In a series of influential studies in the 1970s, researchers consistently demonstrated that the variation in lake NPP or algal biomass across temperate lakes was closely associated with the lake concentration or annual loading rates of phosphorus (Schindler 1974, Vollenweider 1976, Smith 1983, Correll 1998; Figure 8.13). Phosphorus concentrations in the epilimnion are directly related to the total chlorophyll content of the water column, which is directly correlated to net primary productivity (Schindler 1978).

In 1974, David Schindler published the results of a whole-lake experiment in which a small hourglass-shaped lake in the Experimental Lakes Area of Canada was fertilized (Schindler 1974). The two basins of Lake 226 were split in half with a plastic curtain. Both sides of the lake received sucrose and nitrogen additions, but only one basin received phosphate addition. A large algal bloom erupted in the basin receiving C, N, and P, while the water remained clear and algal biomass low in the basin receiving only C and N (Schindler 1974). The aerial photo of this experimental effect (Figure 1.5) is undoubtedly one of the most influential environmental science photographs ever taken. This experimental demonstration and other data from lake ecosystems convinced regulators to remove phosphates from detergents, dramatically reducing municipal P loading to surface waters.

Despite the limited availability of phosphorus in surface waters, we might expect that, as for land vegetation, processes such as denitrification might limit the nitrogen supply in lakes. In a series of studies conducted over the last two decades, nitrogen limitation or N and P co-limitation of lake phytoplankton is frequently reported (Goldman 1988, Morris and Lewis 1988, Downing and McCauley 1992, Elser et al. 2009). Authors of several of these studies have suggested that the preponderance of evidence for P limitation of lake productivity from research throughout the 1970s may be a consequence of making such measurements in areas of North America and Canada that had experienced decades of excess atmospheric nitrogen deposition (Chapter 6) that over time increased the N:P ratio of nutrient inputs to lakes (Elser et al. 2009). Other authors argue that sewage and fertilizer inputs to lakes are typically phosphorus rich and thus may lower the N:P ratio of inputs and enhance internal stores of phosphorus, thereby increasing the potential for N limitation (Downing and McCauley 1992).

While lake phytoplankton productivity may be N, N + P, or P limited, there are several fundamental reasons to expect increases in phosphorus loading to play a disproportionate role in cultural eutrophication (Schindler 1977, Schindler et al. 2008). When phytoplankton grow in limited supplies of nitrogen, the prevalence of nitrogen-fixing algae, primarily cyanobacteria, typically increases, adding nitrogen through fixation and raising the N:P ratio, (compare to [Figure 6.4](#)). In a literature synthesis, Howarth et al. (1988) found that significant nitrogen fixation by lake phytoplankton occurred only when lake N:P ratios were below 16. A subsequent analysis by Smith (1990) suggested that total P loading, rather than N:P ratios, was the best predictor of N fixation rates across lakes globally. When phosphorus is added as a pollutant with low N:P, the algal community shifts to species of blue-green algae and primary productivity increases, with nitrogen inputs through fixation tending to maintain a phosphorus shortage for the growth and photosynthesis of phytoplankton (Smith 1982).

Håkanson et al. (2007) suggest that below N:P ratios of 15, the N:P ratio is a good predictor of cyanobacterial biomass but that in lakes with TN:TP ratios greater than 15, cyanobacterial biomass can be predicted from total phosphorus concentrations or loading alone ([Figure 8.14](#)). With high P loading, nitrogen fixation can supply up to 82% of the nitrogen input to the phytoplankton community (Howarth et al. 1988). Thus lake phytoplankton have a mechanism for acquiring additional inputs of nitrogen, but there is no equivalent biogeochemical process that can increase the supply of phosphorus in lakes when it is in short supply (Schindler 1977).

When the input of phosphorus to a lake ceases, blue-green algae typically decrease in importance and algal productivity declines (Edmondson and Lehman 1981, Schindler et al. 2008). A particularly influential demonstration of the potential for eutrophic lakes to recover following P reductions was recorded in Lake Washington (Edmondson and Lehman 1981).

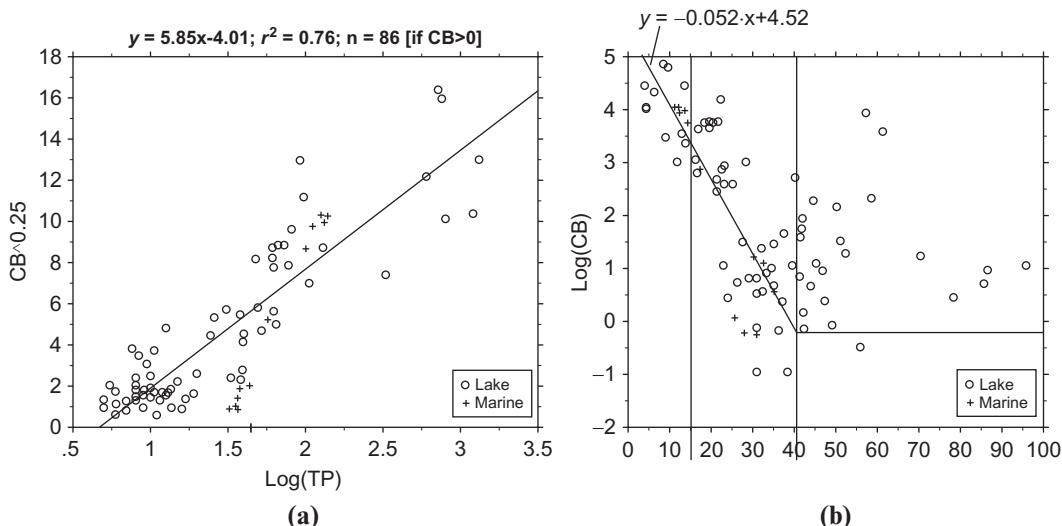


FIGURE 8.14 (a) The relationship between cyanobacterial biomass (CB) and total phosphorus concentrations across 86 lakes and coastal estuaries for which $CB > 0$. (b) The relationship between $\text{log } CB$ and the TN:TP molar ratio. The regression equation given is for systems with TN:TP ratios < 15 . Source: From Håkanson et al. 2007.

Until 1967 the City of Seattle disposed of its sewage directly in Lake Washington; after that year sewage was diverted to the ocean instead of this closed basin. The resulting decline in noxious algal blooms in the lake provided strong evidence for P limitation of lake productivity. The time required for this recovery from eutrophication depends on the extent to which historic P inputs are mineralized and released from lake sediments (Genkai-Kato and Carpenter 2005, Mehner et al. 2008). Historic nitrogen loading is less problematic because significant quantities of nitrogen may be lost from lake sediments through denitrification (McCrackin and Elser 2012). Because of this difference in the persistence of N and P pollution in lakes, Schindler et al. (2008) argued that efforts to reduce N loading are likely to be less effective at reversing cultural eutrophication than reducing P inputs. In contrast, preventing future eutrophication in unpolluted lakes will require reductions in nitrogen as well as phosphorus loading (Conley et al. 2009b, Lewis et al. 2011).

Micronutrient Limitation

The potential for lake phytoplankton to respond to increasing N and P loading with enhanced NPP may be constrained by micronutrient availability. When phosphorus is added to nutrient-poor lakes, the growth of diatoms, single-celled algae with silicate cell walls, may reduce the concentrations of silica to low levels so that diatoms are competitively replaced by nonsiliceous green algae or cyanobacteria (Schelske and Stoermer 1971, Tilman et al. 1986). Similarly, enhanced loading of phosphorus may lead to Fe limitation in clearwater oligotrophic lakes (Sterner et al. 2004). All phytoplankton require Fe for photosynthesis (see [Chapter 2](#)) so Fe limitation may reduce whole ecosystem NPP. Because cyanobacteria typically have higher Fe requirements than eukaryotic algae (Morton and Lee 1974, Brand 1991), and N₂ fixation requires high Fe uptake (Murphy et al. 1976, Glass et al. 2009), increased competition for Fe could also lead to a decline in cyanobacteria or rates of N fixation (Molot et al. 2010). Changes in micronutrient loading or nutrient:micronutrient ratios may lead to more subtle changes in algal community structure. Titman (1976) showed that slight differences in the ratio of silica to phosphorus altered the outcome of competition between two dominant species of diatoms (*Asterionella* and *Cyclotella*). Other studies have shown that N fixation rates can be suppressed by the addition of trace micronutrients, such as Fe (Vrede and Tranvik 2006) or Cu (Horne and Goldman 1974).

Light Limitation of NPP

Much of the research on lake nutrient limitation has been conducted in clearwater lakes without high concentrations of dissolved organic carbon. In lakes stained with DOC, light is the primary limitation on productivity. Across a series of lakes in northern Sweden that ranged in DOC concentrations from about 10 to 100 mg L⁻¹, Ask et al. (2012) found that higher DOC was negatively correlated with GPP and positively correlated with ecosystem respiration (ER) ([Figure 8.15](#)). Similarly, Karlsson et al. (2009) found that phosphorus concentrations were negatively correlated with both primary productivity and the secondary production of fish in 12 nutrient-poor and DOC-rich Swedish lakes. Across these lakes, light availability was a much better predictor of secondary production ([Figure 8.15](#)). For dystrophic lakes (refer to [Table 8.3](#)), nutrient inputs are unlikely to stimulate algal blooms, but may instead enhance the rates of DOM decomposition and CO₂ release (Pace et al. 2007).

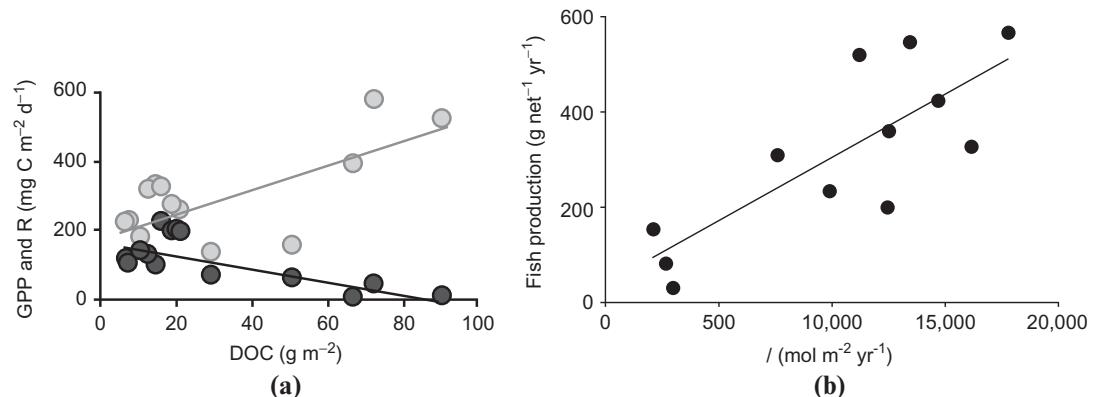


FIGURE 8.15 Light limitation of primary and secondary production in Swedish lakes. (a) Whole-lake gross primary production (GPP, dark gray circles) and respiration (R, light gray circles) for 15 lakes in northern Sweden. (b) Fish production as a function of the annual light climate (I , representing the mean PAR in the whole-lake volume during the ice-free period) for 12 lakes in northern Sweden ($r_2=0.63$, $p=0.002$). Sources: (a) From Ask et al. 2012, used with permission of American Geophysical Union; (b) from Karlsson et al. 2009, used with permission of Nature Publishing Group.

Herbivore Control of NPP

Much of the algal biomass produced by lake phytoplankton is consumed by zooplankton, and changes in the food web can affect whole ecosystem NPP. More productive lakes typically produce higher fish biomass per unit volume (Melack 1976, Karlsson et al. 2009). This trophic linkage works in more than one direction: While nutrient and light availability may increase the productivity of higher trophic levels (“bottom-up” control), the abundance of top predators can influence the intensity of herbivory and alter NPP (“top-down” control; Carpenter et al. 1985). For example, in a series of whole-lake experiments, Carpenter et al. (2001) showed that adding pike to a lake reduced its NPP by a factor of 3 compared to a nearby lake that lacked piscivorous fish. Piscivores, by consuming zooplanktivorous fish, release herbivorous zooplankton from predation and allow them to substantially reduce standing stocks of phytoplankton. This effect has been termed the “trophic cascade.”

In a formal meta-analysis of 54 experimental manipulations of top predators in lakes and ponds, Brett and Goldman (1996) found that nearly all such experimental additions of piscivores led to declines in zooplanktivore biomass and increases in phytoplankton. Not all lake manipulations of top predators, however, have led to changes in NPP (Elser et al. 1998, MacKay and Elser 1998) and it has been suggested that food web interactions are less likely to affect ecosystem productivity in ultraoligotrophic lakes where algae are extremely nutrient limited and in highly eutrophic lakes where algal growth rates are high and algal communities are dominated by unpalatable species (Kitchell and Carpenter 1993).

The Fate of Organic Carbon in Lakes

Organic carbon delivered to lakes from the surrounding catchment or fixed by lake autotrophs may be incorporated into aquatic consumer biomass, respired, sequestered in lake sediments, or transported downstream (Cole and Caraco 2001). Because the sediments of lake

bottoms are frequently anoxic, organic material that reaches the lake bed will decompose slowly (Chapter 7) and lakes typically accumulate sediment carbon over time. In a literature synthesis Einsele et al. (2001) estimated that throughout the Holocene the amount of carbon stored in lake sediments globally is ~ 820 Pg, with small lakes ($< 500 \text{ km}^2$) containing about 70% of this total. Over geologic time lake basins fill with sediments and organic material. This can happen very quickly in manmade reservoirs where inputs of river sediment and organic materials are high (Downing et al. 2006).

Cole et al. (2007) compiled estimates of global lake C storage from the literature, which ranged from 0.03 to 0.07 Pg C yr $^{-1}$ (midrange 0.05 Pg C yr $^{-1}$; Mulholland and Elwood 1982, Meybeck 1993, Dean and Gorham 1998, Stallard 1998, Einsele et al. 2001; Table 8.4). While this global rate is minuscule in comparison with the annual C storage in terrestrial vegetation and soils (about 1.3 Pg C yr $^{-1}$) or in the oceans (1.9 Pg C yr $^{-1}$; Sundquist 1993), it is roughly equivalent to the annual organic C storage in marine sediments (~ 0.12 Pg y; Sarmiento and Sundquist 1992) but occurs within lakes that occupy an area equivalent to only 2% of the ocean area. When lake carbon accumulation is corrected for area, long-term carbon burial rates range from 4.5 to 14 g C m $^{-2}$ y $^{-1}$ (Dean and Gorham 1998, Stallard 1998), which is higher than the long-term soil C accumulation rates estimated for most terrestrial soils (Schlesinger 1990; Figure 5.5).

Carbon burial in lake sediments is predicted to increase with eutrophication as a result of more constant and severe oxygen depletion of sediments coupled with high autochthonous production (Hutchinson 1938, Downing et al. 2008). Examining several lakes, Hutchinson (1938) suggested that the rate of depletion of O₂ in the hypolimnion during seasonal stratification was related to the productivity of the overlying waters. Highly productive waters should contribute large quantities of organic carbon for respiration in the hypolimnion, which is seasonally isolated from sources of oxygen.

The areal hypolimnetic oxygen deficit (abbreviated as AHOD) is a useful concept, but attempts to predict AHOD as a function of nutrient loading have been controversial. Cornett

TABLE 8.4 Carbon Burial Rates in Lakes and Impoundments

Environment	Mean or Median OC Burial (g m $^{-2}$ yr $^{-1}$)	Range
Eutrophic impoundments	2122	148–17,392
Impoundments (Asia)	980	20–3300
Impoundments (Central Europe)	465	14–1700
Impoundments (United States)	350	52–2000
Impoundments (Africa)	260	
Small mesoeutrophic lakes	94	11–198
Small oligotrophic lakes	27	3–128
Large mesoeutrophic lakes	18	10–30
Large oligotrophic lakes	6	2–9

Sources: Downing et al. 2008, Mulholland and Elwood 1982.

and Rigler (1979) concluded that “a simple proportionality between biomass in the epilimnion and area hypolimnetic oxygen deficit does not appear to exist.” They suggested instead that the greatest O₂ consumption occurred in deep lakes with higher water temperatures and a thick hypolimnion (Cornett and Rigler 1979, 1980). It is logical that warmer water temperatures support higher rates of bacterial respiration in the hypolimnion. The relationship between AHOD and hypolimnion thickness, however, was unexpected because it suggests that the greatest deficits are found in deep lakes with large hypolimnetic volume. Their findings, while not without criticism (Chang and Moll 1980), suggest that the consumption of oxygen in the hypolimnion may be largely the result of respiration within the water column, which is greatest in deep lakes where the transit time for sinking detritus is long (Cole and Pace 1995).

Some of this controversy over whether nutrients, temperature, or lake depth drive hypolimnetic anoxia and carbon burial may arise because authors are attempting to find a single relationship that fits lakes of varying nutrient status. In a synthesis of carbon burial rates Downing et al. (2008) found extremely low carbon burial rates in large nutrient-poor lakes but very high rates of carbon burial in midsize eutrophic impoundments despite the fact that the impoundments were typically shallow ([Table 8.4](#)).

Carbon storage in lake sediments is increasing rapidly because of the rapid increase in manmade lakes. Rates of carbon burial in reservoirs are high (estimated at ~400 g C m⁻² yr⁻¹; Mulholland and Elwood 1982, Dean and Gorham 1998, Downing et al. 2008) and because of the rapid expansion of reservoirs, they bury more organic carbon than all natural lake basins combined. Extrapolating this areal rate to the estimated 1,500,000 km² of global reservoir area (St Louis et al. 2000) leads to a global reservoir C storage estimate of 0.6 Pg C y⁻¹ (Cole et al. 2007). Given that reservoirs occupy only ~1% of the continental land surface, this rate of C burial is impressive in comparison with the estimated 1 to 2 Pg C y⁻¹ stored in terrestrial ecosystems and the 0.1 Pg C y⁻¹ buried in ocean sediments ([Chapter 11](#)).

Carbon Export from Lakes

Carbon can be exported from lakes through the degassing of CO₂ or CH₄ or through the downstream export of particulate and dissolved organic matter. Respiration exceeds GPP in most oligotrophic lakes (Sand-Jensen and Staehr 2009, Staehr et al. 2010b, Ask et al. 2012, Jansson et al. 2012). The degree of net heterotrophy is, across many lakes, positively correlated with CO₂ supersaturation and lake DOC concentrations (Roehm et al. 2009, Ask et al. 2012). Globally, lakes may outgas 0.64 Pg C y⁻¹ as CO₂ ([Table 8.1](#); Cole et al. 2007, Aufdenkampe et al. 2011).

In low-sulfate, oligotrophic lakes, methanogenesis is often the dominant form of anaerobic metabolism, but rates of methanogenesis tend to be highly variable in both space and time (Rudd and Hamilton 1978, Kuivila et al. 1989, Zimov et al. 1997). As long as the hypolimnion remains oxygenated, most of the methane produced in hypolimnetic sediments is oxidized by methanotrophs during upward diffusion; however, in shallow sediments a much higher proportion of gross methanogenesis can escape to the atmosphere. Gaining an accurate estimate of lake CH₄ emissions is particularly problematic, since a dominant pathway for CH₄ releases from lakes is through ebullition (Bastviken et al. 2004). In a survey of Siberian thaw lakes, Walter et al. (2006) estimated that ebullition accounted for 95% of CH₄ emissions from

these lakes. Although CH₄ emissions represent a small term within individual lake carbon budgets, the warming potential of CH₄ is $\sim 25 \times$ higher than CO₂ such that CH₄ production may be an important link between lakes and climate change (Tranvik et al. 2009).

The construction of reservoirs is enhancing annual lake CH₄ fluxes by increasing lake area and providing ideal conditions for methanogenesis. Vegetation and organic soils are flooded as impoundments are created, providing a large source of organic matter to fuel methanogenesis in the early years following construction (Kelly et al. 1997, St Louis et al. 2000, Sobek et al. 2012, Teodoru et al. 2012). In some tropical hydroelectric reservoirs large amounts of CH₄ are released as deep methane-enriched waters are passed through turbines; it has been argued that for some reservoirs the resulting greenhouse gas emissions can be greater than that of fossil fuel alternatives these hydropower dams were intended to replace (Fearnside 1995, Abril et al. 2005). St Louis et al. (2000) made the first attempt to estimate the global CH₄ production from reservoirs, suggesting that 0.7×10^{14} g CH₄ per year, or 18% of anthropogenic emissions, could be produced in temperate and tropical reservoirs. Bastviken et al. (2011) arrived at a similar estimate of 0.92×10^{14} CH₄ yr⁻¹ emissions from natural lakes and reservoirs combined. Refining these estimates will require more frequent estimates of CH₄ emissions from a larger number of lakes and reservoirs worldwide.

Nutrient Cycling in Lakes

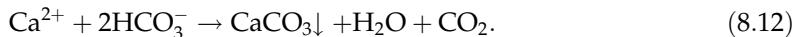
Contemporary lake nutrient budgets are constructed by assessing the inputs of nutrients in precipitation, runoff, and N fixation and the losses of nutrients from lakes due to sedimentation, outflow, and the release of reduced gases. In many cases human impacts now dominate the nutrient budgets of lakes (Edmondson and Lehman 1981). For elements without a substantial gaseous phase (e.g., Fe, Si, P), patterns of element concentration in lake sediments can be used to reconstruct historical loading and retention patterns (Dillon and Evans 1993, Rippey and Anderson 1996). For example, we can use the sedimentary record to solve for changes in lake phosphorus loading over time as

$$L = TPz\rho + TPz\sigma \quad (8.11)$$

where L is total phosphorus loading to the lake (mg m⁻²yr⁻¹), TP is the lake total phosphorus concentration (mg m⁻³), z is lake depth (m), ρ is the hydraulic flushing coefficient ($\sim 1/\text{MRT}$ in yr⁻¹), and σ is the phosphorus sedimentation coefficient (yr⁻¹). Loading can thus be estimated for every layer in a lake sediment core for which investigators can determine the time period over which sediment accumulated (from ¹⁴C dating), lake TP concentrations at the time of sedimentation (inferred from diatom composition), and total P content (Rippey and Anderson 1996). Lake sediments thus retain a record of changes in element exports from terrestrial catchments that can be used to understand how land use change or climate change influences both regional and in-lake nutrient cycling (Davis et al. 1985, Fritz 1996, Mackay et al. 1998, Riding 2000, Smol and Cumming 2000, Muller et al. 2005, Wagner et al. 2009).

Most lakes show a net retention of N, P and Si (Table 7.4; Cross and Rigler 1983; Muller et al. 2005; Harrison et al. 2009, 2012), although in lakes with a substantial annual turnover of water ("open systems"), the net storage of N and P may be relatively small during periods of high flow (Windolf et al. 1996). Iron derived from terrestrial runoff may also be sequestered in lake sediments (Dillon and Evans 2001). Net retention of Ca is seen in lakes where mollusk shells

are accumulating in the sediments (Brown et al. 1992) and in some highly productive, alkaline lakes ($\text{pH} \sim 9$) where calcite (CaCO_3) may precipitate directly as *marl* (Rosen et al. 1995, Hamilton et al. 2009):



These lakes will show a net retention of Ca and a relatively short mean residence time for Ca in the water column (Canfield et al. 1984). Calcite deposition is inhibited in lakes with high allochthonous DOC (Reynolds 1978, Hoch et al. 2000, Lin et al. 2005) and enhanced by high rates of photosynthesis that consume CO_2 (Hartley et al. 1995, Couradeau et al. 2012). In a phosphorus-enrichment experiment in a Michigan Lake, Hamilton et al. (2009) found that calcite deposition was enhanced by P fertilization and that the resulting biogenic calcite-phosphorus sedimentation was a substantial sink for the additional phosphorus. By this mechanism calcite precipitation has the potential to ameliorate eutrophication caused by nutrient loading (Koschel et al. 1983, Robertson et al. 2007).

In general, in-lake retention of nutrients increases with nutrient loading and water residence time (Seitzinger et al. 2006), and declines with lake depth. In deeper lakes, it takes longer for organic matter produced in the epilimnion to fall through the water column and be deposited in sediments. Falling organic matter or carbonates can be decomposed or mineralized during transport through the hypolimnion, reducing the absolute amount of material that reaches the sediments. It is only after sedimentation that elements have the potential to be permanently buried or, in the case of N, denitrified in anoxic sediments (Kelly et al. 1987, Dillon and Molot 1990, Molot and Dillon 1993, Windolf et al. 1996, Saunders and Kalff 2001).

Nitrogen Cycling in Lakes

Nitrogen-fixation rates in lakes range from $0.1 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ to $>90 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ (Howarth et al. 1988), roughly spanning the range of nitrogen fixation reported for terrestrial ecosystems (Chapter 6). Lakes with high rates of nitrogen fixation can show large apparent accumulations of N (Horne and Galat 1985). Because N-fixation is competitively advantageous when N concentrations are low, rates of N fixation within individual lakes typically respond to changes in nitrogen availability. In many seasonally stratified lakes, a seasonal succession from eukaryotic algae to N fixing cyanobacteria is observed as epilimnetic nitrogen concentrations decline over the period of stratification (Sterner 1989) and N fixation rates are reduced when the supply of nitrogen is high (Doyle and Fisher 1994).

Fewer studies have assessed denitrification and other processes of gaseous loss in lakes. Denitrification can be studied by the application of acetylene-block techniques and ^{15}N isotopic labels as discussed in Chapter 6 (Seitzinger et al. 1993). Reported rates of denitrification in individual lakes ranges from 1.8 to $38 \text{ kg ha}^{-1} \text{ yr}^{-1}$ (from a literature synthesis by Piña-Ochoa and Alvarez-Cobelas 2006). The total loss of nitrogen by denitrification exceeds the input of nitrogen by fixation in almost all lakes where both processes have been measured simultaneously (Seitzinger 1988). In a synthesis of more than 100 individual studies, Harrison et al. (2009) found that lakes removed 0 to 99.7% of N inputs. Higher rates of N removal were found for lakes or reservoirs with high N-loading rates, high catchment:lake area ratios, and high settling velocities for N (Harrison et al. 2009).

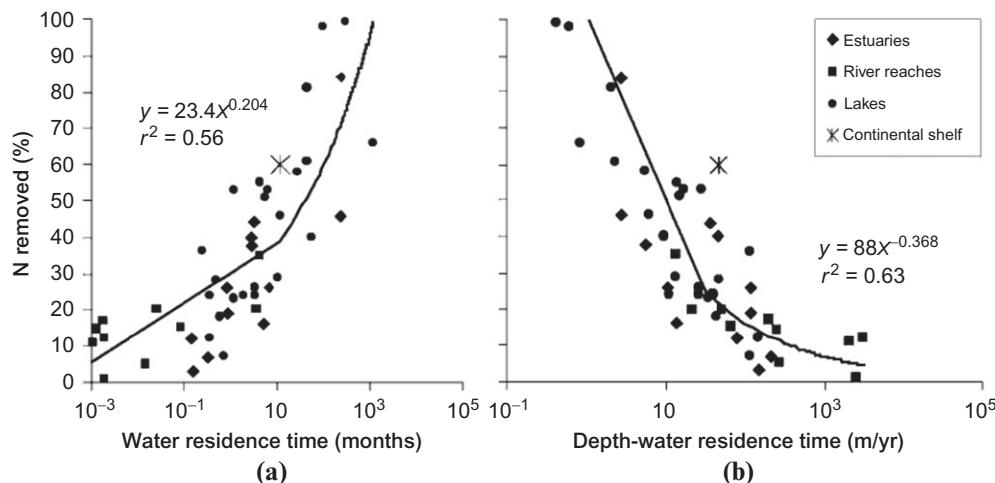


FIGURE 8.16 Relationship between the percentage of N removed (via burial or denitrification) and (a) water residence time (months) or (b) depth/water residence time (m/yr) for lakes, river reaches, estuaries, and continental shelves. Source: From Seitzinger et al. 2006. Used with permission of the Ecological Society of America.

Based on the statistical relationships developed from this dataset, Harrison et al. (2009) estimated that lakes and reservoirs collectively remove 19.7 Tg N yr⁻¹, with small lakes (<50 km²) responsible for nearly 50% of the global total. Often denitrification appears limited by the production and availability of NO₃⁻ in the sediments (Rysgaard et al. 1994), and the proportion of N removed increases with water residence time (Figure 8.16; Yoh et al. 1983, 1988, Mengis et al. 1997, Seitzinger et al. 2006). Because atmospheric N₂O concentrations are so low, most lakes are likely to be supersaturated in N₂O (Whitfield et al. 2011); however, the loss of nitrogen from lakes as N₂ greatly exceeds the loss of N₂O (Seitzinger 1988, Beaulieu et al. 2011). As NO₃⁻ loading to lakes increases (through atmospheric deposition or polluted surface runoff), higher N₂O production is likely to result (McCrackin and Elser 2011).

Lake Phosphorus Cycling

Because P is weathered slowly from rock and effectively bound in soils or assimilated by terrestrial vegetation, under most natural conditions the phosphorus inputs to lake ecosystems are relatively small (Ahl 1988, Reynolds and Davies 2001; Chapter 4). Much of the phosphorus entering lakes is carried with soil minerals, which are rapidly deposited in the sediments (Froelich 1988, Dillon and Evans 1993). The small amounts of inorganic phosphorus entering lakes undergo rapid abiotic precipitation with Fe, Ca, or Mn minerals that are insoluble in well-oxygenated waters, with the form depending on pH (Figure 4.10; Mortimer 1941, 1942; Blomqvist et al. 2004; Hamilton et al. 2009).

Analyses of lake water typically show that a large proportion of the phosphorus is contained in the plankton biomass and only a small portion is found in available forms (Lean 1973, Schindler 1977, Lewis and Wurtsbaugh 2008). Uptake of phosphorus by phytoplankton is an active process that shows a curvilinear relationship to increasing P concentration (Jansson 1993). Continued net primary production by phytoplankton depends on the

rapid cycling of phosphorus between dissolved (e.g., HPO_4^{3-}) and organic forms in the epilimnion (Fee et al. 1994).

Studies of phosphorus cycling have shown that the turnover of phosphorus in the epilimnion is dominated by bacterial decomposition of organic material. Phytoplankton and bacteria excrete extracellular phosphatases to aid in the mineralization of P (Stewart and Wetzel 1982, Wetzel 1992), and planktonic bacteria may immobilize phosphorus when the C:P ratio of their substrate is high (Vadstein et al. 1993). Globally, the molar N:P ratio of freshwater phytoplankton ranges from 6 to 44 (Klausmeier et al. 2004) and net phosphorus mineralization begins at $\text{N:P} < 16$ (Tezuka 1990). Immobilization of N is less common because the C:N ratio of phytoplankton (8–20) is similar to that of bacterial biomass (Tezuka 1990, Downing and McCauley 1992, Elser et al. 2000b). Nutrient turnover in lakes is enhanced by the activities of grazing zooplankton (Porter 1976, Lehman 1980, Elser and Hassett 1994) and fish (Vanni 2002). Grazing zooplankton vary in N:P ratios, with the common cladoceran *Daphnia* having a low N:P ratio ($\sim 14:1$) relative to most copepods ($\sim 30\text{--}50:1$; Sterner et al. 1992); thus, changes in the identity of dominant grazers can alter the ratio as well as the rate of N and P turnover (Elser et al. 2000a).

During a period of stratification, the phosphorus pool in the surface waters is progressively depleted as phytoplankton and other organisms die and sink to the hypolimnion (Levine et al. 1986, Rippey and McSorley 2009). Baines and Pace (1994) found that 10 to 50% of NPP was exported to the hypolimnion of 12 lakes in the eastern United States, with a tendency for a greater fractional export in lakes of lower productivity (Figure 8.17). Higher rates of particle sinking are correlated with higher rates of bacterial respiration in the hypolimnion (Cole and Pace 1995). When fecal pellets and dead organisms sink through the thermocline, phosphorus mineralization continues in the lower water column and sediments (Gachter et al. 1988, Lehman 1988, Carignan and Lean 1991). Anoxic hypolimnetic waters often show high concentrations of P, which is returned to the surface during periods of seasonal mixing. Of course, the turnover of phosphorus through the biotic community is incomplete, so some phosphorus is permanently lost to the sediments.

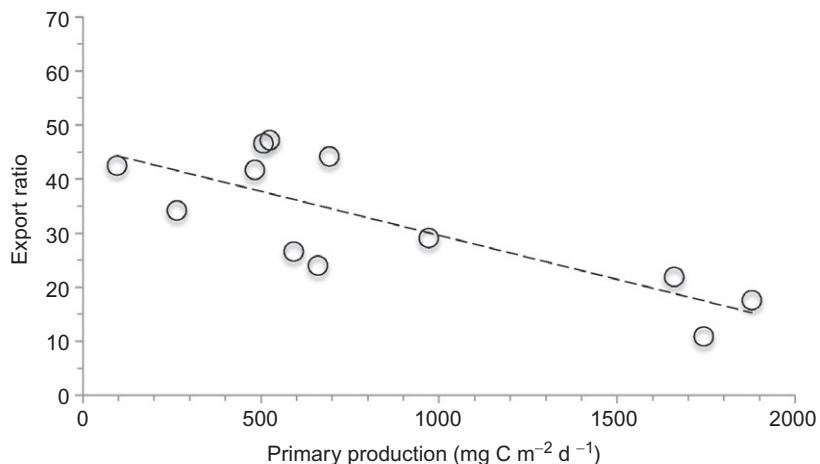


FIGURE 8.17 The percentage of planktonic productivity that sinks to the hypolimnion in lakes as a function of their net primary production. Source: Modified from Baines and Pace 1994. Used with permission of NRC Research Press.

As long as the hypolimnetic waters contain oxygen, a layer of Fe-oxide minerals at the sediment–water interface traps phosphorus that diffuses upward from bacterial decomposition of organic matter in the sediments or from the dissolution of Fe-P minerals at a lower redox potential at depth. However, when hypolimnetic waters become anoxic, this “iron trap for phosphorus” is lost as oxidized Fe minerals are reduced, releasing P to the overlying waters (Mortimer 1941, 1942; Caraco et al. 1990; Golterman 2001; Blomqvist et al. 2004). Interactions between elements may be important in determining the release of P from sediments. In most freshwaters the concentration of SO_4^{2-} is low, and P is strongly adsorbed by Fe minerals in the sediment. In the sea, concentrations of SO_4^{2-} are higher, and P limitation is less apparent (Chapter 9). Increasing concentrations of SO_4^{2-} in lakes due to acid rain or due to mining of pyrite-rich minerals may act through the anion exchange reactions to drive P into solution (Caraco et al. 1989, Wang and Chapman 1999).

In many cases the dissolution of Fe minerals is limited, and there is no regeneration of phosphorus from sediments (Davison et al. 1982, Levine et al. 1986, Caraco et al. 1990, Davison 1993, Golterman 1995). Sedimentary accumulations of undecomposed organic matter and Fe minerals contain P that is effectively lost from the ecosystem (Cross and Rigler 1983).

Sulfur Cycling in Lakes

In the sediments and low-oxygen bottom waters of lakes, as in the saturated sediments of wetlands, sulfur can play an important role in both carbon and nitrogen cycling. Sulfate concentrations in lakes are generally low; however, particularly in eutrophic lakes, where hypolimnetic oxygen concentrations are reduced, sulfate reduction is an important component of lake carbon cycling (Holmer and Storkholm 2001; Figure 8.18). In a highly eutrophic Michigan lake, Smith and Klug (1981) found that sulfate reduction was responsible for 7% of carbon mineralization.

In a review of the literature, Holmer and Storkholm (2001) concluded that sulfate reduction can account for a significant fraction (12–81%) of the total anaerobic carbon mineralization in lake sediments, although rates of sulfate reduction were typically lower than methanogenesis

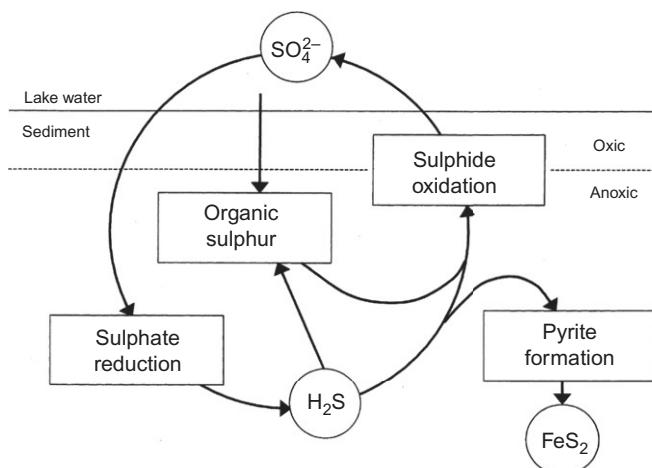


FIGURE 8.18 A simplified lake sediment sulfur cycle. Source: From Holmer and Storkholm 2001.

within the same lake. Sulfate reduction is enhanced in eutrophic lakes where more organic carbon is supplied to the sediments in deep water and shallow sediments are more likely to be anoxic. When reduced forms of sulfur are cycled through reoxidation pathways, high rates of SC_4^{2-} reduction can occur in lake sediments, despite low concentrations of SO_4^{2-} in lake water (Holmer and Storkholm 2001). Urban et al. (1994) found that rates of sulfide oxidation in the sediments of an oligotrophic lake in Wisconsin were nearly as rapid as sulfate reduction, indicating rapid fluxes of S despite the small pool sizes of S in the sediments.

Recent work has demonstrated that anaerobic sulfide oxidation during dissimilatory nitrate reduction or denitrification can be important sinks for NO_3^- in lake sediments, with sulfur bacteria gaining energy by oxidizing reduced sulfide to SO_4^{2-} and reducing NO_3^- either to N_2 or NH_4^+ (Chapter 7; Burgin and Hamilton 2008, Laverman et al. 2012). Although volatile losses of sulfur occur (Brinkman and Santos 1974), most H_2S appears to be reoxidized as it passes through the upper sediments (Dornblaser et al. 1994) or the water column (Mazumder and Dickman 1989), so little escapes to the atmosphere (Nriagu et al. 1987; Figure 8.10).

RIVERS

Rivers differ from lakes in several important ways that influence their biogeochemistry (Figure 8.19). The unidirectional flow of water in rivers maintains a constant supply of nutrients, water turbulence constantly mixes particulates into the water column, and frequent scouring flows limit the capacity for permanent burial of elements in sediments. In addition, the boundaries of rivers, both laterally and longitudinally, are extremely dynamic, with river flows expanding to encompass their floodplains and to include their ephemeral headwaters during periods of high runoff and contracting to a limited portion of their channels during periods of drought.

Like lakes, river biota can significantly alter the magnitude, timing, and form of chemical delivery to downstream waters (Meyer et al. 1988). Although “streams are the gutters down which flow the ruins of continents” (Leopold et al. 1964), stream channels are physically and

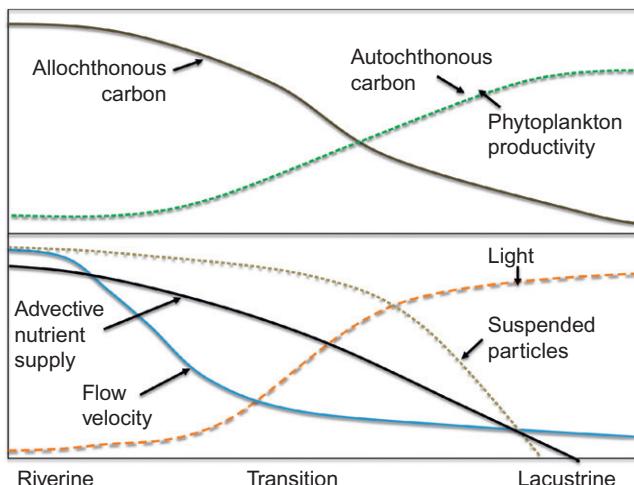


FIGURE 8.19 Commonly observed shifts in flow, light, nutrients, and sources of organic matter in the transition between rivers and lakes.

biologically complex and thus trap, delay, and attenuate the water, chemicals, and sediment pulses delivered from upslope and upstream (Bencala and Walters 1983). The communities of organisms within stream ecosystems largely survive by consuming and transforming terrestrial materials before passing them to the atmosphere or downstream, further altering the timing and quantity of chemical exports (Wallace and Webster 1996, Wallace et al. 1997).

Although materials accumulate in floodplains and large pools, rivers are not net aggrading systems and are less retentive of chemicals and solutes in comparison to hillslopes, wetlands, or lakes (Wagener et al. 1998, Essington and Carpenter 2000, Grimm et al. 2003). Because of the comparatively high velocities of flow in channels (i.e., limited residence time), chemicals and solutes that reach streams are routed much more rapidly to downstream receiving waters than would occur via subsurface flowpaths. Once introduced to streams, the only fate for elements that have no gaseous form (e.g., the limiting nutrient phosphorus, most trace metals) is transport to downstream floodplains, lakes, reservoirs, or coastal zones, although this transport may require anywhere from days to millennia.

For elements with a gaseous form at ambient conditions, substantial conversion and thus permanent export to the atmosphere can occur in rivers. In particular, denitrification can convert ~16 to 50% of nitrate (NO_3^-) inputs to N_2 (Galloway et al. 2008, Seitzinger et al. 2002, Mulholland et al. 2008) and >50% of the fixed carbon inputs are respiration as CO_2 (Battin et al. 2009, Aufdenkampe et al. 2011).

Riverbeds provide ideal conditions for a variety of metabolic processes because of the large area where oxygenated waters flow over anoxic sediments; thus rivers typically have disproportionately high rates of nutrient transformations and decomposition (mass per unit area) compared to adjacent surrounding soils (Lohse et al. 2009). Anoxic habitats within streams and their associated riparian zones are often the primary locations where significant denitrification and methanogenesis occur within temperate and arid landscapes.

River Water Budgets and Mixing

Water may enter a segment of river channel as flow delivered from upstream segments, as direct precipitation delivered to the channel surface, or as lateral inflows that are delivered overland, through shallow subsurface pathways or via exchange with deep groundwater (Figure 8.20). In small headwater streams, lateral inputs can dominate the water balance, but as streams grow larger in size, inflow from upstream segments quickly becomes the

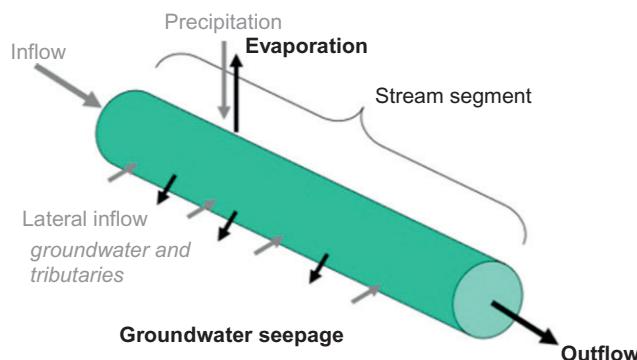


FIGURE 8.20 The water budget for a river segment.

dominant water source. Water may leave a channel through downstream flow, through evaporation, or through net losses to regional groundwater. Even when there is no net loss to groundwater, gross exchanges of water between the channel and groundwater can be quite large (Covino and McGlynn 2007, Poole et al. 2008). In some arid ecosystems the surface flow of large rivers is ultimately lost through net fluxes into regional groundwaters and during periods of high flow, rivers may overtop their banks and lose water to their floodplains. Under most conditions, however, the dominant route of water export is downstream flow.

The flow of water through terrestrial ecosystems to stream waters is often modeled using simplifying assumptions about the rate of plant uptake and the downward flow of water through the soil profile (Freeze 1974). Downward movement is assumed to occur during any period in which the percolation of water to a particular depth is in excess of the water-holding capacity of that depth and the rate of plant uptake during the interval. Water-holding capacity is commonly called *field capacity*, which is the water content that a soil can retain against the force of gravity. Excess water draining to the bottom of the soil profile will be transported to groundwater or receiving streams.

Long-term observations of streams show that hydrographs are affected by topography, vegetation, and soil characteristics, as well as the pattern and intensity of rainfall in individual storms (Ward 1967, Bosch and Hewlett 1982, McGuire et al. 2005). Stormflows tend to increase when vegetation is removed because bare soil allows a greater proportion of precipitation to leave via overland flow (Bosch and Hewlett 1982, Schlesinger et al. 2000; [Figure 8.21](#)). Stream hydrographs provide information about how rapidly rainwater or snowmelt is transported to channels, and how frequently channels are flooded or dry ([Figure 8.22](#)). Stream flow comprises surface runoff, which may carry organic debris and soil particles, and together with the drainage

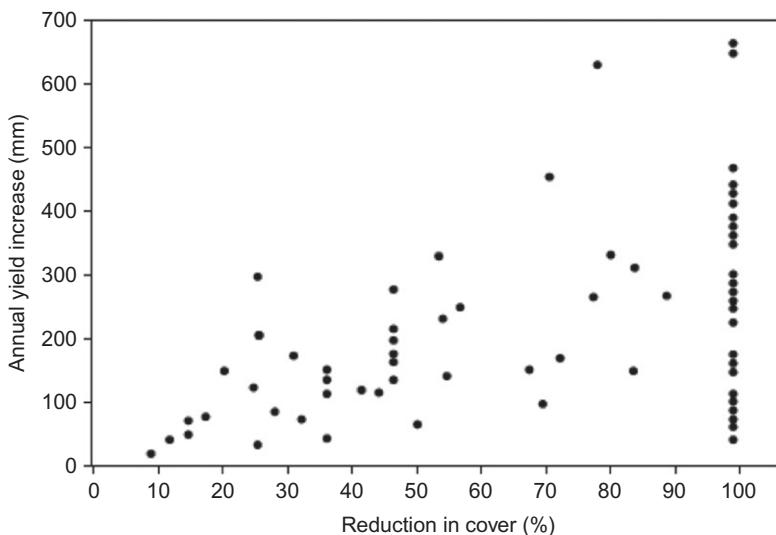


FIGURE 8.21 Water yield increases following changes in vegetation cover. *Source: Adapted from Bosch and Hewlett 1982.*

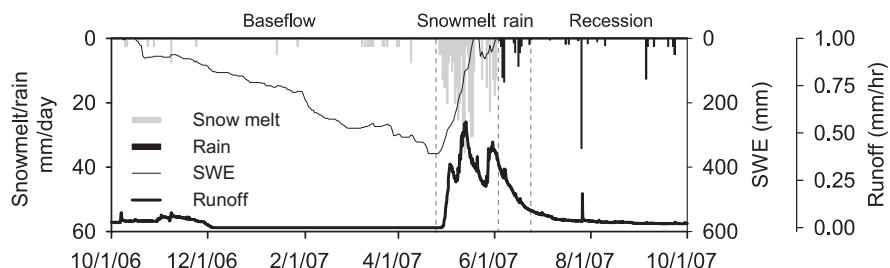


FIGURE 8.22 The annual hydrograph for a snowmelt-dominated river in Montana is shown in *black*. Stream flow reaches its peak during the late spring snowmelt period, but also floods following an intense summer rainstorm. The mass of snowpack is recorded as snow water equivalent (SWE) and is indicated by the gray line. Rain is shown with black bars and snowmelt is shown in gray bars. *Source:* From Jensco *et al.* 2009. Used with permission of the American Geophysical Union.

of permanently inundated soils or groundwater, the relative proportion changes both seasonally and on the scale of individual storms (refer to Figure 8.2; Bonell 1993, Sidle *et al.* 2000).

The relative importance of short flowpaths (~quickflow = overland flow + shallow soil flowpaths) versus baseflow (provided by groundwater and permanently saturated soil flowpaths) can vary greatly between biomes as a function of climate, and between watersheds as a function of soil depth and topography (McGuire *et al.* 2005, Lutz *et al.* 2012). Streams dominated by groundwater have consistent baseflows and tend to have stable channels with obvious headwaters. In contrast, streams with flows derived predominantly from precipitation, such as those in arid or urban watersheds, have dynamic and inconsistent flow origins (Stanley *et al.* 1997), such that the extent of headwater streams and the expanse of the channel network itself vary dramatically over time (Figure 8.23).

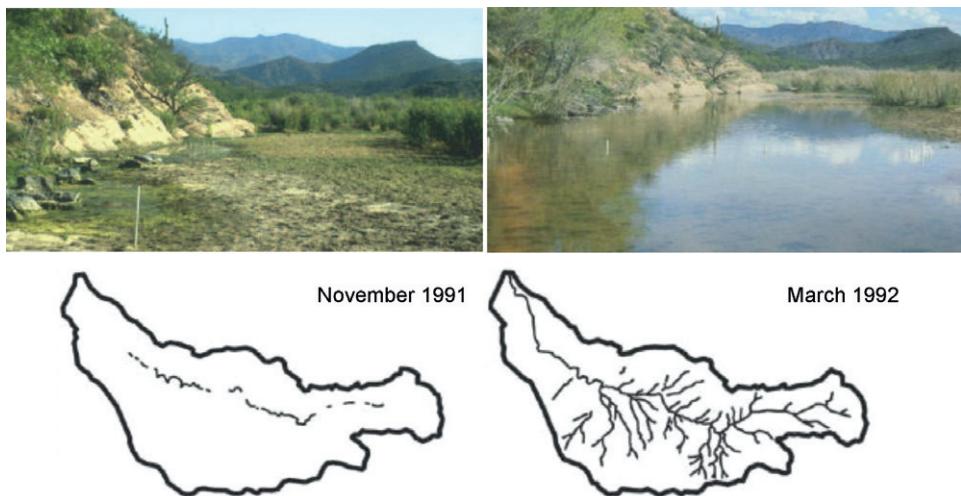


FIGURE 8.23 Changes in the longitudinal and lateral surface water area of Sycamore Creek, a desert stream in Arizona. *Source:* Maps from Stanley *et al.* 1997. Used with permission of the University of California Press. Photos provided by Emily Stanley.

Carbon Cycling in Rivers

While some fraction of the organic carbon in rivers is derived from internal productivity, much of the organic carbon entering a stream reach is DOC leached from the terrestrial landscape (Fisher and Likens 1973, Meyer 1981, Webster and Meyer 1997, Meyer et al. 1998, Mayorga et al. 2005). Dissolved organic carbon (DOC) becomes an increasingly important fraction of allochthonous organic carbon with increasing river size. The compounds of DOC include soluble carbohydrates and amino acids, which are leached from decomposing leaves and plant roots (Suberkropp et al. 1976), and humic and fulvic acids from soil organic matter (McDowell and Likens 1988, Qualls and Haines 1992; [Chapter 5](#)). A significant amount of the DOC in the Amazon River is of recent origin (Mayorga et al. 2005), but some fraction of the DOC exported to rivers is ancient. Using ^{14}C dating, Raymond and Bauer (2001) report DOC ages in the Susquehanna, Rappahannock, and Hudson rivers of 688, 736, and 1384 years bp.¹⁰

Although the age and composition of this terrestrial DOC would suggest that it is highly recalcitrant in soil, aquatic microbes assimilate and respire most terrestrial DOC during river transport (Wallace et al. 1999, Richey et al. 2002, Mayorga et al. 2005, Battin et al. 2009) and virtually no terrestrial DOC makes its way to the open ocean (Hedges et al. 1997). As discussed in the preceding section, DOC that was recalcitrant in dark soils or anoxic sediments may become labile in well-lit and well-oxygenated rivers.

Particulate matter dominates the carbon budget of many small streams. The leaves, needles, twigs, branches, and trunks of vegetation that fall into streams support diverse aquatic food webs as they are shredded and decomposed during downstream transport (Webster et al. 1999). Along river networks, the ratio of dissolved to particulate allochthonous carbon inputs generally increases as larger rivers have a smaller proportion of terrestrial “edge” from which to acquire particulate material and because CPOM delivered to tributaries is degraded rather than transported downstream (Vannote 1980, Webster and Meyer 1997, Webster et al. 1999). In narrow, shaded headwaters terrestrial inputs are the dominant energy source and R greatly exceeds NPP. Autochthonous production by benthic algae (periphyton) and aquatic macrophytes (vascular hydrophytes) becomes increasingly important as channels widen. This frequently observed pattern led Vannote et al. (1980) to predict increases in ecosystem productivity with stream size, or along the river continuum. The model predicts that in very large rivers, allochthonous inputs and heterotrophy will again dominate the carbon budget because large rivers are often too deep to support benthic autotrophs and too fast and turbid to support significant phytoplankton productivity.

New Inputs of C—Primary Productivity in Rivers

Where light is not limiting, primary production by benthic algae and aquatic macrophytes is an important carbon source to rivers. Biomass estimates or measures of chlorophyll are often misleading indicators of river productivity because scouring disturbances and variable light regimes drive substantial temporal variation in GPP (Grimm and Fisher

¹⁰ Note that this ^{14}C dating provides a single age for the bulk pool of DOC, which will include DOC molecules that were fixed in photosynthesis seconds, hours, days, seasons, years, and millennia before the sample was collected.

1989, Hill 1996) and also because grazing invertebrates are capable of consuming a large fraction of GPP (Wallace and Webster 1996). Because algae and macrophyte tissues are more nutrient rich and palatable than terrestrial organic matter, autotrophic production often contributes disproportionately to secondary production in river food webs (McCutchan and Lewis 2002).

River NPP estimates are typically made using one of two approaches: respirometer chamber estimates or in situ dissolved oxygen change (Bott 2006). Respirometer chamber estimates are analogous to the light/dark bottle methods described above for lakes, and involve isolating stream sediments and water in closed containers and measuring changes in the dissolved oxygen concentration of the overlying water over time. Although chamber estimates are useful for comparative studies and experimental manipulations, NPP estimates derived from chambers are difficult to extrapolate to whole ecosystems for several reasons. First, enclosing stream sediments in a closed vessel dramatically alters the flow, nutrient supply, and gas exchange conditions typical of natural streams (Bott 2006). Second, because river sediments are typically very heterogeneous, scaling to the whole ecosystem requires adequate sampling of all benthic habitat types.

Finally, because chamber methods typically do not include subsurface sediments, they tend to considerably underestimate rates of ecosystem respiration because they do not measure oxygen consumption in the hyporheic zone¹¹ (Fellows et al. 2001). In general, chamber methods have indicated that primary production often exceeds respiration in well-lit streams (Minshall et al. 1983, Bott et al. 1985) while open channel methods are far more likely to find net heterotrophy for any 24-hour period (Mulholland et al. 2001, Hall and Tank 2003a, Bott et al. 2006, Bernot et al. 2010).

The open channel technique involves measuring diel patterns of stream-water oxygen, or less commonly CO₂ concentrations, and linking these diel changes in gas concentration to the processes of production, respiration, and groundwater or atmosphere exchange (Odum 1956; Figure 8.9). For any time step,

$$\Delta O_2 = GPP - R \pm E, \quad (8.13)$$

where E is atmospheric exchange as estimated using a gas tracer (Wanninkhof et al. 1990). These data are analyzed as described in the lake metabolism section above. The chief difference is that, in rivers, flow turbulence is a more important driver of gas diffusion than is wind, and so gas-tracer-derived estimates of diffusion must be made for the same flows at which oxygen changes are measured. In two years of continuous monitoring of GPP in Walker Branch, Tennessee, Roberts et al. (2007) showed high day-to-day and seasonal variability in GPP that was largely predicted by light availability (Figure 8.24). In this stream, and probably many similar streams draining intact deciduous forests, the highest rates of stream metabolism are recorded outside of the terrestrial growing season.

¹¹ The hyporheic zone is the volume of subsurface sediments where groundwaters and surface waters are actively exchanged. Hyporheic zone volume varies widely across streams; there is no hyporheic zone in bedrock-constrained channels but the hyporheos may extend 10s to 100s of meters in coarse alluvial channels.

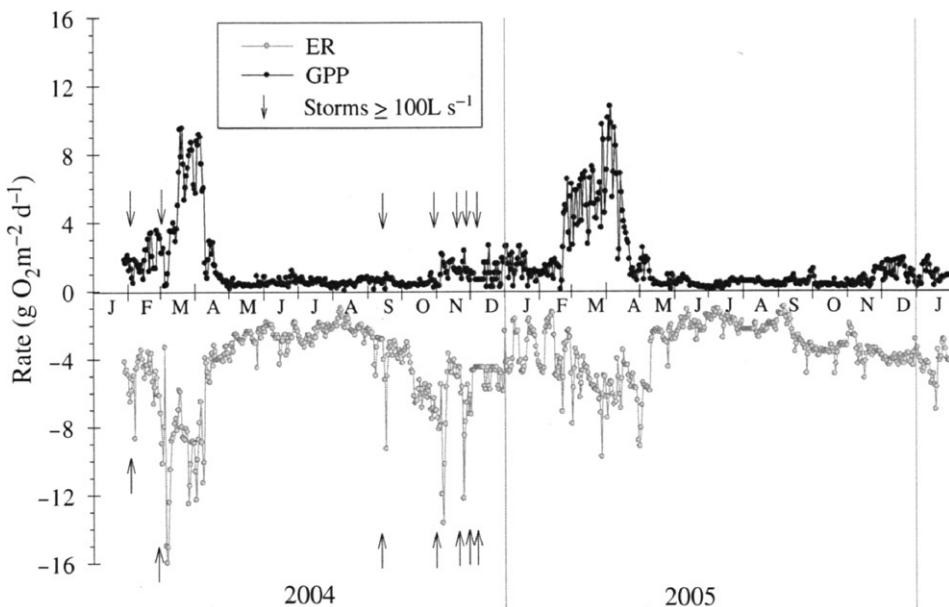


FIGURE 8.24 Daily estimates of gross primary production (GPP) and ecosystem respiration (ER) rates for Walker Branch, Tennessee, derived from open channel oxygen measurements over two years. Arrows indicate when large storms occurred. *Source: From Roberts et al. 2007. Used with permission of Springer.*

Limits to Autochthonous Production in Flowing Waters

In small streams light is often the primary factor limiting GPP (Hill 1996, Hall and Tank 2003b, Roberts et al. 2007) and surveys of algal standing stocks and stream nutrient concentrations typically fail to see the same strong positive correlations that have been observed in lakes (Biggs 1996, Francoeur 2001). The nutrient limitation status of benthic algae is often assessed using nutrient-diffusing substrates (NDS), which are agar-filled containers that slowly release nutrient solution through a porous membrane into the stream. The biomass of algae can be compared between substrates containing nutrient-enriched or nutrient-free agar (Pringle 1987).

In a comprehensive synthesis of 237 separate NDS experiments, Francoeur (2001) found that 43% of experiments measured no algal response to either N or P additions, while colimitation by both N and P (23%) was more common than limitation by either N (17%) or P (18%) alone. Results may vary seasonally according to light availability. For example, Bernhardt and Likens (2004) measured significant nutrient limitation of benthic algae for 10 streams of the Hubbard Brook experimental forest only in the spring before canopy leafout, with no nutrient-enrichment effects observed during summer or fall.

In well-lit streams, factors other than nutrient supply may constrain the response of river autotrophs to nutrient loading. Many rivers experience floods, which either scour or bury riverbeds with transported sediments. Thus the algae and macrophytes in many rivers are nearly always at some stage of recovery from the most recent flood (Grimm and Fisher 1989, Death and Winterbourn 1995). It is not surprising, then, that some of the most productive

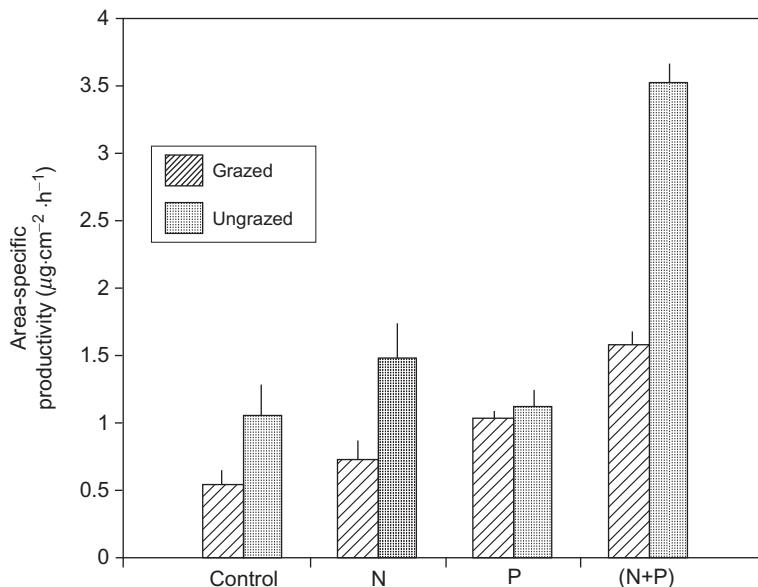


FIGURE 8.25 Effects of nutrient enrichment and grazing by snails on algal productivity in a series of streamside channels (measured by ^{14}C incorporation) in Walker Branch, Tennessee. Source: From Rosemond et al. 1993. Used with permission of the Ecological Society of America.

river systems on Earth are spring-fed rivers that never experience scouring flows and which are dominated by lush growths of aquatic macrophytes (Odum 1957). As in lakes, grazing invertebrates or fish can substantially reduce the standing crops and productivity of river autotrophs (Wallace and Webster 1996, Taylor et al. 2006), and can constrain the photosynthetic response to nutrient enrichment (Figure 8.25; Rosemond et al. 1993, Taylor et al. 2006).

Carbon Budgets for Rivers

Carbon budgets are often used to understand the relative importance of autochthonous and allochthonous carbon inputs to river systems. In the first such complete carbon budget, constructed for a small headwater stream in New Hampshire, Fisher and Likens (1972) were unable to find any algae in the sediments of Bear Brook. In these heavily shaded and acidic streams the only autotrophs were stream bryophytes, which contributed less than $\sim 0.1\%$ of annual C inputs (Table 8.5). In one year of monitoring surface and lateral carbon inputs and outputs, Fisher and Likens (1973) estimated that of the ~ 3260 kg of C delivered as leaves and branches to a segment of Bear Brook, ~ 2930 kg were respired by stream microbes. The energetics of this stream were almost completely dominated by allochthonous inputs with a P:R ratio <0.01 .

In a compilation of subsequent stream organic matter budgets for 35 streams, Webster and Meyer (1997) documented a wide range in P:R ratios, from 0 (as in Bear Brook) to 1.7. Generally the P:R ratio increased with stream size; however, desert streams were far more productive, and the single blackwater river included in the study was far less productive than

TABLE 8.5 Annual Carbon Budget for Bear Brook, a Small New Hampshire Stream

Item	Kg—whole stream ^a	Kcal/m ²	Percentage
Inputs			
Litterfall			
Leaf	1990	1370	22.7
Branch	740	520	8.6
Miscellaneous	530	370	6.1
Wind transport			
Autumn	422	290	4.8
Spring	125	90	1.5
Throughfall	43	31	0.5
Fluvial transport			
CPOM	640	430	7.1
FPOM	155	128	2.1
DOM, surface	1580	1300	21.5
DOM, subsurface	1800	1500	24.8
Moss production	13	10	0.2
Input total	8051	6039	99.9
Outputs			
Fluvial transport			
CPOM	1370	930	15.0
FPOM	330	274	5.0
DOM	3380	2800	46.0
Respiration			
Macroconsumers	13	9	0.2
Microconsumers	2930	2026	34.0
Output total	8020	6039	100.2

^a Budget in kg does not balance because of different caloric equivalents of budgetary components.

Source: Adapted from Fisher and Likens 1976.

predicted for their size (Figure 8.26; Webster and Meyer 1997). For desert streams, which drain a landscape of low-stature vegetation, stream size is not an effective indicator of light availability (Jones et al. 1997). For the blackwater Ogeechee River, as for dystrophic lakes, high concentrations of allochthonous DOC in rivers attenuated light availability (Meyer et al. 1997).

Much of the coarse particulate material provided to rivers from terrestrial vegetation is respired by microbes. While only a small fraction of terrestrial carbon is consumed by aquatic invertebrates (Fisher and Likens 1973), in shaded streams this is the primary resource for aquatic food webs. Terrestrial carbon thus contributes substantially to secondary production of aquatic insects. In a whole-ecosystem experiment, Wallace et al. (1997) excluded terrestrial litter inputs to a small mountain stream in North Carolina for four years and observed substantial declines in the biomass production of aquatic insects (Figure 8.27).

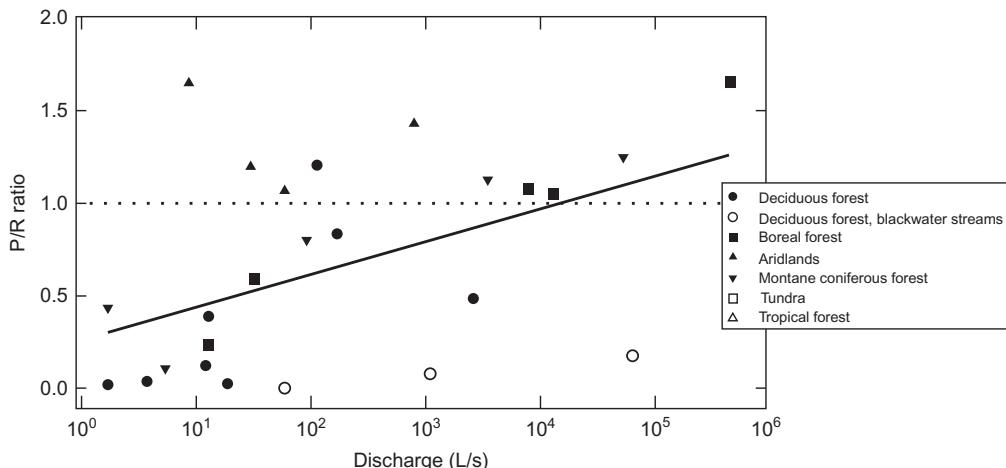


FIGURE 8.26 P:R ratios from a synthesis of 26 organic matter budgets reported in the literature. Source: From Webster and Meyer 1997. Used with permission of the North American Benthological Society.

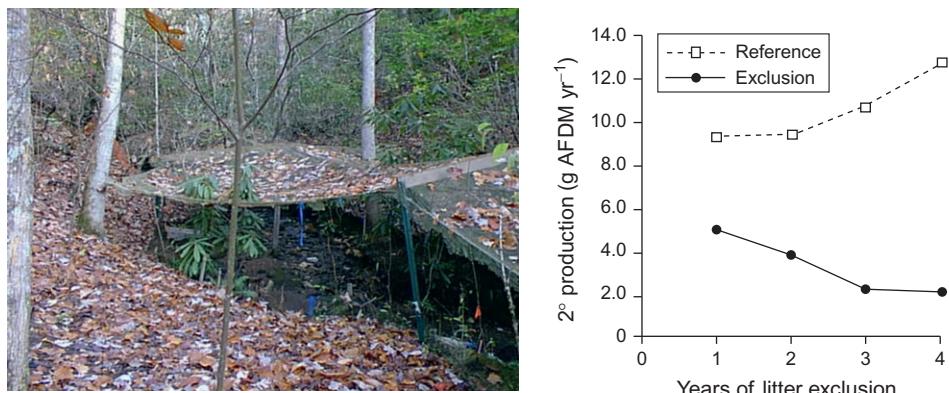


FIGURE 8.27 Effects of a multiyear leaf litter exclusion experiment on the secondary production (~total biomass of stream macroinvertebrates) of a small forested stream (Coweeta, North Carolina). Source: From Wallace et al. 1997. Used with permission of the American Association for the Advancement of Science.

Nutrient Spiraling in Rivers

An effective theory for nutrient cycling in stream ecosystems is the concept of nutrient spiraling, which recognizes that lotic nutrient cycles are constantly displaced downstream by advective flow (Figure 8.28; Webster and Patten 1979, Newbold et al. 1981, Newbold 1992, Webster and Ehrman 1996). During downstream transport, dissolved ions are accumulated by bacteria and other stream organisms and converted to organic forms. When these organisms die, they are degraded to inorganic forms that are returned to the water, only to be taken up again by organisms that are involved in the further degradation of organic

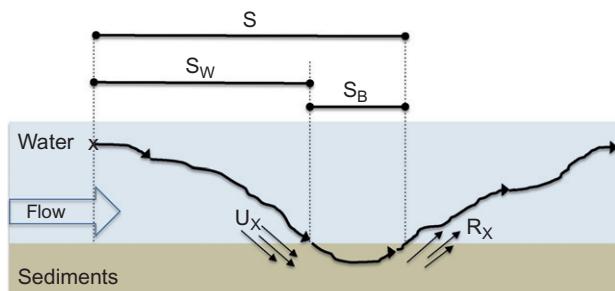


FIGURE 8.28 A nutrient spiral is a nutrient cycle that is displaced by advective flow. In this diagram the black line represents the path of an average nutrient molecule during downstream transport as it is moved downstream prior to uptake into sediments (U) and then transported yet further downstream prior to remineralization (R) and release to the water column. The spiraling length (S) is composed of the uptake length (S_w), which is the transport distance prior to removal from the water column, and the remineralization length (S_B), which is the downstream distance transported within benthic sediments or biota. Source: Modified from Newbold 1992.

materials. The cycle between inorganic and organic forms may be completed many times before a nutrient atom is ultimately exported from the river.

Biogeochemists often compare the downstream transport of nutrients and conservative solutes (~elements available far in excess of biological demand and not effectively sorbed onto sediments) in order to understand the role of biota in determining element fate and transport. If a solution of conservative ions (e.g., Cl, Br) is injected into a river, their concentration will decline with distance downstream of the injection point as a function of dilution (Stream Solute Workshop 1990) or permanent loss to groundwater (Covino and McGlynn 2007, Poole et al. 2008). If the slope of the downstream decline in the concentration of a coinjected nutrient is steeper than measured for the conservative tracer, this indicates biological or chemical uptake in addition to dilution and mass loss. The uptake length (S_w) is thus calculated as the inverse slope of the line describing the downstream decline of tracer-corrected nutrient concentrations:

$$\ln A_x = \ln A_0 + k A_x, \quad (8.14)$$

where A_x is the corrected solute concentration x meters downstream from the point of addition, A_0 is the corrected concentration of the solute at the addition site, and k_A is the per meter uptake rate of solute A. Solute concentrations are corrected for dilution by dividing them by the concentration of a coinjected conservative tracer (Tr) measured at the same location:

$$A_x = [N_x]/[Tr_x]. \quad (8.15)$$

From this and basic measures of stream flow and geomorphology, uptake lengths, velocities, and rates can be derived. The uptake length of a solute (S_w) represents the average downstream distance that a dissolved nutrient molecule travels before it enters the particulate phase:

$$S_w = 1/k_A. \quad (8.16)$$

The nutrient spiral (between dissolved and particulate phases) is equivalent to a nutrient cycle (between organic and inorganic forms) for solutes that are not strongly sorbed onto mineral particles, but it conflates both physical sorption and biological assimilation for ions such

as NH_4^+ or PO_4^{2-} , which can also be removed from solution through abiotic sorption (see [Chapter 4](#)). Elements that are in greater biological demand will have shorter spiraling lengths. The spiraling length can be used to estimate whole ecosystem uptake rates (U) by

$$U = [Q \times C_{\text{bkgrnd}}] / [S_w \times w], \quad (8.17)$$

where Q is stream flow in $\text{m}^3 \text{ min}^{-1}$, C_{bkgrnd} is the concentration of the solute of interest prior to the experimental enrichment, and w is the average width of the study reach in m. Spiraling length estimates can be made using either nutrient enrichments or isotopic tracers (^{15}N and ^{32}P) together with a conservative tracer (e.g., Cl^- , Br^- , or a fluorescing dye). Because uptake rates tend to increase with increasing concentration and demand can become saturated (Peterson et al. 2001, Bernhardt 2002, Mulholland et al. 2002, Covino et al. 2010), additions are likely to overestimate uptake lengths and underestimate uptake rates.

Across streams, nutrient uptake rates decline strongly with increasing flow velocities and increase with increasing sediment–water contact time indicating that hydrology ultimately constrains biological assimilation (Peterson et al. 2001, Hall et al. 2002, Webster et al. 2003, Wollheim et al. 2006). To allow comparisons of uptake efficiency across streams with very different flows, biogeochemists sometimes calculate uptake velocities, or mass transfer coefficients (V_f):

$$V_f = [Q/w]/S_w, \quad (8.18)$$

which measures the efficiency of benthic uptake accounting for differences in flow.

Modifications of the spiraling technique have made it possible to calculate from a single addition both the ambient uptake rate and the maximum potential uptake rate of a stream ecosystem (Covino et al. 2010). Coinjection of nutrient solutes (e.g., DOC together with NO_3^- , or inorganic N and P added simultaneously) can be compared to single nutrient injections to compare the relative strength of whole-ecosystem nutrient-limitation (Bernhardt and McDowell 2008, Lutz et al. 2012).

Most forms of land use change increase surface runoff and nitrogen (N) loading to streams. Receiving stream channels, regardless of their condition, will dampen these terrestrial signals through downstream dilution. Intact stream ecosystems will lead to more rapid attenuation of nutrient pulses than can be explained by dilution alone through biological assimilation and transformation (Alexander et al. 2000, Seitzinger et al. 2002, Bernhardt et al. 2003, Green et al. 2004).

Ecosystem nutrient demand can also be assessed using mass-balance approaches. Annual mass balances are very time consuming to construct and are rare in the literature ([Table 8.6](#); Meyer et al. 1981, Triska et al. 1984). In a comprehensive annual N budget for a small stream in the U.S. Pacific Northwest, Triska et al. (1984) showed that one-third of the nitrogen delivered to the ~100-m study reach was effectively stored or converted into nitrogen gas or secondary production over the course of a year ([Figure 8.29](#)).

Several recent efforts have estimated the instantaneous mass flux difference between the upstream and downstream ends of a study reach. Roberts et al. (2007) compared upstream and downstream nitrogen fluxes (flux (mg/s) = concentration (mg/L) \times discharge (L/s)) two to three times per week for two years in Walker Branch, Tennessee. They used this information together with continuous estimates of stream GPP and R (refer to [Figure 8.24](#)) to show that variation in GPP could explain nearly 80% of instantaneous NO_3^- flux (Roberts et al. 2007). Since GPP in this stream is nearly entirely explained by light, they were able

TABLE 8.6 Yearly Fluxes of Organic Carbon, Nitrogen, and Phosphorus in Bear Brook

	Organic carbon (g/m ²)	Nitrogen (g/m ²)	Phosphorus (g/m ²)	Atomic Ratio C:N:P
Inputs				
Total dissolved	200	56	0.39	1700:320:1
Total fine particulate	12	0.27	0.55	54:1:1
Total coarse particulate	340	8.2	0.7	1300:26:1
Total gaseous	1	<0.1	0	
Total inputs	620	64	1.6	990:89:1
Outputs				
Total dissolved	260	57	0.29	2300:440:1
Total fine particulate	25	0.43	1.1	59:0.9:1
Total coarse particulate	100	1.8	0.38	720:10:1
Total gaseous	230	?	0	
Total outputs	620	59	1.8	890:72:1

Source: Meyer *et al.* 1981. Used with permission of VG Wort, Germany.

to show that solar energy supply directly and rapidly drives nitrogen uptake capacity in the stream. Heffernan and Cohen (2010) provide a more extreme example of the tight linkages between light availability, stream GPP, and ecosystem scale NO_3^- uptake rates. Using oxygen and nitrate sensors recording every few minutes in a macrophyte-dominated spring system in south Florida, they estimated continuous metabolism and stream nitrate uptake (Heffernan and Cohen 2010). They documented dramatic diel covariation in GPP and NO_3^- uptake (Figure 8.30) that could be almost perfectly predicted by light availability.

River Nitrogen Cycling

Measurements and models of stream nitrogen cycling using spiraling approaches generally conclude that biological uptake within stream ecosystems significantly reduces the downstream flux of inorganic nitrogen (e.g., Alexander *et al.* 2000, Seitzinger *et al.* 2002, Bernhardt *et al.* 2002, Kemp and Dodds 2002b, Peterson *et al.* 2001, Mulholland *et al.* 2008, Wollheim *et al.* 2008). Across sites, much of the variation in nitrogen uptake lengths can be explained by differences in stream flow and depth (Peterson *et al.* 2001, Wollheim *et al.* 2008). Nutrients travel longer distances in streams with faster flow and reduced water-sediment contact.

In a cross biome survey of $^{15}\text{NH}_4^+$ uptake in streams of North America, Peterson *et al.* (2001) found that ammonium was typically removed from the water column within tens to hundreds of meters, while nitrate tended to travel much longer distances in the same streams. Rapid uptake of dissolved NH_4^+ by stream sediments is likely due to preferential uptake of NH_4^+ (Chapter 6) as well as cation exchange (Chapter 4) (Peterson *et al.* 2001). Much of the NH_4^+ that enters streams is immediately nitrified, with the proportion returning to the water column increasing with stream nitrate concentrations (Peterson *et al.* 2001, Bernhardt *et al.* 2002). Nitrification facilitates the downstream transport of nitrogen as nitrate, which

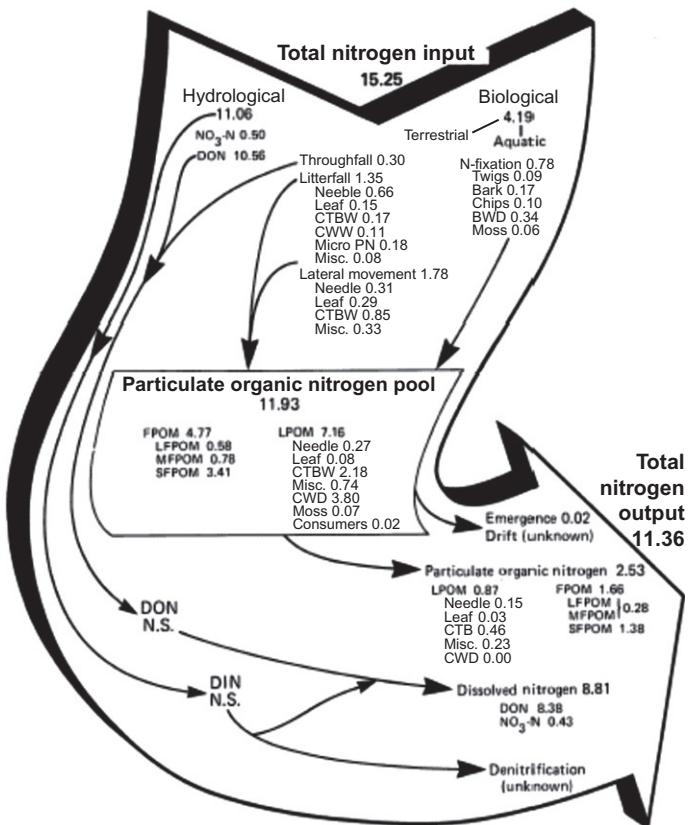


FIGURE 8.29 Nitrogen budget for the stream at watershed 10 of the H.J. Andrews Long Term Ecological Research site, indicating the source and magnitude of annual nitrogen inputs, mean pool size, and annual exports. DON and DIN as an instantaneous pool are not significant (NS). Source: From Triska et al. 1984. Used with permission of the Ecological Society of America.

DON = dissolved organic nitrogen; DIN = dissolved inorganic nitrogen; CTBW = cones, twigs, bark, and wood (>1.0 mm and <15.0 cm); CWD = coarse wood debris (>15.0 cm); BWD = wood blocks used to estimate the N fixation rate on woody debris; Micro PN = nitrogen input associated with microparticulate litterfall ($<800 \mu\text{m}$ diameter); LPOM = large particulate organic matter (>1.0 mm diameter); FPOM = fine particulate organic matter (<1.0 mm diameter)

may exacerbate downstream nitrogen pollutant loading (Bernhardt et al. 2002). Nitrification may also be an important source of N₂O from stream ecosystems. There are few direct measures of nitrification-derived N₂O for streams, but most models assume, and limited field measurements support, the assumption that nitrification and denitrification generate low rates of N₂O production in streams as compared to terrestrial soils or wetlands (Beaulieu et al. 2011).

Nitrate spiraling is controlled almost entirely by biological processes because it is poorly sorbed. Generally, nitrate uptake rates tend to increase with nitrate loading, although this capacity can be easily saturated by high loading rates (Mulholland et al. 2008). Variations in

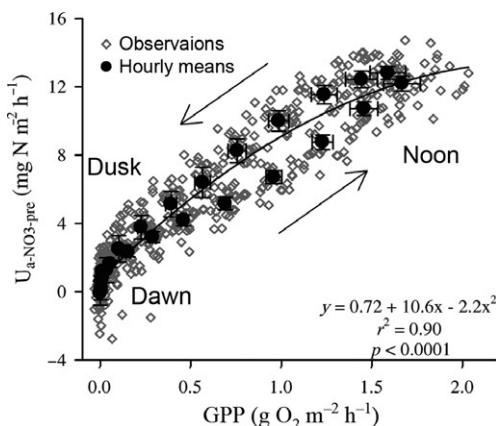


FIGURE 8.30 Nitrate uptake rate (U_{NO_3}) varies as a function of GPP over the course of a single day in the macrophyte-dominated Ichetucknee River, Florida. The small circles represent individual data points, the large circles represent hourly averages. The arrows show the hysteresis of the relationship from predawn on day 1 to predawn on day 2. Source: From Heffernan and Cohen 2010. Used with permission of the Association for the Sciences of Limnology and Oceanography. All Rights Reserved.

carbon supply and carbon processing (metabolism) are good correlates of nitrogen uptake both within and among streams (Baker et al. 1999, Baker et al. 2000, Bernhardt and Likens 2002, Crenshaw et al. 2002, Hall and Tank 2003b, Roberts and Mulholland 2007). Tight linkages between carbon and nutrient processing are expected given stoichiometric and thermodynamic constraints on organisms, yet it can be difficult to conceive of small, forested streams as carbon limited. However, carbon can be strongly limiting even in streams with high organic matter standing stocks. Experimental additions of labile carbon to stream sediment samples have consistently been shown to decrease nitrification (Strauss and Lamberti 2000, Strauss and Lamberti 2002, Strauss et al. 2002). Organic carbon addition to hyporheic flowpaths have been shown to stimulate N assimilation and denitrification (Hedin et al. 1998, Baker et al. 1999, Sobczak et al. 2003, Crenshaw et al. 2002). During a two-month DOC enrichment to a stream in the Hubbard Brook Experimental Forest, Bernhardt and Likens (2002) were able to reduce inorganic nitrogen export from an entire watershed to below analytical detection throughout the period of C enrichment, indicating that the biological capacity for nitrate uptake was limited by labile carbon.

The flux of organic matter can strongly influence N cycling activity, often creating a patchy distribution of NO_3^- sources and sinks along a stream length (Triska and Oremland 1981, Holmes et al. 1996, Kemp and Dodds 2002a, McClain et al. 2003). Both organic matter storage and nitrogen uptake rates are strongly influenced by hydrologic factors such as stream size, water residence time, and the abundance of physical features to trap organic material (Bilby 1981, Triska 1989, Valett et al. 1996, Peterson et al. 2001, Wollheim et al. 2001, Hall et al. 2002, Webster et al. 2003); thus it is possible that a positive correlation between benthic C storage and N processing rates reflects similar hydrologic controls.

Since streams are not aggrading systems, a large portion of the net loss of N within stream ecosystems must be attributed to denitrification. In a series of $^{15}\text{NO}_3$ -addition experiments in 72 North American streams, Mulholland et al. (2008) found that NO_3^- uptake rates varied widely ($0.01\text{--}1000 \text{ mg N m}^{-2} \text{ hr}^{-1}$). Across this series of isotopic enrichment experiments, anywhere from 0 to 100% of added $^{15}\text{NO}_3$ uptake was converted, within 24 hours, to $^{15}\text{N}_2$ (Mulholland et al. 2008, Mulholland et al. 2009). The median rate was 16% of NO_3^- uptake converted to N_2 over the course of the single-day experiments. Given that these estimates do not

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 may be lost 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

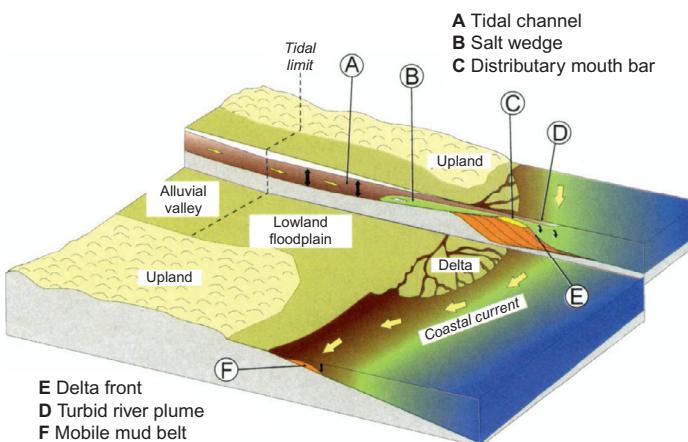


FIGURE 8.31 Generic diagram of a river estuary. The estuary boundaries are defined as the upper limit of the tidal influence within the river inflow to the coastal boundary of freshwater influence. Source: From Bianchi and Allison 2009. Used with permission of the National Academy of Sciences.

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 (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 ($>+200$ 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.

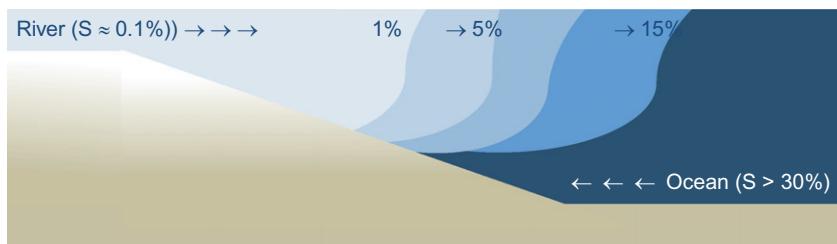


FIGURE 8.32 A diagram of a generic salinity gradient within a coastal estuary. River waters interacting with ocean waters lead to a gradient from fresh to full-strength ocean waters. The greater density of saltwater often leads to a salt wedge underlying a plume of less saline surface waters.

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 thermo-haline 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 super-saturated in CO₂. In a synthesis of literature estimates of air–water CO₂ 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 CO₂, that is the air–water flux (FCO_2 ¹²) was 3.9 mol C m⁻² yr⁻¹ (from Kone and Borges 2008). For the other estuaries FCO₂ values ranged from -3.6 mol C m⁻² yr⁻¹ in Finland's Bothnian Bay (Algesten et al. 2004) to -76 mol C m⁻² yr⁻¹ in Portugal's Douro estuary (Frankignoulle et al. 1998). While acknowledging the wide variation in reported FCO₂ 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 CO₂ of ~0.50 Pg C yr⁻¹ to the atmosphere (Figure 8.33).

Mounting evidence based on pCO₂ measurements and mass-balance calculations seems to indicate that the continental shelves are sinks for atmospheric CO₂ (Borges 2005, Chen and Borges 2009). Annual FCO₂ estimates on continental shelves average ~1.1 mol CO₂ m⁻² yr⁻¹, which, scaled to a global continental shelf area of $26 \times 10^6 \text{ km}^2$, yields an annual CO₂ uptake of about 0.35 Pg C yr⁻¹ (Chen and Borges 2009). Because of their much greater spatial extent, coastal shelves more than offset the atmospheric CO₂ 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 SO₄ 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 FCO₂ indicates the ecosystem is a net sink for atmospheric CO₂ while a negative FCO₂ value indicates that the system is a net source of CO₂ to the atmosphere.

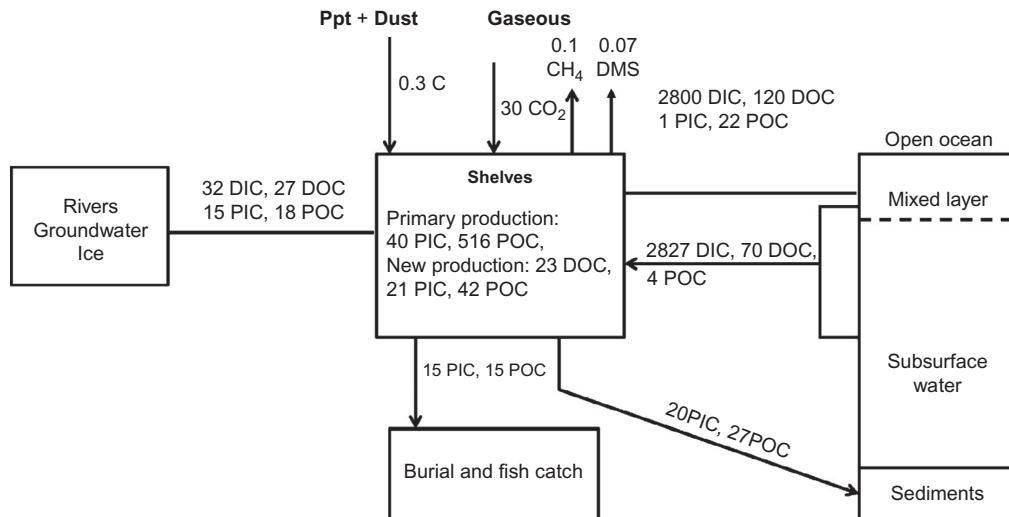


FIGURE 8.33 Mass balance of carbon in continental shelves (flows are in $10^{12} \text{ mol C yr}^{-1}$). Source: From Chen-Tung and Borges 2009.

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)	FCO ₂ Air–Water CO ₂ flux (mol C m $^{-2}$ yr $^{-1}$)	Air–Water CO ₂ flux (Pg C yr $^{-1}$)
60°–90°			
Open oceanic waters	30.77	-0.75	-0.28
Inner estuaries	0.4	46	0.22
Open shelf	6.79	-1.88	-0.15
Subtotal	37.96	-0.46	-0.21
30°–60°			
Open oceanic waters	122.44	-1.4	-2.05
Inner estuaries	0.29	46	0.16
Non-estuarine salt marshes	0.14	23.45	0.04
Coastal upwelling systems	0.24	1.09	0.003
Open shelf	14.47	-1.74	-0.3
Subtotal	137.58	-1.3	-2.15
30°N–30°S			
Open oceanic waters	182.77	0.35	0.77
Inner estuaries	0.25	16.83	0.05
Coastal upwelling systems	1.25	1.09	0.02
Coral reefs	0.62	1.52	0.01
Mangroves	0.2	18.66	0.04
Open shelf	1.35	1.74	0.03
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.

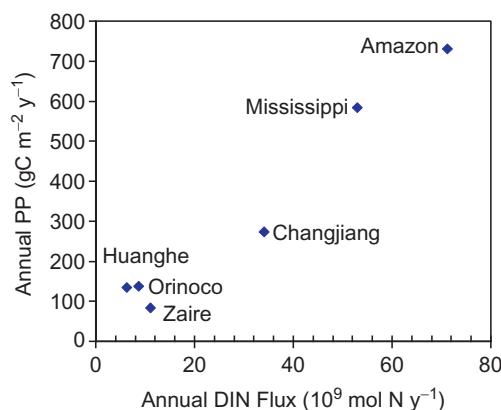


FIGURE 8.34 Relationship between primary production in coastal shelf waters impacted by major rivers and riverine DIN flux. Source: Adapted from Dagg et al. 2004.

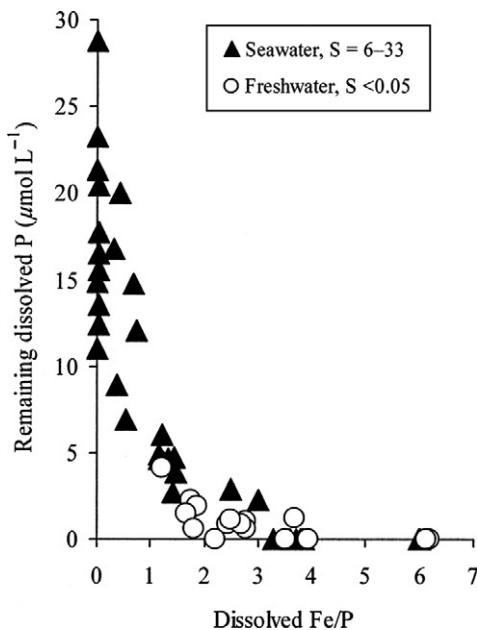


FIGURE 8.35 In experimental oxygenation of anoxic waters collected from the brackish northwestern Baltic Sea and adjoining freshwater Lake Malaren of Sweden, the amount of P remaining in solution following oxygenation was dependent on the dissolved molar Fe:P ratio, irrespective of salinity. Very little 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

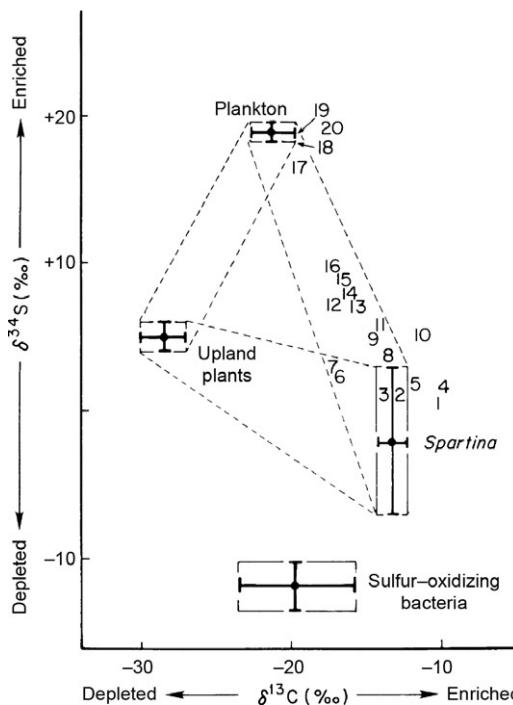


FIGURE 8.36 The isotope ratio for C and S in consumers is shown in relation to their ratios in upland plants, plankton, the salt marsh grass *Spartina*, and sulfur-oxidizing bacteria for Cape Cod's Great Sippewissett Salt Marsh in Massachusetts. The isotope ratios in sulfur-oxidizing bacteria are very 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 $\delta^{15}\text{N}$ (Horriigan 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.

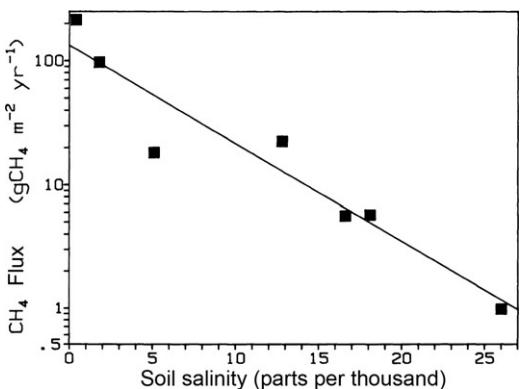


FIGURE 8.37 Annual methane flux as a function of average soil salinity across three southeastern United States salt marshes. Source: From Bartlett et al. 1987. Used with permission of Springer.

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, Attrai 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 CH₄ to the atmosphere (Chapter 11). Some salt marsh soils also appear to be a small source of phosphine (PH₃) 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

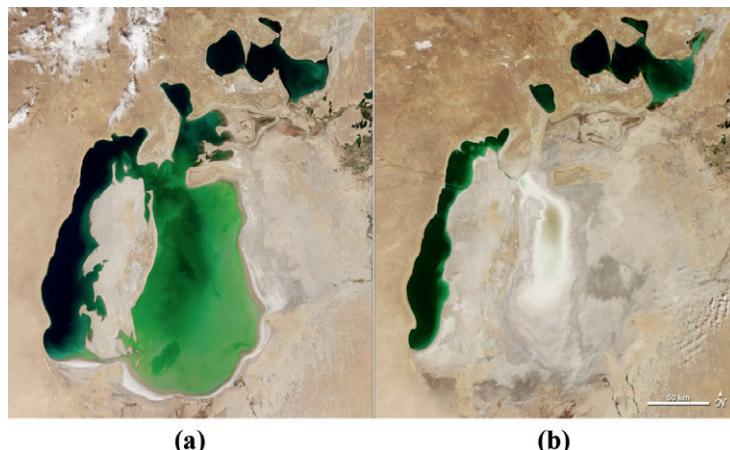


FIGURE 8.38 NASA satellite imagery shows the boundaries of the Aral Sea in 2000 (a) and in 2009 (b). Once the fourth largest lake in the world, the Aral Sea today is an example of a terminal lake that is both shrinking and becoming saltier as irrigation in the lake basin reduces annual river inflows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

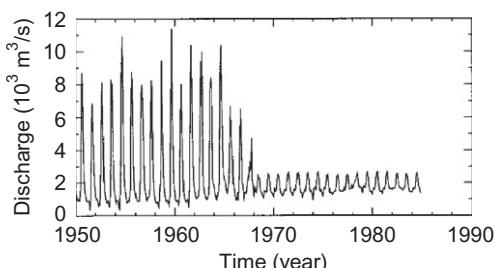


FIGURE 8.39 The effect of dam construction on river flows for the Nile River before and after construction of Aswan High Dam. Discharge is recorded just below the dam. The stabilization of flow is apparent, and it is not difficult to identify the time at which the dam was constructed and the Lake Nasser 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 wastewater 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

	$10^3 \text{ tonnes yr}^{-1}$	
	P	N
The Nile		
Pre-Aswan High Dam		
Dissolved	3.2	6.7
On sediments	4–8	?
	Total	7–11
		6.7
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.

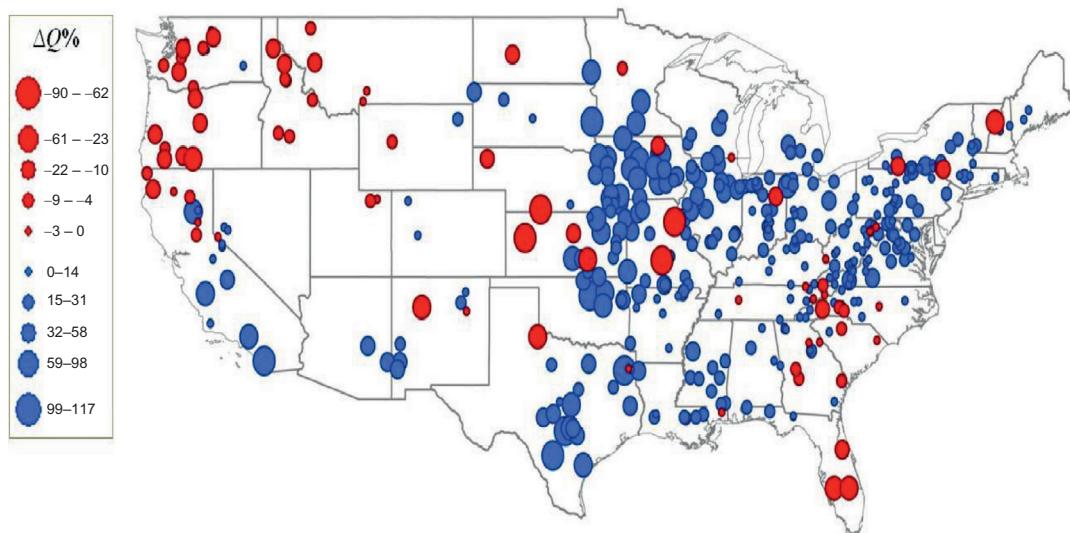


FIGURE 8.40 Spatial distribution of the change in stream flow (Q) recorded for 413 U.S. watersheds between the periods 1948–1970 and 1971–2003. Source: From Wang and Hejazi 2011. Used with permission of the American Geophysical Union.

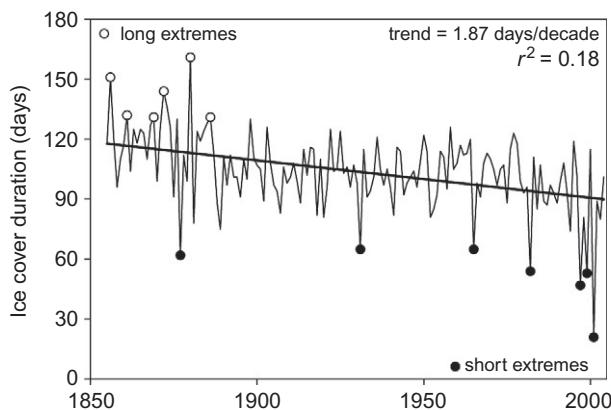


FIGURE 8.41 Graphic of the ice cover duration and extremes for the winters of 1855–1856 through 2004–2005 for Lake Mendota, Wisconsin. Over the 150-year record the six most extreme short and long ice duration winters (25-year events) are marked as closed or open circles. Source: From Benson et al. 2012.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

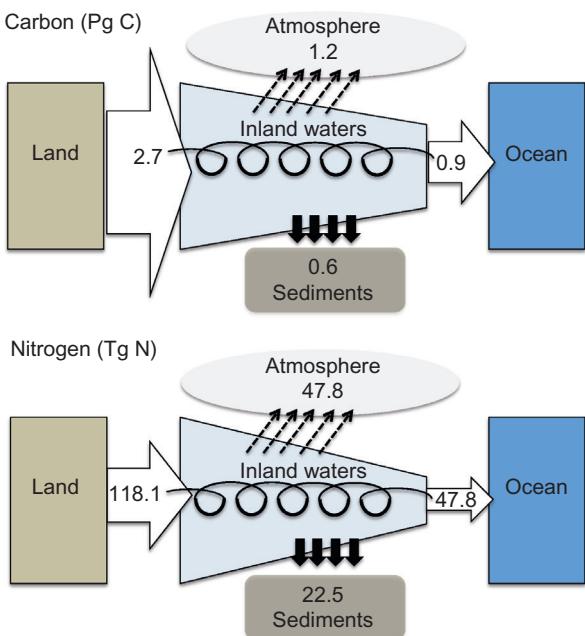


FIGURE 8.42 The cumulative effect of inland waters on global C and N cycling. Note that rivers and lakes deliver as much C and N to the atmosphere as to the ocean, indicating that biological processing of these elements within freshwaters is as important as their physical transport. Source: Numbers for 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 ~40% and store ~20% of the 2.7 Pg of allochthonous carbon, and denitrify or store ~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.
- Dodds, W. K. 2002. *Freshwater Ecology: Concepts and Environmental Applications*. Academic Press.
- Hauer, R. H., and G. Lamberti. 2006. *Methods in Stream Ecology* (second ed.). Academic Press.
- Stumm, W., and J. J. Morgan. 1996. *Aquatic Chemistry Chemical Equilibria and Rates in Natural Waters* (third ed.). Wiley.
- Wetzel, R. G., and G. E. Likens. 2000. *Limnological Analyses* (third ed.). Springer-Verlag.
- Wetzel, R. G. 2001. *Limnology* (third ed.). Academic Press.

PROBLEMS

1. Assume, as per Dean and Gorham (1998), that the average sedimentation rate of particulate material in reservoirs is 2 cm y^{-1} , that the average bulk density of lake sediments is 1 g cm^{-3} , and that the average C content of lake sediments is 2%. Under these assumptions, how much C might be stored annually in reservoir sediments if the total area of global reservoirs increased to twice their current land area of $1,500,000 \text{ km}^2$ (from St Louis et al. 2000)? Since methane efflux is also high from reservoirs, what average reservoir CH_4 flux would be necessary to completely offset this enhanced carbon sequestration (assume that CH_4 has a global warming potential $25\times$ that of CO_2)? How does this calculated rate compare to estimates of reservoir CH_4 flux in the literature?
 2. If global warming induces a 15% increase in DOC export from Scandinavian soils to receiving streams, what will the likely consequences be for GPP, ER, NEP, and pCO_2 in the 15 northern Swedish lakes shown in [Figure 8.15](#) (from Ask et al. 2012)?
 3. Go to the Hubbard Brook Ecosystem Study website and download the chemistry of stream water for experimental watersheds #6 from www.hubbardbrook.org/data/dataset_search.php and the instantaneous stream-flow data for watershed #6 from www.hubbardbrook.org/data/dataset.php?id=1. Match up weekly chemistry data with the discharge recorded for the sampling date. Prepare concentration x discharge (CxQ) relationships for NO_3^- , Ca^{2+} , and Cl^- for the entire record. Now compare these CxQ relationships for the first and last decades of the long-term record. Are the ranges of discharge or concentrations different between the two time periods? Now use these subsamples of the data to calculate volume-weighted concentrations for the two time periods. How have volume-weighted concentrations changed? For a more challenging assignment, take these volume-weighted concentrations and multiply them by annual flow to estimate the annual export of each solute.
 4. Calculate the actual free energy yield for sulfate reduction in freshwater and in full-strength seawater. Assume $\text{pH}=8$, 1 atm of pressure, and unlimited CH_2O . Compare this free energy yield to methanogenesis under the same conditions.
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