Wetland Ecosystems

INTRODUCTION

Aquatic and terrestrial ecosystems differ in the relative importance of hydrology as a critical factor in their biogeochemistry. In terrestrial ecosystems water may limit autotrophic or heterotrophic activity directly. In aquatic ecosystems where water is abundant, hydrology plays other fundamental roles. First, because oxygen diffuses 10^4 more slowly in water than it does in air, water indirectly limits biogeochemical activity by constraining oxygen supply. As a result there are many places in aquatic ecosystems where oxygen consumption exceeds rates of delivery, so anoxia is the typical condition of most sediments in wetlands, lakes, streams, and oceans. The plants and microbes controlling the biogeochemistry of aquatic
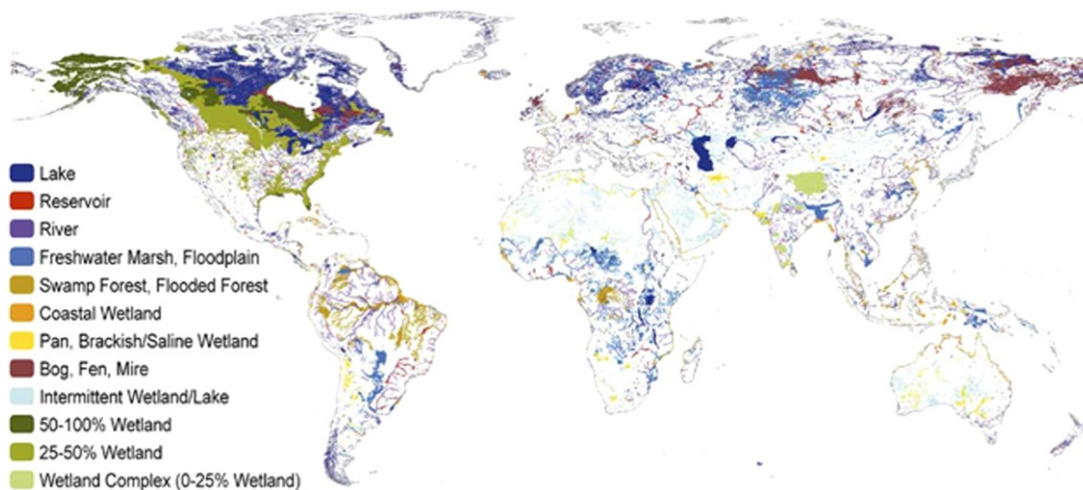
- ■ Lake
- ■ Reservoir
- ■ River
- ■ Freshwater Marsh, Floodplain
- ■ Swamp Forest, Flooded Forest
- ■ Coastal Wetland
- ■ Pan, Brackish/Saline Wetland
- ■ Bog, Fen, Mire
- ■ Intermittent Wetland/Lake
- ■ 50-100% Wetland
- ■ 25-50% Wetland
- ■ Wetland Complex (0-25% Wetland)

FIGURE 7.1   The distribution of global wetlands. *Source: From Lehner and Doll (2004).*

ecosystems must cope with limited oxygen supplies. Second, because of their low topographic positions where surface waters collect or groundwaters emerge, aquatic ecosystems receive substantial inputs from the surrounding terrestrial catchments.

The importance of these subsidies from terrestrial ecosystems depends to a great extent on the ratio of shoreline to the volume of the ecosystem. In many aquatic ecosystems these *allochthonous* (i.e., externally derived) inputs of energy and elements can exceed *autochthonous* (in situ) inputs by deposition, photosynthesis, or fixation, such that the biogeochemical cycles of many (perhaps most) aquatic ecosystems are net heterotrophic, or reliant on surrounding terrestrial ecosystems to provide the majority of their annual supply of organic matter and essential elements.

For many aquatic ecosystems, ecosystem boundaries can be difficult to assess on the ground, and even more difficult to estimate using remote sensing. All estimates of wetland area are thus fraught with uncertainty. Improvements in remote sensing will offer refined estimates of the areal extent of aquatic systems and the contribution of aquatic ecosystems to global biogeochemical cycles. The current global estimates of lakes, rivers, and wetlands are shown in Figure 7.1 and Table 7.1.

Although there are a wide variety of wetland types (e.g., marshes, bogs, fens, swamps), all wetlands are characterized by the unique features of their hydrology, vegetation, and soils. All wetlands have water at or near the surface for at least some portion of the year; as a result they have hydric soils[1] that exhibit intermittent to permanent anoxia. Hydrophytic (water-loving) plants capable of living in saturated soils dominate wetland vegetation. Estimates of the global wetland area are extremely variable, ranging from 5.3 to 12.8×10^6 km^2 depending on the stringency of the wetland definition applied (Matthews and Fung 1987, Aselmann and Crutzen 1989, Lehner and Doll 2004, Mitsch and Gosselink 2007). Despite their relatively

[1] Soils that are formed under conditions of periodic or continuous saturation sufficient to develop anoxic conditions in the upper horizons.

TABLE 7.1   Estimated Global Spatial Extent of Inland Waters

Class	Global Area	
	10^3 km^2	%
1. Lake	2428	1.8
2. Reservoir	251	0.2
3. River	360	0.3
4. Freshwater Marsh, Floodplain	2529	1.9
5. Swamp Forest, Flooded Forest	1165	0.9
6. Coastal Wetland	660	0.5
7. Pan, Brackish/Saline Wetland	435	0.3
8. Bog, Fen, Mire	708	0.5
9. Intermittent Wetland/Lake	690	0.5
10. Wetland Complexes		
50–100% Wetland	882–1764	0.7–1.3
35–50% Wetland	790–1580	0.6–1.2
0–25% Wetland	0–228	0–0.2
Total lakes and reservoirs (1–3)	2679	2.0
Total Wetlands (4–10)	8219–10,119	6.2–7.6

Source: Data from Lehner and Doll (2004). In these analyses, they assumed a total global land surface area (excluding Antarctica and glaciated Greenland) of 133 million km².

small proportional area, wetlands play an important role in global carbon cycling. In some instances, wetlands have the highest average productivity of any ecosystem type (1300 g C m^{-2} yr^{-1}) (Houghton and Skole 1990). Wetlands contribute 7 to 15% of global terrestrial productivity, and collectively store more than half of all the soil carbon on Earth (peatlands alone are estimated to store >50% of the world's soil carbon) (Gorham 1991, Eswaran et al. 1993, Roulet 2000, Tarnocai et al. 2009). The importance of wetlands as a global soil carbon sink is considerably offset by their production of the greenhouse gas CH$_4$ for which wetlands are the dominant global source, contributing 20 to 33% of global methane emissions (refer to Table 11.2; Bousquet et al. 2006, Bloom et al. 2010, Ringeval et al. 2010).

Wetlands support ideal conditions for the removal of reactive nitrogen by denitrification (Jordan et al. 2011) and for the sequestration of nitrogen and phosphorus in organic matter (Reddy et al. 1999). At the same time, wetlands can be important sources of dissolved organic matter (and organic nutrients) to downstream and coastal ecosystems (Schiff et al. 1998, Pellerin et al. 2004, Harrison et al. 2005). Despite the high potential for denitrification within wetlands, there are no good estimates of their contribution to global N$_2$O emission, and it has generally been assumed that N$_2$O production is much lower in wetlands than in upland soils (Bridgham et al. 2006, Mitsch and Gosselink 2007, Schlesinger 2009).

The heightened capacity for denitrification, CH_4 production, and soil carbon storage in wetlands are all a result of a lack of oxygen in wetland sediments. While aerobic oxidation ($CH_2O + O_2 \rightarrow CO_2 + H_2O$) dominates organic matter decomposition in most terrestrial ecosystems, microbes in flooded soils must use a variety of anaerobic metabolic pathways to obtain energy from organic matter. Microbial consumption of oxygen in wet soils and sediments frequently exceeds O_2 supply through diffusion. Without oxygen, microbes cannot use oxidative phosphorylation to decompose organic polymers to CO_2, and instead must rely on the alternate electron acceptors NO_3^-, Fe^{3+} and Mn^{4+}, SO_4^{2-}, or, in the most highly reducing environments, fermentation products such as acetate or CO_2 itself. Many of these primitive metabolic pathways evolved prior to the oxygenation of the Earth (Chapter 2), and continue to dominate the biogeochemistry of anoxic wetland sediments. These pathways yield less energy than aerobic respiration and the supply of alternate electron acceptors is often limiting, leading to far less efficient decomposition in wetlands and ultimately to large stores of organic matter. Over geologic time, the organic detritus accumulated in wetlands of the Carboniferous was buried and lithified to become modern coal deposits (Cross and Phillips 1990, McCabe 2009).

TYPES OF WETLANDS

The great variety of wetland types can be classified using hydrologic and physical properties that collectively constrain biogeochemical cycling and determine how wetlands influence the form, timing, and magnitude of chemical exports from catchments (Brinson 1993). Among the most important factors are water residence time, the degree of hydrologic connectivity between the wetland and regional rivers or groundwater, and the frequency, intensity, and duration of inundation. Wetlands may also be characterized by their soils and vegetation, which both respond to and exert control over wetland hydrology.

Wetland Hydrology

Water may enter a wetland by precipitation, tributary inflows, near-surface seepage, and exchange with deeper groundwater; water leaves wetlands through groundwater recharge, surface outflows, and evapotranspiration (Figure 7.2).

$$\text{Wetland volume } (V) = \text{Inputs } (P_n + S_i + G_i) - \text{Outputs } (ET - G_o - S_o). \qquad (7.1)$$
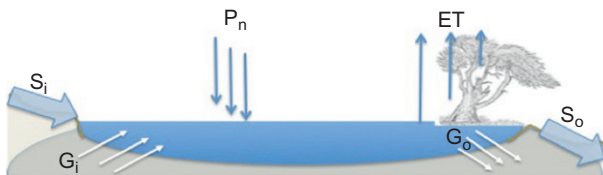

FIGURE 7.2   A wetland water budget. P_n represents precipitation inputs; ET represents evapotranspiration losses. S denotes surface water; G denotes groundwater. Subscript i indicates inputs; o indicates outputs.

The residence time of water within a wetland is calculated as the wetland volume (V) divided by the total inputs or outputs (MRT = V/Inputs or V/Outputs).[2] Wetlands in which precipitation and evapotranspiration are the only modes of water exchange usually have long water residence times and are sometimes referred to as closed systems because the rate of internal element turnover vastly exceeds the exchange of elements across ecosystem boundaries. In contrast, wetlands where runoff and outflow dominate the water budget are known as open systems, since water residence times are short and the flux of materials through the system may approach or exceed nutrient turnover within the ecosystem. The residence time of water ultimately limits the capacity of biota to change the composition of waters passing through a wetland.

The degree of hydrologic connectivity between a wetland and its catchment affects not only the source but the composition of biogeochemically important elements in the wetland, as well as the degree to which the wetland can affect biogeochemical patterns at larger, catchment scales. Comparisons of northern peatlands and riverine wetlands are instructive. The extensive peatlands at high latitudes tend to be hydrologically isolated wetlands, known as *ombrotrophic*[3] bogs, which receive all or most of their water from precipitation (Gorham 1957). In contrast, the wetlands that border many rivers experience episodic flooding and inundation accompanied by high rates of sediment deposition and erosion, and thus experience active biogeochemical exchange with adjacent surface waters.

Just as the amount and timing of annual precipitation is a key determinant of vegetation composition and productivity in terrestrial ecosystems, the annual hydroperiod of wetlands is a defining characteristic of their biological and biogeochemical properties (Brinson 1993). A wetland's hydroperiod describes the depth, duration, and frequency of inundation during a typical year (Figure 7.3). Some wetlands are permanently flooded, while others never have standing surface water. The periodicity and predictability of flooding in wetlands varies, with some wetlands flooded seasonally while other wetlands are only inundated following heavy rainfall. Wetlands subject to lunar tides will have predictable diel flooding frequencies, while wind tides lead to dynamic and unpredictable flooding in wetlands on low-lying coastal plains. The duration and intensity of flooding drives temporal variation in soil oxygen availability in wetland sediments, which places strong constraints on wetland vegetation. Flood pulses can also provide critical subsidies of material from upland and upstream ecosystems that fuel wetland productivity and food webs (Brinson et al. 1981, Megonigal et al. 1997).

Salinity merits special consideration. Wetlands that are hydrologically connected to the oceans or to inland salt lakes have intermittently or permanently high concentrations of sea-salts. In salt marshes salinity may change from freshwater to full-strength seawater over the course of a single tide cycle, while more inland coastal wetlands may experience saltwater intrusion only during rare droughts or extreme wind tides associated with hurricanes. Only a few species of herbaceous vegetation have successfully adapted to life in full-strength seawater, since the high ionic strength of saltwater makes it difficult for plants to maintain osmotic balance.

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[2] See Footnote 1, Chapter 3.

[3] Ombrotrophic, literally meaning "to feed on rain," is a term often used to describe vegetation dependent on atmospheric nutrients.
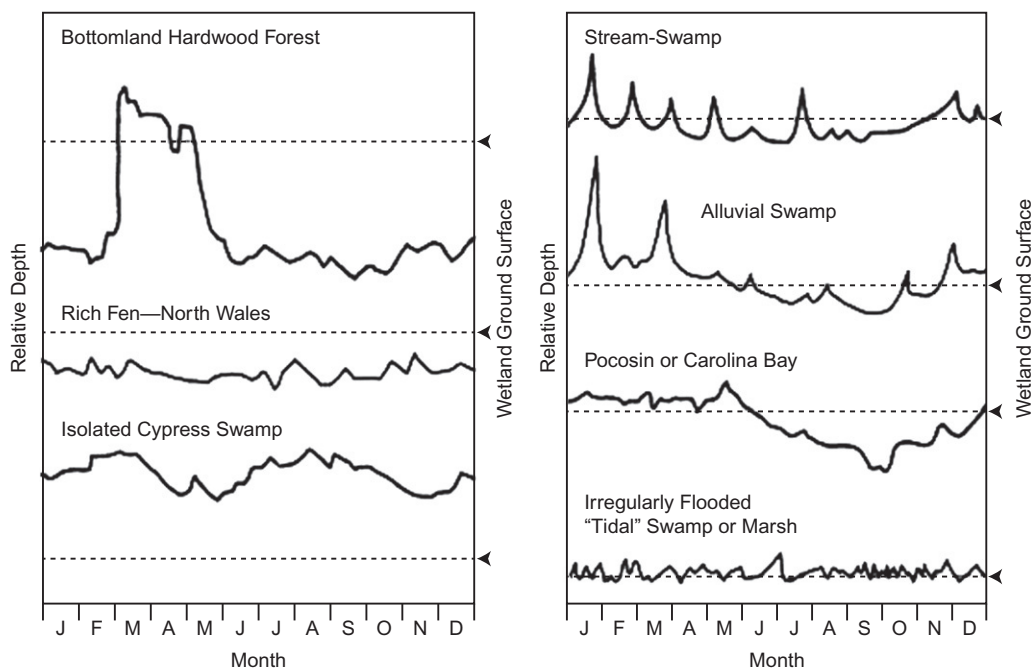
FIGURE 7.3   A comparison of wetland hydroperiods. Note that the duration and frequency of surface water vary greatly between wetland types. While the Bottomland Hardwood Forest and Carolina Bay are seasonally flooded, the hydrologically isolated cypress swamp is permanently flooded. In contrast, wetlands adjacent to rivers such as the stream-swamp and alluvial swamp shown here may undergo periodic inundation in conjunction with river floods. Tidal marshes may be flooded and drained on a daily basis, while some rich fens and bogs never have standing surface water. *Source: From Brinson (1993). Used with permission of Springer.*

Wetland Soils

Generally, wetland soils can be classified into three categories:

1. Soils permanently inundated with water above the soil surface
2. Saturated soils with the water table at or just below the soil surface
3. Soils where the water table depth is always below the surface

In saturated wetland soils, oxygen typically does not diffuse more than a few millimeters below the water table and reduced compounds and trace gases (N_2O, H_2S, CH_4) produced from anaerobic metabolic pathways can accumulate at high concentrations. Iron is a convenient indicator of anoxic conditions in the field because oxidized iron is easily recognized in soils by its red color, whereas reduced iron is grayish (Megonigal et al. 1993). Soil layers with reduced iron are called gley (Figure 7.4). In saturated wetland soils, the soil volume is generally 50% solids and 50% water, while in upland soils as much as 25% of the soil volume can consist of air-filled pore space. In upland soils only the interior of soil aggregates is typically anoxic (Chapter 6) and gases diffuse readily between the soil and the atmosphere. Wetland soils can
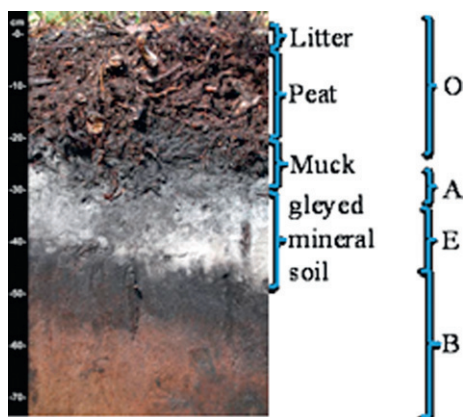
FIGURE 7.4   A hydric soil profile, with a thick dark layer of organic soil overlying a grey mineral soil characteristic of reduced iron. The traditional soil horizons for this Spodosol are indicated on the right. The organic (O) horizon overlies a mineral (A) horizon enriched in humic materials. The zone of eluviation (E) is characterized by a loss of silicate clays, iron, or aluminum and overlies the B horizon, or zone of illuviation. *Source: Image from NRCS 2010 Field Indicators of Hydric Soils in the United States; see* www.nwo.usace.army.mil/html/od-rwy/hydricsoils.pdf.

be converted to upland soils through drainage. The global loss of wetlands has largely resulted from efforts to drain wetlands so that formerly saturated sediments can support agriculture.

Wetland Vegetation

Having saturated sediments but sufficiently shallow surface water that allows vascular plants to dominate, wetlands occupy a special place along the terrestrial-to-aquatic continuum. The dominant autotrophs in wetlands have similar light and nutrient requirements to those of the plants of upland systems (Chapter 6) but must overcome the additional constraint of rooting in waterlogged soils with low O_2 concentration. Wetlands may be dominated by autotrophs ranging from sphagnum moss, sedges, reeds, and grasses to shrubs or trees—with the dominant vegetation both a function of and a control on wetland water balance and hydroperiod. Vascular plants growing in wetland ecosystems must cope with periodic or permanent saturation of their root tissues, a physiological challenge that prevents many plants from growing successfully in wetlands (Bailey-Serres and Voesenek 2008). A lack of oxygen in saturated soils directly interferes with root metabolism, creating root oxygen deficiency (Keeley 1979, Gibbs and Greenway 2003). In addition, anoxic sediments support microbial production of some metabolic products that are toxic to plants (e.g., H_2S from sulfate reduction; Eq. 2.12) (Lamers et al. 1998, Wang and Chapman 1999).

Wetland plants have developed a variety of morphological and physiological traits that allow them to persist in saturated sediments. Some wetland plants have the capacity to use anaerobic fermentation in their roots during periods of low or no oxygen (Keeley 1979, Gibbs and Greenway 2003, Greenway and Gibbs 2003); however, metabolism of organic compounds via fermentation is far less efficient than aerobic respiration. Many wetland plants have airspaces within their cortex (*aerenchyma*) that facilitate gas exchange between the atmosphere and the sediments surrounding their roots (Brix et al. 1992, Jackson and Armstrong 1999; Figure 7.5). Still other wetland plants, such as the bald cypress and coastal mangrove trees, have specialized aerial rooting structures (*pneumatophores*) that appear to facilitate gas exchange (Kurz and Demaree 1934, Scholander et al. 1955).
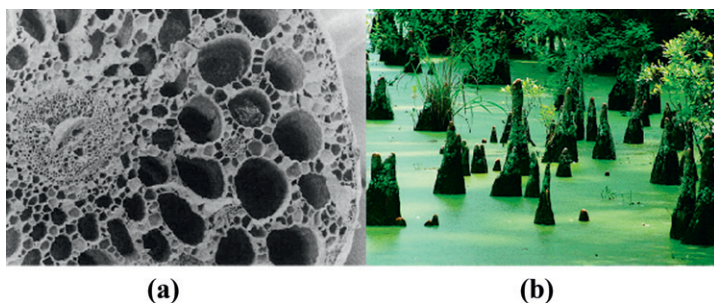
FIGURE 7.5 (a) Electron micrograph of a cross-sectioned stem of the aquatic macrophyte *Potamageton*; (b) photograph of Cypress pneumatophores. *Source: (a) From Jackson and Armstrong (1999). (b) From Wikipedia Commons.*

(a) **(b)**

Facilitated gas exchange between the atmosphere and the rhizosphere, in addition to alleviating oxygen stress for plants, can also increase the oxygen content of wetland soils around plant roots (Wolf et al. 2007, Schmidt et al. 2010a), allowing aerobic metabolism by soil microbes in flooded soils. For many wetland plants the extent of aerynchymous tissues depends on the intensity or duration of inundation, suggesting that there is some physiological cost associated with these specialized tissues (Justin and Armstrong 1987). These adaptations allow wetland plants to persist in suboxic or anoxic conditions and to alter soil oxygen availability. Some plants are only found in wetland ecosystems (obligate wetland plants) whereas others are capable of growing across a broader range of hydrologic conditions (facultative wetland plants) and are merely more common in wetland ecosystems.

PRODUCTIVITY IN WETLAND ECOSYSTEMS

Emergent plants dominate the vegetation of most wetlands and net primary production is usually estimated using the harvest or eddy-covariance approaches outlined in Chapter 5. Net primary productivity varies widely across wetland ecosystems depending on nutrient supply (Brinson et al. 1981, Brown 1981). Unlike terrestrial ecosystems, where variation in vegetation type and stature is largely predictable from climate, the differences in wetland productivity is more strongly influenced by edaphic[4] factors (Brinson 1993). Variation in wetland hydroperiod has important consequences for productivity, because autotrophic respiration is less efficient in saturated soils (as discussed in the previous section) and because a high proportion of nutrients are sequestered in undecomposed soil organic matter, leaving low concentrations (and slow turnover) of available nutrients in the soil. Areas that are less frequently flooded tend to have higher productivity, since periodic soil drying allows for more rapid nutrient mineralization by aerobic microbes (Figure 7.6).

In contrast to upland terrestrial ecosystems, where numerous experiments have documented nutrient limitation of primary productivity, there have been far fewer experimental manipulations of nutrient supply in wetland ecosystems (Bedford et al. 1999). Venterink et al. (2001) reported that nearly half of 50 fertilization experiments in wetlands found

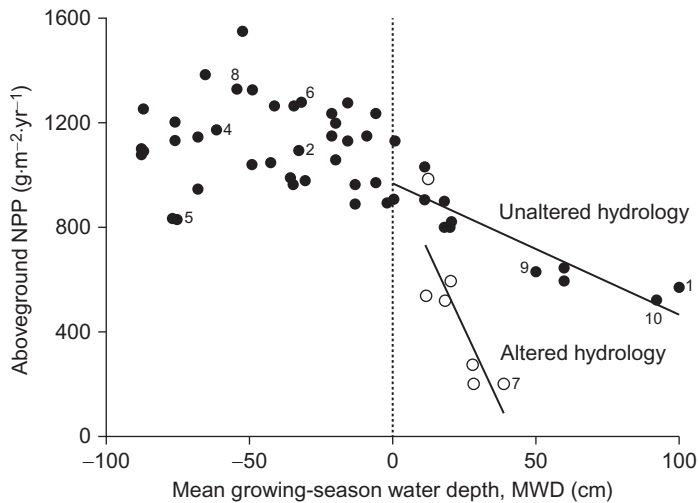[4] Resulting from or influenced by the soil.

FIGURE 7.6 Water depth was negatively correlated with aboveground NPP for southern coastal wetlands. The effect of inundation was more pronounced when levees were built to maintain permanent flooding (plots shown in open circles). *Source: From Megonigal et al. 1997. Used with permission of Springer.*

significant N limitation of plant biomass, 8 experiments reported P limitation, and 13 reported colimitation by N with either P or K. In wetlands spanning gradients of atmospheric N deposition across Europe and Canada, N inputs appear to be correlated with increasing vascular plant biomass and reduced biomass of low stature mosses (Berendse et al. 2001, Turunen et al. 2004, Limpens et al. 2008). In a long-term (5-year) fertilization experiment in the Mer Bleue peatland in Ottawa, Canada, Bubier et al. (2007) saw no change in total aboveground plant biomass and lower net ecosystem production (NEP) in fertilized plots. They attributed this paradoxical finding to a nutrient stimulation of vascular plant growth that was accompanied by declines in the abundance of mosses, particularly *Sphagnum,* leading to a decline in organic matter accumulation. The loss of *Sphagnum* mosses due to N deposition, fertilization, or drainage-induced increases in N turnover could lead to substantial reductions in peat accumulation because replacement species typically produce higher-quality litter and have higher rates of evapotranspiration than *Sphagnum* (van Breemen 1995).

In closed wetland systems such as the extensive boreal peatlands at high latitudes in the Northern Hemisphere, nitrogen and phosphorus are typically both in short supply for plant growth and decomposition (Chapin et al. 1978, Damman 1988). In the tundra of Alaska, Chapin et al. (1978) found that the soil organic matter contained 64% of the total phosphorus in the ecosystem and had a mean residence time of 220 years, while available phosphorus in soil solution comprised 0.3% of the total phosphorus and had a residence time of 10 hours. Low temperatures and high water tables together limit nutrient mineralization in the tundra (Marion and Black 1987), and as a result of slow decomposition many boreal bogs show a net accumulation of nitrogen and phosphorus in peat (Hemond 1983, Damman 1988, Urban et al. 1989a). In a fertilization experiment, Shaver and Chapin (1986) found that the response of *Eriophorum vaginatum* in tussock tundra was greater for N than for P. Rates of nitrogen fixation within boreal wetlands can be very high (Barsdate and Alexander 1975, Waughman and Bellamy 1980, Schwintzer 1983). A variety of arctic plants are capable of assimilating low-molecular-weight

organic nitrogen molecules (e.g., Chapin et al. 1993, Nasholm et al. 1998), which suggests that in isolated wetlands, nitrogen limitation is frequently severe.

Determining nutrient limitation of primary productivity in hydrologically open wetlands is more difficult because hydrologic losses complicate fertilization experiments. Wetlands receiving surface runoff can have high inputs of phosphorus and other elements derived from rock weathering (Mitsch et al. 1979, Waughman 1980, Frangi and Lugo 1985). In these ecosystems phosphorus and sulfur are retained on iron and aluminum minerals that are constituents of soil organic matter (Richardson 1985, Mowbray and Schlesinger 1988). With greater surface and groundwater inputs, net primary production is more likely to be limited by N than P (e.g., Tilton 1978) because large amounts of nitrogen can be lost through denitrification, while P tends to accumulate in soil organic material. Many wetlands receive high inorganic N loading from fertilizer, sewage-derived runoff, or N deposition, which can lead to substantial changes in plant composition (Bedford et al. 1999).

Net primary production (NPP) is highest in wetlands receiving nutrient enrichment or with high nutrient turnover. The degree, duration, and periodicity of flooding affect wetland productivity more than rainfall or temperature. Drainage can promote enhanced productivity by increasing nutrient mineralization. Tree growth and nitrogen content increase when northern wetlands are drained (Figure 7.7; Lieffers and Macdonald 1990, Westman and Laiho 2003, Choi et al. 2007, Turetsky et al. 2011). Flooding can enhance wetland productivity when it brings subsidies of nutrients from the contributing catchment, but can also stress wetland plants by suppressing organic matter mineralization and promoting the production of H_2S. This subsidy-stress relationship (*sensu* Odum et al. 1979) precludes a general relationship between water availability and NPP in wetland ecosystems. In a survey of temperate forested wetlands, Megonigal et al. (1997) found that intermittently flooded wetlands had higher litterfall and NPP than permanently flooded wetlands (Figure 7.8) and suggested that intermittent flooding allows soils to dry, which increases decomposition and promotes nutrient mineralization. In contrast, other studies have suggested that inundation by flowing water can deliver nutrients from upland areas to wetland forests (Conner and Day 1976, Conner et al. 2011). Several studies in forested floodplain wetlands found the highest litterfall in the wettest sites but little clear evidence that plant growth was affected by flooding regime (Clawson et al. 2001, Conner et al. 2011). The discrepancy in findings may be due to the type of inundation, with stagnant inundation suppressing nutrient mineralization and reducing productivity (e.g., Schlesinger 1978, Megonigal et al. 1997) and flowing water providing nutrient subsidies (e.g., Conner and Day 1976, Clawson et al. 2001).

ORGANIC MATTER STORAGE IN WETLANDS

Decomposition is impeded in flooded and saturated soils so that primary production in wetlands will often exceed decomposition, leading to a net accumulation of soil organic matter. As a result, over decadal to millennial timescales many wetlands have accumulated large standing stocks of soil organic matter (Table 7.2). If the plant remains are still recognizable, these organic materials are called peat. As decomposition removes carbon and the relative mineral fraction increases, oxidation of soil humus leads to a darker muck without recognizable plant tissues (see Figure 7.4). The rate of peat accumulation is determined by the rates of
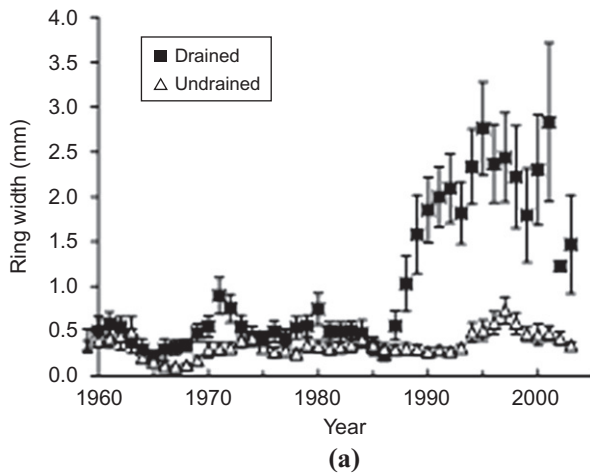
FIGURE 7.7 Drainage of a forested boreal fen in western Canada in 1986 doubled the rate of peat C accumulation through increases in tree biomass and detritus (indicated here by tree ring growth) (a), but also made the drained fen more susceptible to catastrophic losses of carbon in fire (b). In 2001, a wildfire burned ~450 years of accumulated peat in the drained portion while removing only ~58 years of accumulated peat in the undrained portions of the fen. *Source: Modified from Turetsky et al. (2011).*
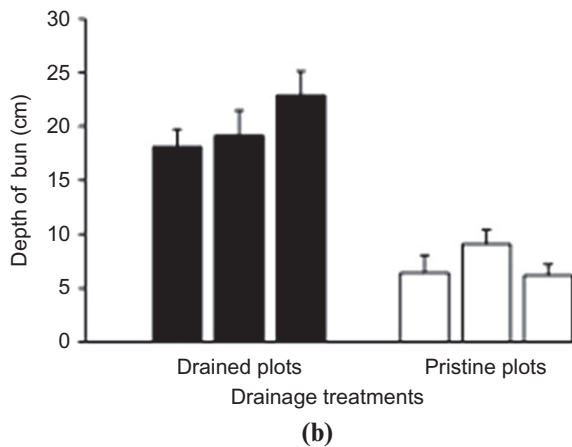
decomposition in both the oxic upper level and the lower level of the deposit. Through time, older layers of organic material are buried and compacted beneath the weight of newly deposited plant detritus (Figure 7.7). The transport of solutes and diffusion of gases slow with depth as a result of water saturation and compaction. It is useful to differentiate between the biogeochemically active *acrotelm*, the surface layer of peat above the lowest water table elevation that experiences fluctuations between oxic and anoxic conditions, and the *catotelm*, or underlying layers that are permanently saturated.

Peatland ecosystems can be perceived as a special category of wetland wherein plants build the terrain through the deposition of litter into saturated soils. Accretion occurs in these low-energy environments through biogenic processes rather than by sediment deposition (Gosselink and Turner 1978, Brinson et al. 1981). Clymo (1984) proposed a model for peat accumulation which predicts that peatlands will eventually attain a steady state when the input of detritus from primary production at the peat surface is balanced by the loss of organic
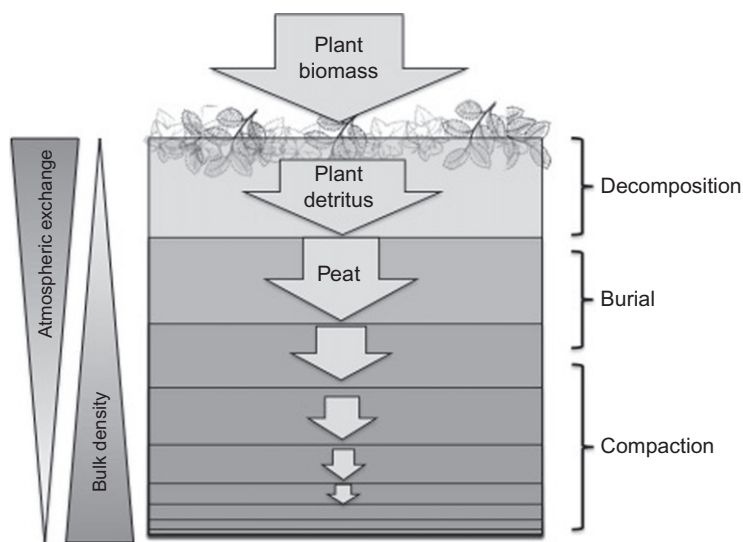
FIGURE 7.8   A model of peat accumulation and compaction over time. Fresh litter is deposited in the surface layers, where decomposition rates are highest due to oxygen diffusion and the supply of alternate electron acceptors. Organic matter that escapes decomposition is buried beneath new litter inputs and over time becomes compacted through the accumulation of overlying material. Models of peat accumulation predict that eventually peatlands reach a steady state where new biomass inputs are balanced by carbon losses through decomposition. *Source: Adapted from Clymo (1984).*

TABLE 7.2   Carbon Accumulation in Wetland Sediments: a Compilation of Reported Rates

Location	Wetland and/or vegetation type	Accumulation interval (yrs)	Accumulation rate (g C m^{-2} yr^{-1})	References
Peatlands			12–25	Malmer (1975)
Global wetlands			20–140	Mitra et al. (2005)
North America	Peatlands		29	Gorham (1991)
Boreal Wetlands			**8–80**	
Alaska and Canada	Peatlands		8–61	Ovenden (1990)
Alaska	*Picea* and *Sphagnum*	4790	11–61	Billings (1987)
Russia	Mires, bogs, and fens	3000–7000	12–80	Botch et al. (1995)
Manitoba	*Picea* and *Sphagnum*	2960–7939	13–26	Reader and Stewart (1972)
Western Canada	*Sphagnum* bogs	9000	13.6–34.9	Kuhry and Vitt (1996)
Sweden	Bogs		20–30	Armentano and Menges (1986)

TABLE 7.2 Cont'd

Location	Wetland and/or vegetation type	Accumulation interval (yrs)	Accumulation rate (g C m^{-2} yr^{-1})	References
Alaska	*Eriophorum vaginatum*	7000	27	Viereck (1966)
Ontario	*Sphagnum* bogs	5300	30–32	Belyea and Warner (1996)
Russia	Siberian mires	8000–10,000	12.1–23.7	Turunen et al. (2001)
Finland	Mires		18.5	Turunen et al. (2002)
Canada	Mer Bleue ombrotrophic bog	2700	10–25	Roulet et al. (2007)
Canada	23 ombrotrophic bogs	150	73 ± 17	Moore et al. (2005)
Finland	795 bogs and fens	5000	21	Clymo et al. (1998)
Sweden	Store Mosse mire	5000	14–72	Belyea and Malmer (2004)
Canada	Continental western Canadian peatlands	Current	19.4	Vitt et al. (2000)
Temperate Wetlands			**17–317**	
Georgia	Floodplain cypress gum forests	100	107	Craft and Casey (2000)
Georgia	Depressional wetlands	100	70	Craft and Casey (2000)
Wisconsin	*Sphagnum*	8260	17–38	Kratz and DeWitt (1986)
Massachusetts	Thoreau's bog		90	Hemond (1980)
North America	Protected prairie potholes		83	Euliss et al. (2006)
Ohio	Created marshes		180–190	Anderson and Mitsch (2006)
North America	Restored prairie potholes		305	Euliss et al. (2006)
Ohio	Depressional wetlands	42	317 ± 93	Bernal and Mitsch (2012)
Ohio	Riverine, flow-through	42	140 ± 16	Bernal and Mitsch (2012)
Eastern U.S.	Circumneutral freshwater peatlands	30	49 ± 11	Craft et al. (2008)
Eastern U.S.	Acidic freshwater peatlands	30	88 ± 20	Craft et al. (2008)
Subtropical Wetlands			**70–387**	
Louisiana	Salt marsh		200–300	Hatton et al. (1983)
Florida	*Cladium* swamp	25–30	70–105	Craft and Richardson (1993)

I. PROCESSES AND REACTIONS

TABLE 7.2   Carbon Accumulation in Wetland Sediments: a Compilation of Reported Rates—Cont'd

Location	Wetland and/or vegetation type	Accumulation interval (yrs)	Accumulation rate (g C m^{-2} yr^{-1})	References
Florida Everglades	*Cladium sp.*		86–140	Reddy et al. (1993)
Florida Everglades	*Typha sp.*		163–387	Reddy et al. (1993)
Tropical Wetlands			**39–480**	
Amazon	Lowland peatlands	1700–2850	39–85	Lahteenoja et al. (2009)
Kenya	Papyrus wetlands		160	Jones and Humphries (2002)
Uganda	Papyrus wetlands		480	Saunders et al. (2007)
Costa Rica	Humid tropical wetland	42	255	Mitsch et al. (2010)
Mexico	Mangroves		100	Twilley et al. (1992)
Range of reported values			**8–480**	

matter by decomposition throughout the peat profile. The saturated soils of tundra and boreal forest region contain about 50% of the total storage of organic matter in soils of the world (Tarnocai et al. 2009, Frolking et al. 2011). Many of these ecosystems have accumulated soil carbon since the retreat of the last continental glaciers (Harden et al. 1992).

The unique aspect of wetland ecosystems is the dominance and diversity of anaerobic metabolic pathways employed by microbes for metabolism in the absence of oxygen. The drainage of wetland soils (through natural droughts or anthropogenic drainage) leads to rapid oxidation of their large stocks of organic matter by aerobic microbes (Armentano and Menges 1986, Turner 2004). The resulting decrease in soil elevation, or subsidence, has been notably documented for inland wetlands in England, Germany, and the Florida Everglades, where posts have been anchored in a stable subsurface layer and changing surface elevations are recorded relative to the immobile post. Soil elevation has declined more than 4 m in the past 130 and 150 years in the German and English sites, respectively (Heathwaite et al. 1990), and more than 3 m since 1924 at the Everglades site (Stephens and Stewart 1976). The rapid oxidation of soil organic matter in drained wetlands provides clear evidence that much of the organic material stored in wetland sediments is not inherently recalcitrant. Decomposition in flooded soils is extremely inefficient due to a lack of oxygen (Figure 7.9).

To understand how flooding constrains decomposition, we must compare the mechanisms and energy yield derived from anaerobic respiration and aerobic respiration. Both decomposition pathways are initiated by the cleavage of organic monomers from large complex organic polymers by extracellular enzymes. Aerobic respiration can
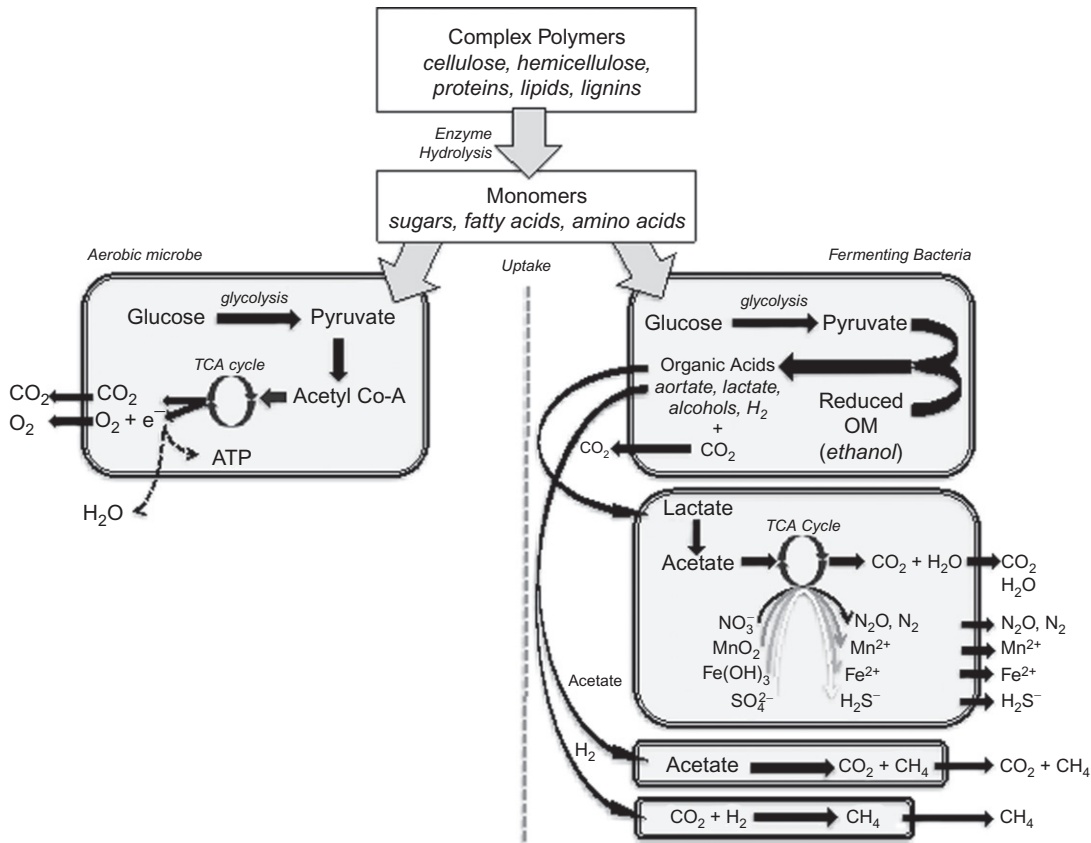
FIGURE 7.9 Contrasting the single aerobic respiration pathway with the multistage pathway involved in decomposition in the absence of oxygen. *Source: Figure drawn with inspiration from Megonigal et al. (2003) and Reddy and DeLaune (2008).*

completely degrade the resulting organic monomers to CO_2 using glycolysis followed by the Kreb's cycle (Figure 7.9). When oxygen is available, a single molecule of glucose yields 2 moles of ATP from glycolysis and a further 36 moles of ATP through the Kreb's cycle (Madigan and Martinko 2006). Without oxygen, this reaction sequence stops at pyruvate, and further degradation requires fermentative metabolism, which has a low energy yield (Figure 7.9). Aerobic respiration results in the complete degradation of monomers to CO_2, whereas fermentation results in the accumulation of a variety of organic acids and alcohols. The resulting fermentation products are subsequently further degraded to CO_2 by bacteria using NO_3^-, Mn^{4+}, Fe^{3+}, or SO_4^{2-} as alternative electron acceptors in place of O_2, or they may undergo additional fermentation steps to produce CH_4. These alternative respiratory pathways have lower energy yields, and thus support a smaller microbial biomass that in turn produces lower concentrations of extracellular enzymes (McLatchey and Reddy 1998).

There are two mechanistic explanations for the inefficient decomposition typical of wetlands. Until recently, decomposition was primarily assumed to be limited by the supply of oxygen and alternative electron acceptors necessary for the terminal steps in organic matter decomposition. Recent work has suggested additional enzyme-mediated constraints at earlier stages of the decomposition pathway (Limpens et al. 2008). The activity of phenol oxidase, a critical extracellular enzyme involved in the degradation of lignin and phenolics,[5] is substantially reduced under low-oxygen conditions, leading to an accumulation of phenolic compounds in wetland sediments (McLatchey and Reddy 1998, Freeman et al. 2001b). High concentrations of phenolic compounds can then further inhibit organic matter decomposition (Appel 1993, Freeman et al. 2001b, Ye et al. 2012).

When one or more alternate electron acceptors are abundant, the rate of soil organic matter decomposition will be limited by the pace of enzymatic hydrolysis or fermentation (Freeman et al. 2001b, Megonigal et al. 2003). In contrast, when alternate electron acceptors are in short supply, fermentation products may accumulate until sediments are resupplied with oxygen or alternative electron acceptors. Decomposition of soil organic matter in wetlands can be enhanced either by lowering the water table (allowing oxygen to penetrate to deeper soil layers) or by increasing the supply of alternate electron acceptors. Nitrogen deposition, amendments with oxidized Fe, and enhanced SO_4 availability resulting from acid rain or saltwater intrusion have all been shown to significantly enhance decomposition rates (Van Bodegom et al. 2005, Bragazza et al. 2006, Gauci and Chapman 2006, Weston et al. 2006). Decomposition in wetland sediments is typically highest at the wetland surface, where recently synthesized, more labile organic material comes into contact with the greatest potential supply of electron acceptors.

MICROBIAL METABOLISM IN SATURATED SEDIMENTS

In a closed aqueous system containing a large supply of organic material together with appreciable concentrations of oxidants (O_2, NO_3^-, Mn^{4+}, Fe^{3+}, and SO_4^{2-}), we can easily predict the order in which the oxidants will be depleted (Table 7.3). The exergonic (energy-yielding) oxidation of organic matter (A) would be paired first with oxygen respiration (B), then NO_3^- respiration (C), then Mn^{4+} (D), Fe^{3+} (E), and SO_4^{2-} (F) respiration would follow in sequence (Table 7.3). If organic matter remained after all of these oxidants were depleted, we might subsequently measure an accumulation of CH_4 in our closed vessel. This predictable sequence of biologically mediated chemical reactions occurs because there is a tendency for the highest energy yielding metabolic pathways to take precedence over lower energy yielding processes (Stumm and Morgan 1996). The same reaction sequence observed in a closed vessel can also be observed in wetland ecosystems examined through time following flooding or with depth in the soil profile (Figure 7.10).

Common reduction and oxidation half reactions are shown in Table 7.3 together with the standard electrical potential of each reaction. Standard electrical potentials are expressed per mol of electrons transferred; thus each reaction has been written to transfer one mol of

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[5] Phenolics are a class of chemical compound consisting of a hydroxyl group bonded directly to an aromatic hydrocarbon. In wetlands, soluble humic acids make up a large fraction of phenolics.

TABLE 7.3 Common Reduction and Oxidation Half Reactions

Part A

Reduction	E° (V)	Oxidation	E°(V)
(A) $1/4O_2(g) + H^+ + e^- = 1/2H_2O$	+0.813	(L) $1/4CH_2O + 1/4H_2O = 1/4CO_2 + H^+ + e^-$	−0.485
(B) $1/5NO_3^- + 6/5H^+ + e^- = 1/10N_2 \; 3/5H_2O$	+0.749	(M) $1/2CH_4 + 1/2H_2O = 1/2CH_3OH + H^+ + e^-$	+0.170
(C) $1/2MnO_2(s) + 1/2HCO_3 + 3/2H^+ + e^- = 1/2MnCO_3 + H_2O$	+0.526	(N) $1/8HS^- + 1/2H_2O = 1/8SO_4^{2-} + 9/8H^+ + e^-$	−0.222
(D) $1/8NO_3^- + 5/4H^+ + e^- = 1/8NH_4^+ \; 3/8H_2O$	+0.363	(O) $FeCO_3(s) + 2H_2O = FeOOH(s) + HCO_3(10^{-3}) + 2H^+ + e^-$	−0.047
(E) $FeOOH(s) + HCO_3(10^{-3}) + 2H^+ + e^- = FeCO_3(s) + 2H_2O$	−0.047	(P) $1/8NH_4^+ \; 3/8H_2O = 1/8NO_3^- + 5/4H^+ + e^-$	+0.364
(F) $1/2CH_2O + H^+ + e^- = 1/2CH_3OH$	−0.178	(Q) $1/2MnCO^3(s) + H_2O = 1/2MnO_2(s) + 1/2HCO_3(10^{-3}) + 3/2H^+ + e^-$	+0.527
(G) $1/8SO_4^{2-} + 9/8H^+ + e^- = 1/8HS^- + 1/2H_2O$	−0.222		
(H) $1/8CO_2 + H^+ + e^- = 1/8CH_4^+ \; 1/4H_2O$	−0.244		
(I) $1/6N_2 + 4/3H^+ + e^- = 1/3NH_4$	−0.277		

Part B

Examples	Combinations	ΔG° (W) pH=7 (kJ eq−1)
Aerobic respiration	A+L	−125
Denitrification	B+L	−119
Nitrate reduction to ammonium	D+L	−82
Fermentation	F+L	−27
Sulfate reduction	G+L	−25
Methane fermentation	H+L	−23
Methane oxidation	A+M	−62
Sulfide oxidation	A+N	−100
Nitrification	A+P	−43
Ferrous oxidation	A+O	−88
Mn(II) oxidation	A+Q	−30

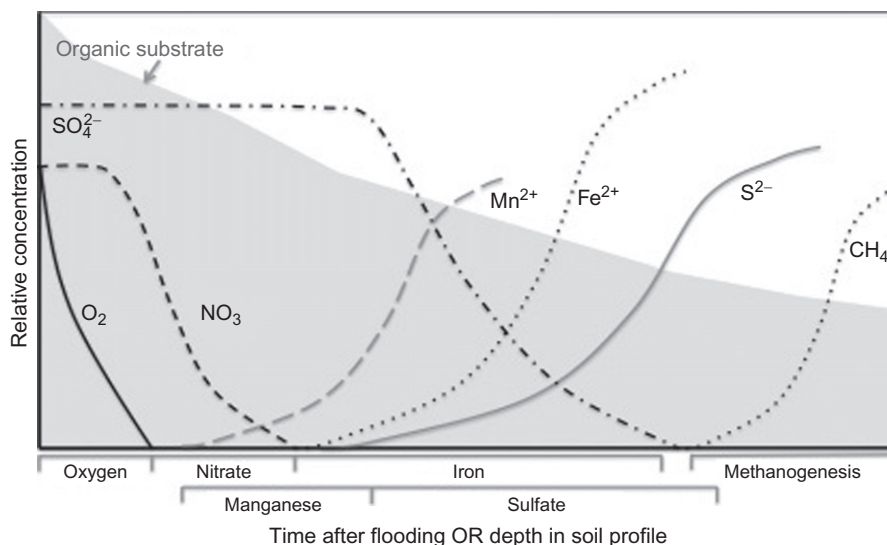*Source: Modified from Stumm and Morgan (1996, p. 474).*

FIGURE 7.10   The concentrations of reactants and products of terminal decomposition pathways are shown for a wetland sediment over time following flooding. Rotating the figure 90° to the right shows the pattern of substrate concentrations (and the order of metabolic pathways) with depth in a soil profile.

electrons. Where $E° > 0$ the reaction will proceed spontaneously as written. Where $E° < 0$ the reaction will proceed in the opposite direction. The greater the difference in $E°$ between two half reactions, the greater the resulting free energy yield from their combination will be. In Part B the standard free energies of common redox couplets are shown. These are calculated from the $E°$ values in Part A using Equation 7.2. In the table, CH_2O represents an "average" organic substance. The actual free energy yield of different organic substances may differ from that given for CH_2O. This difference may be very large, particularly for anoxic processes involving carbon substrates with very different oxidation states than that assumed for CH_2O.

The terminal decomposition steps in wetlands are dominated by anaerobic metabolic pathways that yield a variety of reaction products in addition to the CO_2 and H_2O generated by aerobic oxidation. These pathways are responsible for the production of N_2, N_2O, and CH_4, the abundance of reduced H_2, Fe^{2+}, and H_2S, and the production of pyrite (FeS_2) in wetland soils. In any wetland the relative importance of these metabolic pathways to overall ecosystem carbon and nutrient cycling depends on the external supply or reoxidation of the various electron acceptors. The order of redox reactions results from the very limited supply of fermentation products. Since fermentation is slow and fermentation products are scarce, the metabolic pathways that maximize energy gain are highly favored. Successful metabolic strategies (and thus successful microbes) are those that garner the greatest energy given available substrates. The "redox ladder," the predictable sequence of reactions following flooding or with depth, thus arises from competitive interactions between microbes (Postma and Jakobsen 1996, Stumm and Morgan 1996). It seems at first paradoxical that in these carbon-rich systems we see such fierce competition for carbon substrates that the chemical reaction sequence is closely matched by an ecological succession of microorganisms (aerobic

heterotrophs → denitrifiers → fermenters → sulfate reducers → methanogens). This paradox can be explained if we consider that the rate of decomposition is determined by fermentation while the relative dominance of terminal electron acceptor processes is predictable from their energy yield (Postma and Jakobsen 1996).

To understand and predict which microbial metabolisms will dominate at any given time or place in wetland sediments, we must understand how the possible reactions vary in the amount of energy generated (free energy yield). Thermodynamics allows us to predict the dominant metabolisms because particular microbial species, with different metabolic strategies, become competitively superior under different chemical conditions.
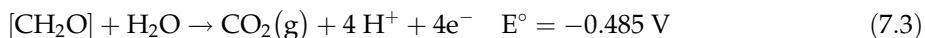
Free Energy Calculation

To calculate the energy yield from the oxidation of organic matter paired with the reduction of any electron acceptor, we calculate the standard Gibb's free energy yield ($\Delta G°$) for a redox couplet as:

$$\Delta G° = -nF\Delta E, \tag{7.2}$$

where n is the number of electrons, F is Faraday's constant (23.061 kcal volt^{-1}), and ΔE is the difference in electrical potential (V) between the oxidation and reduction reactions (Table 7.4). Reactions with a negative ΔG are energy yielding (exergonic) while reactions with a positive ΔG require energy (endergonic).

For aerobic respiration of a generic organic molecule (CH_2O), we can calculate the standard free energy yield $\Delta G°$. The standard free energy assumes that all substrates are available in abundance and that the reaction occurs at a standard temperature of 25°C. The free energy yield of each reaction is higher for carbon compounds that have more reduced chemical bonds and lower for more oxidized organic molecules. Here we will use a generic carbon molecule with 1/6 the free energy of glucose, which has six carbon atoms.

Oxidation 1/2 reaction:

$$[CH_2O] + H_2O \rightarrow CO_2(g) + 4\,H^+ + 4e^-   E° = -0.485\ V \tag{7.3}$$

Reduction 1/2 reaction:

$$O_2(g) + 4H^+(W) + 4e^- \rightarrow 2H_2O   E° = +0.813\ V \tag{7.4}$$

Joint reaction:

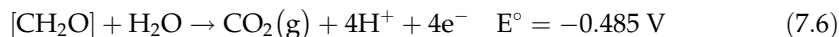$$[CH_2O] + O_2 \rightarrow CO_2 + 2H_2O   \Delta E° = +1.30\ V \tag{7.5}$$

Thus,

$$\begin{aligned}
\Delta G° &= -nF\Delta E \\
&= -(4)(23.061\ \text{kcal})(+1.30\ V) \\
&= -119.9\ \text{kcal per mol } CH_2O
\end{aligned}$$

or, since 1 kcal = 4.184 kJ = -502 kJ per mol CH_2O
or divide by 4 to determine = -29.9 kcal per e^{-1}
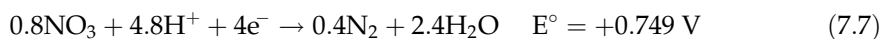or, since 1 kcal = 4.184 kJ = -125 kJ per e^{-1}

Note that the reduction step requires energy $(+E°)$ while the oxidation step yields energy $(-E°)$. We can express the energy yields for each equation per mole of carbon substrate or per mole of electrons transferred. The net energy yield of the paired reaction is $\sim$125 kJ for every mole of electrons transferred. Expressing energy yield per mole of electrons is useful for comparing processes that oxidize inorganic reduced energy sources (e.g., sulfide oxidation, ferrous oxidation, or manganese oxidation) with those that oxidize organic matter.

If we pair the same organic matter oxidation reaction with the reduction of NO_3 as an alternative electron acceptor, we calculate a lower energy yield.
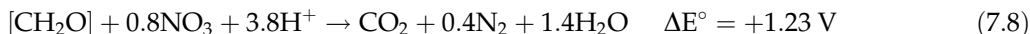
Oxidation 1/2 reaction:

$$[CH_2O] + H_2O \rightarrow CO_2(g) + 4H^+ + 4e^- \quad E° = -0.485 \text{ V} \tag{7.6}$$

Reduction 1/2 reaction:

$$0.8NO_3 + 4.8H^+ + 4e^- \rightarrow 0.4N_2 + 2.4H_2O \quad E° = +0.749 \text{ V} \tag{7.7}$$

Joint reaction:

$$[CH_2O] + 0.8NO_3 + 3.8H^+ \rightarrow CO_2 + 0.4N_2 + 1.4H_2O \quad \Delta E° = +1.23 \text{ V} \tag{7.8}$$

And since

$$\begin{aligned}
\Delta G° &= -nF\Delta E \\
&= -(4)(23.061 \text{ kcal V}^{-1})(1.23 \text{ V}) \\
&= -113 \text{ kcal per mol CH}_2\text{O} \\
\text{or} &= -474 \text{ kJ per mol CH}_2\text{O} \\
\text{or} &= -28.5 \text{ kcal per e}^{-1} \\
\text{or} &= -119 \text{ kJ per e}^{-1}
\end{aligned}$$

In comparing the $\Delta G°$ for these two reactions, we see that in denitrification nitrate respiration releases only 95% of the energy contained in our generic organic molecule (CH_2O) relative to aerobic respiration. Because of this difference in efficiency, whenever O_2 is available, heterotrophs utilizing aerobic respiration should outcompete denitrifiers for organic substrates.

Aerobic heterotrophs and denitrifiers often coexist in upland soils; indeed, many heterotrophic microbes are facultative denitrifiers that switch between aerobic respiration and denitrification depending on the supply of O_2 versus NO_3 (Carter et al. 1995; Chapter 6). In the previous comparisons we assume that substrates are not limiting. The "actual free energy yields" (ΔG) for these reactions, which take into account the concentrations of all reactants, indicate that under the conditions found in most oxic soils, aerobic respiration has a much higher ΔG than denitrification because oxygen is far more available than nitrate. In contrast, in wet soils where oxygen concentrations are low and nitrate concentrations are high (as in wet agricultural fields or wetlands receiving nitrogen-rich runoff), the two pathways may have nearly equivalent ΔG.

To calculate the actual free energy yield (ΔG) of a reaction we use the equation

$$\Delta G = \Delta G° + RT \ln Q, \tag{7.9}$$

where R is the universal gas constant (1.987×10^{-3} kcal K^{-1} mol^{-1}), T is temperature in °K, and Q represents the reaction quotient, or the concentration of reaction products relative to the concentration of reactants. For a generic reaction $^{a}Ox_1 + ^{b}Red_2 \rightarrow ^{c}Red_1 + ^{d}Ox_2$, the reaction quotient would be calculated as

$$Q = [Red_1]^c [Ox_2]^d / [Ox_1]^a [Red_2]^b. \tag{7.10}$$

Actual free energies thus modify our energy yield predictions by taking into account the relative abundance of reactants and products in the environment. This is a critical adjustment because the assumption of standard activities of all reactants inherent to the standard free energy calculations is rarely met in natural ecosystems. In most salt marsh ecosystems, for example, the dominant pathway for organic matter decomposition is sulfate reduction (Howarth 1984), a pathway that is not energetically favored according to standard free energy predictions (Table 7.4) but which becomes important in anoxic sediments where sulfate is abundant.

In a comparison of a freshwater and a brackish wetland in coastal Maryland, Neubauer et al. (2005) measured high rates of Fe^{3+} reduction in the early summer in both wetlands giving way later in the season to methanogenesis in the freshwater wetland (low SO_4^{2-}) and sulfate reduction in the brackish wetland receiving marine-derived SO_4^{2-} (Figure 7.11). We can use the actual free energy calculations to understand the environmental conditions under which we would
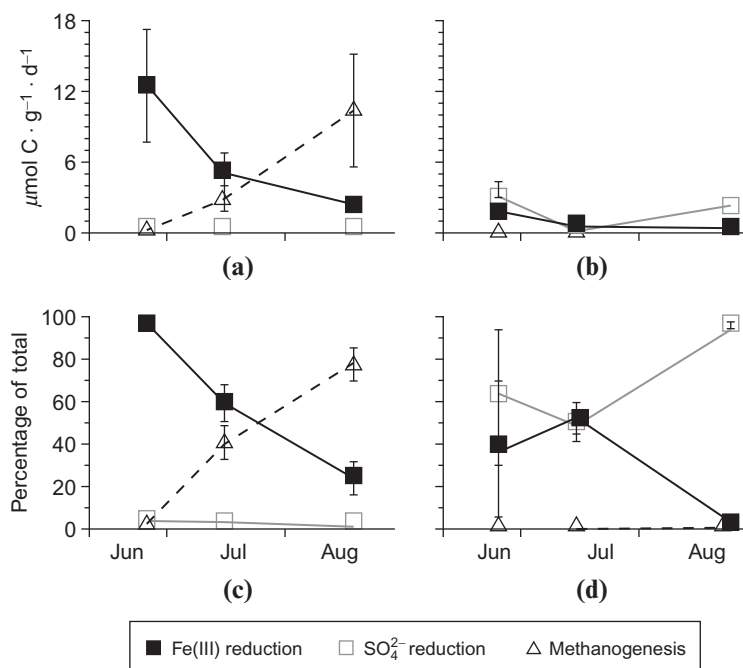

FIGURE 7.11   Seasonal changes in the rates and relative importance of Fe(III) reduction, SO_4^{2-} reduction, and methanogenesis during summer 2002 in (a) and (c) Jug Bay, a freshwater wetland, and (b) and (d) Jack Bay, a brackish wetland on the coastal plain of Maryland. *Source: From Neubauer et al. (2005). Used with permission of the Ecological Society of America.*

predict these shifts in the dominant metabolic pathways. Terminal electron acceptors that are extremely abundant will be likely to dominate decomposition pathways.

While the energy yield from sulfate reduction and methane fermentation is very low, the reduced products of sulfate reduction (HS^-) and methanogenesis (CH_4) are themselves energy-rich reduced substrates for other organisms. In the presence of oxygen, sulfide oxidation generates $100 \, \text{kJ eq}^{-1}$ of free energy, which, when combined with the free energy yield of sulfate reduction ($25 \, \text{kJ eq}^{-1}$), achieves the same total free energy yield as aerobic respiration of the same original carbon molecules (Table 7.4, Part B). This explains why very little sulfide gas or methane escapes from wetlands relative to the amounts produced in wetland sediments. There is energy to be extracted from these highly reduced gases.

Most wetlands undergo both flooding and drying cycles, and many wetlands are shallow enough to support rooted vegetation that can passively or actively transport gases between the atmosphere and sediments. Because of this variation in water level and in plant-facilitated gas exchange, oxygen depletion within wetlands is far from uniform in either time or space. As a result, wetland sediments are characterized by complex temporal and spatial gradients in the dominant metabolic pathways and rates of organic matter oxidation. Oxygen concentrations are typically high in shallow surface waters or drained surface sediments that are in direct contact with the atmosphere, but O_2 levels decline rapidly with depth in organic-rich sediments. However, the rhizospheres (root-associated sediments) of aerenchymous plants can remain well oxygenated and can support higher rates of mineralization that, in turn, may help alleviate nutrient limitation of wetland plant growth (Weiss et al. 2005, Laanbroek 2010, Schmidt et al. 2010b; Figure 7.12). Greater root biomass can thus be indirectly

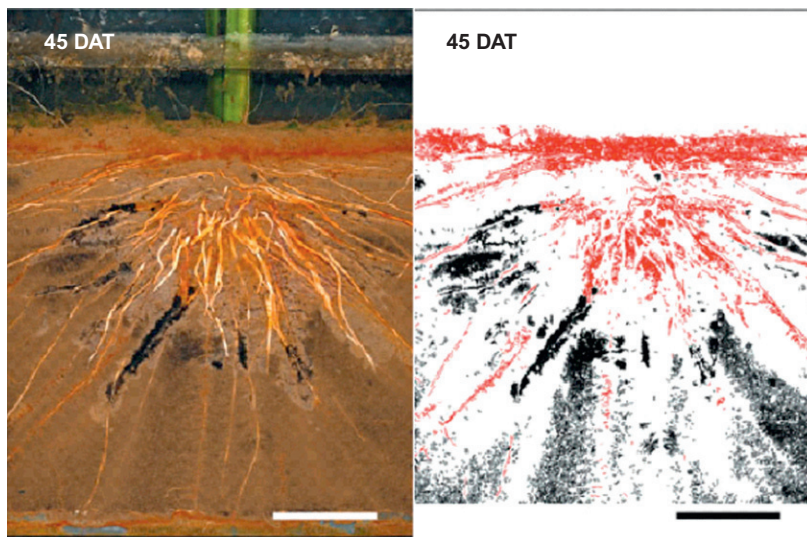FIGURE 7.12   Schmidt et al. (2010) grew rice seedlings (*Oryza sativa*) in experimental containers (rhizotrons) with a clear plastic side. On the *left* is a photograph of the rhizosphere of a single rice seedling grown in a paddy soil for 45 days. On the *right* the same image is highlighted to show areas that are oxic in red and anoxic in black. *Source: From Schmidt et al. (2010b). Used with permission of Springer.*

associated with higher rates of organic matter mineralization due to rhizosphere oxidation (Wolf et al. 2007).

Measuring the Redox Potential of the Environment

We can measure the development of anoxic conditions in sediments by measuring redox potential (pe). Just as pH expresses the concentration of H^+ in solution, redox potential is used to express the tendency of an environmental sample (usually measured in situ) to either receive or supply electrons. Oxic environments have high redox potential because they have a high capacity to attract electrons (oxygen is the most powerful electron acceptor), while anoxic environments have a low redox potential (reducing conditions) because of an abundance of reduced compounds already replete with electrons. When a metal probe is inserted into a soil or sediment, the metal surface will begin to exchange electrons with its surroundings, and the net direction of the exchange will depend on both the reactivity of the metal and the relative abundance of electrons in the environment. To measure the direction and strength of this electron exchange, the metal probe can be connected to a reference electrode, with a voltmeter placed in between. The redox potential is then measured as the voltage necessary to stop the flow of electrons within the electrode.

In a laboratory setting, the redox potential of chemical mixtures is determined by connecting the redox probe to a standard hydrogen electrode. The relative abundance of electrons in the solution will alter the equilibrium constant for the exchange of electrons within the electrode, where electrons are shuttled between sulfuric acid and a hydrogen gas atmosphere:

$$H^+ + 4e^- \longleftrightarrow 2H_2 \; (g). \tag{7.11}$$

In the field it is not easy to maintain standard hydrogen electrodes, so investigators typically use either an Ag/AgCl electrode or a calomel reference electrode that has been calibrated against a hydrogen electrode (Fiedler 2004, Rabenhorst 2009). The Ag/AgCl electrode consists of a silver wire surrounded by AgCl salt that is contained within a concentrated KCl solution. The solid Ag exchanges electrons with the AgCl solution:

$$Ag \longleftrightarrow Ag^+ + e^-. \tag{7.12}$$

When the reference electrode is connected to the platinum probe and inserted into an oxic soil, oxygen will consume electrons along the platinum probe:

$$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O. \quad E_h = +700 \text{ to} + 400 \text{ mV}. \tag{7.13}$$
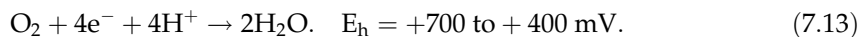
The reaction within the Ag/AgCl electrode (Eq. 7.12) will go to the right (Ag is oxidized) and the voltmeter will record a positive flow of electrons (Figure 7.13(a)). If instead the platinum probe is inserted into a highly reduced sediment, electrons will flow toward the reference electrode. The reaction (Eq. 7.12) will proceed to the left (Ag is reduced), and the voltmeter will record a negative flow of electrons (Figure 7.13(b)). Charge balance is maintained within the reference electrode by the diffusion of ions through a porous ceramic or membrane tip. Potassium ions (K^+) will be released through the ceramic tip when the redox potential is positive, and Cl^- ions will be released to the soil when the redox potential is negative (Figure 7.13)
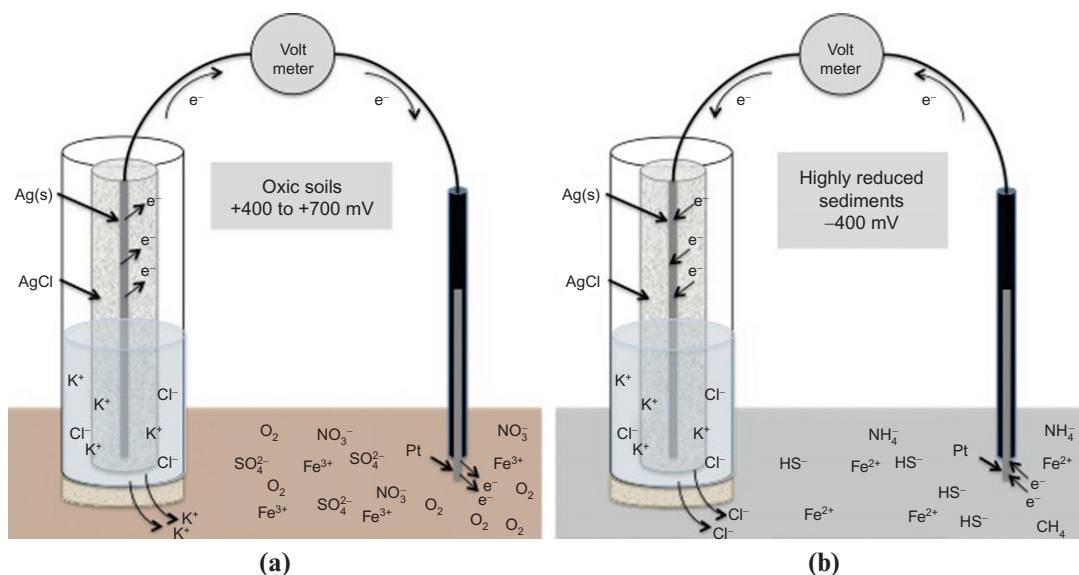
FIGURE 7.13   Schematic of an Ag/AgCl reference electrode and platinum electrode inserted into (a) an oxic soil and (b) a highly reduced sediment, demonstrating how the direction of electron flow depends on the availability of electron acceptors at the platinum electrode. Depending on the direction of e^- flow, either K^+ or Cl^- will be released through the ceramic or membrane tip of the reference electrode into the soil to maintain charge balance within the electrode.

The oxidizing or reducing potential of the soil is thus estimated relative to the reference electrode. Redox potential must be corrected when one uses Ag/AgCl rather than a standard hydrogen electrode using a correction factor (~ 200 mV for an Ag/AgCl electrode and ~ 250 mV for a calomel electrode). Typically, the redox potential in soils with any oxygen present varies only between $+400$ mV and $+700$ mV. As oxygen is depleted, other constituents, such as Fe^{3+} may accept electrons, but a lower voltage will be recorded since Fe^{3+} has a reduced capacity for attracting electrons relative to O_2.

$$Fe^{2+} + 3H_2O \leftrightarrow Fe(OH)_3 + 3H^+ + e^- \quad \text{and} \quad E_h = +100 \text{ to} -100 \text{ mV} \qquad (7.14)$$
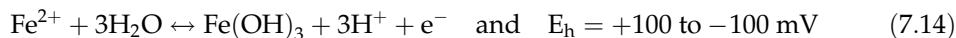
In aqueous environments, redox potential can range from $+400$ mV to -800 mV (Figure 7.14). A negative sign means that the reducing environment has excess electrons, a situation in which excess electrons will form H_2 gas via Eq. 7.11.

The pH of the environment will affect the redox potential established by oxygen and other alternate electron acceptors (Figure 7.14). Aerobic oxidation, which generates H^+ ions (shown in Eq. 7.13), is more likely to proceed under neutral or alkaline conditions while anaerobic pathways that consume H^+ ions (shown in Eq. 7.14) are chemically more favorable in acidic environments (e.g., Weier and Gilliam 1986). Because of the pH sensitivity of redox reactions, it is often useful to express the redox potential of a reaction in units of pe, a constant that is derived from the equilibrium constant of the oxidation–reduction reaction (K) and which incorporates information on pH. For any reaction,

$$\text{Oxidized Species} + e^- + H^+ \longleftrightarrow \text{Reduced Species}, \qquad (7.15)$$
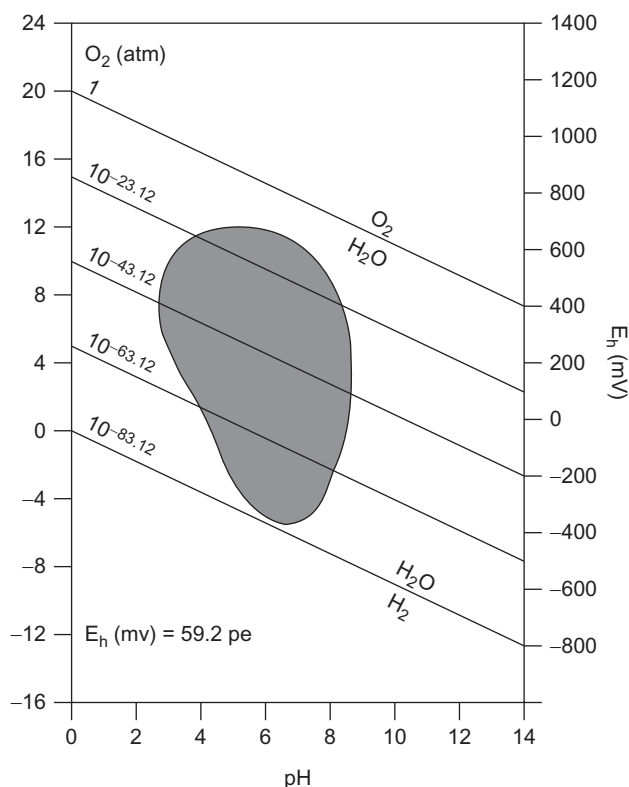
FIGURE 7.14 This stability diagram shows the relationship between pH and redox potential. Diagonal lines are the redox potential at different oxygen partial pressures. The *shaded zone* in the center of the figure shows the range of redox potentials that are found in natural aqueous environments. *Source: Modified from Lindsay (1979), which was based on the original compilation by Baas Becking et al. (1960). Used with permission of The University of Chicago Press.*

and the equilibrium constant can be determined by

$$\log K = \log[\text{reduced}] - \log[\text{oxidized}] - \log[e^-] - \log[H^+]. \tag{7.16}$$

If we assume that the concentrations of oxidized and reduced species are equal, then

$$pe + pH = \log K. \tag{7.17}$$

Here pe is the negative logarithm of the electron activity $(-\log[e^-])$, and it expresses the energy of electrons in the system (Bartlett 1986). Because the sum of pe and pH is constant, if one goes up, the other must decline. When a given reaction occurs at a lower pH, it will occur at a higher redox potential, expressed as pe. Measurements of redox potential that are expressed as voltage can be converted to pe following

$$pe = E_h/(RT/F)2.3, \tag{7.18}$$

where R is the universal gas constant ($1.987\,\text{cal}\,\text{mol}^{-1}\,\text{K}^{-1}$), F is Faraday's constant ($23.06\,\text{kcal}\,\text{V}^{-1}\,\text{mol}^{-1}$), T is temperature in Kelvin, and 2.3 is a constant to convert natural to base-10 logarithms.

Environmental chemists use E_h-pH or pe-pH diagrams to predict the likely oxidation state of various constituents in natural environments based on these chemical relationships (e.g.,
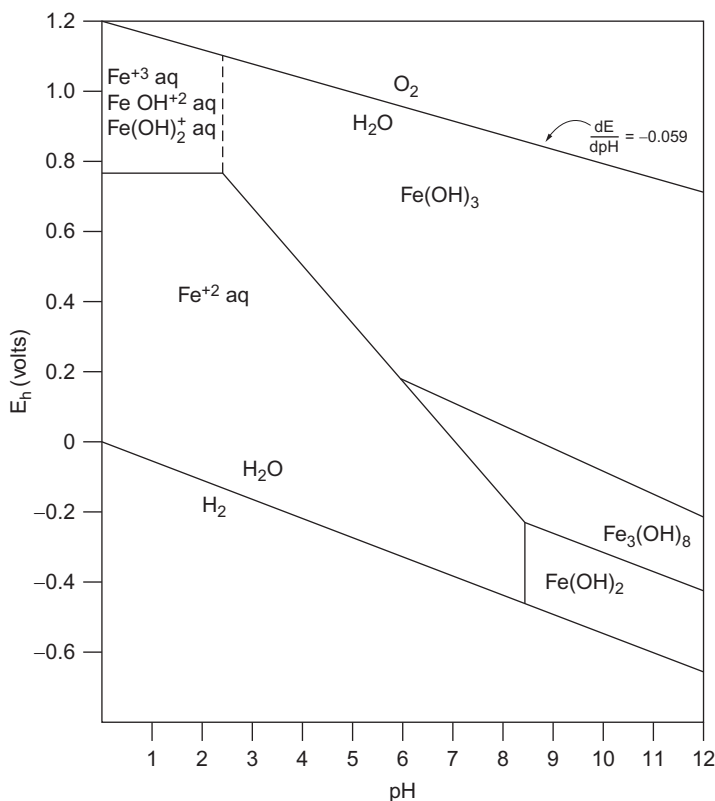
FIGURE 7.15 This stability diagram shows the expected form of iron in natural environments of varying pH and E_h. In interpreting such diagrams it is important to remember that E_h and pH are properties of the environment determined by the total suite of chemical species present. Thus, E_h predicts the forms of iron that will be present under a set of chemical conditions using a set of simplifying assumptions. Because iron is interacting with a variety of chemicals in solution, these predictions are not always accurate due to competing reactions. Important to biogeochemistry, E_h can be used to predict what modes of microbial activity are possible in a given environment, and E_h-pH predictions can be useful against which to compare field patterns. *Source: Modified from Lindsay (1979).*

Figure 7.15). Two lines bound all such diagrams. At any redox potential above the upper line, even water would be oxidized (Eq. 7.12 in reverse)—a condition not normally found on the surface of the Earth. Similarly any condition below the lower line would allow the reduction of water, again a condition rarely seen on Earth. These boundary redox conditions vary predictably with pH, with E_h declining by 59 mV with each unit of pH increase, reflecting that oxidation proceeds at a lower redox potential under more alkaline conditions.

In most cases organic matter contributes a large amount of "reducing power" that lowers the redox potential in flooded soils and sediments (Bartlett 1986). High concentrations of Fe^{2+} will be found in flooded low-redox potential environments where impeded decomposition leaves undecomposed organic matter in the soil and humic substances impart acidity to the soil solution. Where organic matter is sparse, iron may persist in its oxidized form (Fe^{3+}) even when the soils are flooded (e.g., Couto et al. 1985). Aeration and liming are each used as techniques for ameliorating acid mine drainage because iron tends to precipitate in oxidized forms at high redox potential or high pH.

Redox potential measurements do not actually measure the number of electrons in the environment, but instead provide a standard method for comparing their relative availability. Because individual anaerobic metabolic pathways vary predictably in their energy yield, they tend to dominate in a fairly narrow range of redox potentials so that a measure of field redox

potential can provide a good prediction of the likely metabolic pathways at the point of measurement. The measure of a field redox potential is not equivalent to the measurement of the redox potential of a component chemical reaction (except when measurements are made in the lab in solutions where only one equilibrium reaction is possible). Instead, field redox potential provides a way of comparing the degree to which electron acceptor abundance and oxidizing efficiency vary in space and time.

Soils and sediments that resist change in their redox potential are said to be highly poised. Conceptually, poise is to redox as buffering capacity is to pH (Bartlett 1986). As long as soils are exposed to the atmosphere, they will appear to be highly poised, since O_2 will maintain a high redox potential under nearly all conditions. Soils with high concentrations of Mn^{4+} and Fe^{3+} are less likely to produce substantial amounts of H_2S or CH_4 during short-term flooding events because it is unlikely that microbes will be able to sufficiently deplete these electron acceptors and turn to the less efficient oxidizing constituents (SO_4, CO_2) (Lovley and Phillips 1987, Achtnich et al. 1995, Maynard et al. 2011). Such soils are also poised but at a lower redox potential than oxic soils. Because of the large differences in free energy yield for each anaerobic metabolic pathway, we can predict what metabolic products are likely to accumulate from a measure of redox potential (see Figure 7.14).

ANAEROBIC METABOLIC PATHWAYS

Prior to the oxidation of the Earth's atmosphere about 2.5 bya, anaerobic metabolism dominated the biosphere (Chapter 2). In the anoxic sediments of wetlands, lakes, rivers, and oceans, these metabolic pathways continue to dominate biogeochemical cycling today. Table 7.3 listed the more important overall reactions involved in anaerobic oxidation of organic matter in wetland sediments and allowed comparison among the resulting free energy yield from each reaction. These reactions have different biogeochemical consequences.

Fermentation

Fermentation of organic matter (Table 7.4) is a required precursor or accompaniment for each of the subsequent anaerobic metabolic pathways in Table 7.3 (Figure 7.9). Fermenting bacteria in wetlands are obligate anaerobes that use a variety of organic substrates, including

TABLE 7.4 Examples of Chemical Reactions and Associated Free Energy Yield (per mol of organic matter or sulfur compound) and Catalyzing Organisms Performing Fermentation

Reaction		$-\Delta G^{\circ}$ (kJ mol^{-1})	Organisms catalyzing these reactions
(1) $3(CH_2O)$	$\rightarrow CO_2 + C_2H_6O$	23.4	For example, yeasts, *Sarcina ventriculi*, *Zymonas*, *Leuconostoc* sp., clostridia, *Thermonanaerobium brockii*, etc.
(2) $n(CH_2O)$	$\rightarrow mCO_2$ and/or fatty acids and/or alcohols and/or H_2	5–60	For example, yeasts, *clostridia, enterobacteria, lactobacilii, streptococci, propionibacteria*, and many others

Source: Adapted from Zehnder and Stumm (1988).

alcohols, sugars, and organic and amino acids, and convert them into CO_2 and various reduced fermentation products (predominantly C1–C18 acids and alcohols, molecular hydrogen, and CO_2) (Zehnder and Stumm 1988). Fermentation occurs inside microbial cells and does not require an external supply of electron acceptors. During fermentation ATP is produced by substrate-level phosphorylation. Fermentation pathways themselves have very low energy yield, but the low-molecular-weight organic acids, alcohols, and molecular hydrogen that are produced during fermentation ultimately determine the rate of terminal decomposition steps (Freeman et al. 2001b, Megonigal et al. 2003).

Although often ignored as an important pathway for the production of CO_2, a number of recent studies have suggested that fermentation (together with humic acid reduction; Lovley et al. 1996) can account for a significant fraction of anaerobic carbon mineralization in wetland sediments (Keller and Bridgham 2007). In addition to producing CO_2 or facilitating organic matter mineralization to CO_2 or CH_4, fermentation products can also accumulate as dissolved organic compounds (DOC) that are susceptible to leaching and hydrologic export.

Dissimilatory Nitrate Reduction

After O_2 is depleted by aerobic respiration, nitrate becomes the best alternative electron acceptor, and in anoxic sediments nitrate will be rapidly consumed whenever there are suitable organic substrates or reduced chemical compounds available for metabolism (Table 7.5). The term denitrification is typically used to refer to the process by which bacteria convert nitrate to gaseous N_2O or N_2 during the oxidation of organic matter (see Eqs. 1 and 2 in Table 7.5). These reactions are dissimilatory since the nitrogen used for denitrification is not incorporated into the biomass of denitrifying microbes. This type of denitrification is primarily performed by facultative anaerobes, organisms that switch from aerobic oxidation of organic matter when oxygen is present to denitrification when oxygen is depleted. The standard free energy yield of the reaction is only marginally lower than that of aerobic respiration

TABLE 7.5   Chemical Reactions and Associated Free Energy Yield (per mol of organic matter or sulfur compound) for Dissimilatory Nitrate Reduction Pathways

Reaction	$-\Delta G°$ (kJ mol^{-1})	Organisms catalyzing these reactions
(1) $2\,NO_3^- + (CH_2O) \rightarrow 2\,NO_2^- + CO_2 + H_2O$	82.2	For example, members of the genus *Enterobacter, E. coli* and many others
(2) $4/5\,NO_2^- + (CH_2) + 4/5\,H^+ \rightarrow 2/5\,N_2 + CO_2 + 7/5\,H_2O$	112	For example, members of the genus *Pseudomonas, Bacillus lichenformis, Paracoccus denitrificans,* etc.
(3) $1/2\,NO_3^- + (CH_2O) + H^+ \rightarrow 1/2\,NH_4^+ + CO_2 + 1/2\,H_2O$	74	Members of the genus *Clostridium*
(4) $6/5\,NO_3^- + S^0 + 2/5\,H_2O \rightarrow 3/5\,N_2 + SO_4^{2-} + 4/5\,H^+$	91.3	Member of the genus *Thiobacillus*
(5) $8/5\,NO_3^- + HS^- + 3/5\,H^+ \rightarrow 4/5\,N_2 + SO_4^{2-} + 4/5\,H_2O$	93	*Thoiosphaera pantotropha* and members of the genus *Thiobacillus*

Source: Adapted from Zehnder and Stumm (1988).

(refer to Table 7.3). Standard free energy calculations assume unlimited supplies of reactants; however, the NO_3^- in flooded soils is never as abundant as the O_2 in oxic soils. Thus even highly NO_3^--enriched wetland sediments are likely to have lower soil respiration rates once oxygen is depleted. In many flooded soils denitrification is limited by the availability of NO_3^-, a problem exacerbated by the fact that nitrification (Eqs. 2.17 and 2.18) cannot proceed without oxygen.

Although often discussed as a single process (e.g., Eq. 2.20), the denitrification process occurs in multiple steps whereby NO_3^- is converted sequentially to NO_2^-, NO, and N_2O (Figure 6.13). Particularly in nitrogen-enriched agricultural fields N_2O can be a significant fraction of the total gaseous nitrogen produced (Stehfest and Bouwman 2006) and dissolved nitrite (NO_2^-) can become a more important dissolved export than NH_4^+ (Stanley and Maxted 2008). It appears that the ratio of $N_2O:N_2$ production from denitrification in wetlands is typically lower than in upland soils (Schlesinger 2009), but there are concerns that continued nitrogen loading to wetlands from nitrogen deposition or fertilizer runoff may enhance N_2O yields since incomplete denitrification (with N_2O as a terminal product) becomes increasingly energetically favorable when the supply of NO_3^- is high (Verhoeven et al. 2006).

An alternative metabolic process to denitrification is dissimilatory nitrogen reduction to ammonium (usually referred to by the acronym DNRA), in which NO_3^- is converted to NH_4^+ through fermentation by obligate anaerobes (Zehnder and Stumm 1988, Megonigal et al. 2003; Eq. 3 in Table 7.5). DNRA appears to be a dominant process in some wet soils and wetland sediments (Scott et al. 2008, Dong et al. 2011), particularly in anoxic habitats where nitrate availability is very low and labile carbon supplies are high. Under these conditions, selection may favor microbes that retain fixed N over denitrifiers that further deplete limited N supplies (Tiedje 1988, Burgin and Hamilton 2007).

Anaerobic oxidation of NH_4^+ to N_2, or anammox, is another dissimilatory pathway, wherein NH_4^+ is oxidized by reaction with NO_2^- under anaerobic conditions to produce N_2. This process was only recently identified in wastewater treatment systems, but appears to be an important pathway for N_2 production in some coastal and marine sediments (Dalsgaard and Thamdrup 2002, Zehr and Ward 2002). Anammox appears to be competitively advantageous when carbon is highly limiting (Dalsgaard and Thamdrup 2002), but thus far there has been little research on its importance in freshwater ecosystems.

Nitrate may also be used in the oxidation of reduced sulfur, iron, or manganese compounds in anoxic sediments. Indeed, anaerobic sulfide oxidation using NO_3^- as an electron acceptor is an energetically favorable process accomplished by chemolithotrophic sulfur bacteria, which may occur in preference to denitrification or DNRA in situations where reduced sulfur compounds are abundant (refer to Table 7.5; Zehnder and Stumm 1988). Anaerobic oxidation of Fe^{2+} using NO_3^- by microbes is known to occur, but the ecosystem-level importance of this process is not currently well understood (Clement et al. 2005, Burgin and Hamilton 2007). Anaerobic Fe and Mn oxidation might both be expected to be important consumption pathways for NO_3^- when organic substrates are limiting and the concentrations of reduced Fe or Mn compounds are high.

Burgin and Hamilton (2007) proposed a useful conceptual model summarizing current understanding of the many alternative pathways for NO_3^- utilization under anoxic conditions (Figure 7.16). The relative importance of these processes is a function of the actual free
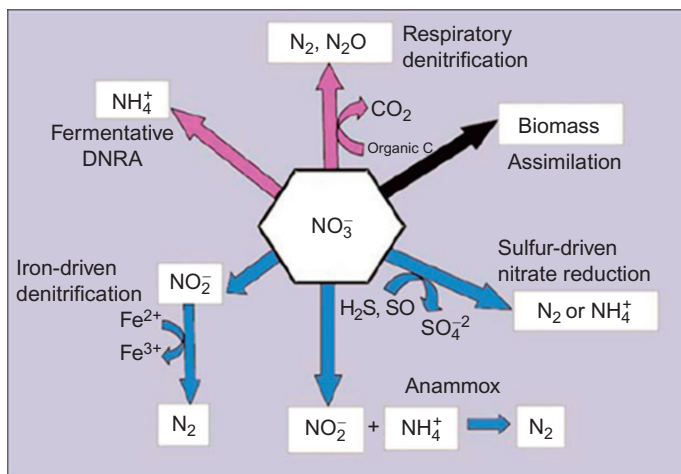
FIGURE 7.16　A conceptual diagram of important nitrate removal pathways in the absence of oxygen. *Blue arrows* denote autotrophic pathways and *dark pink* arrows denote heterotrophic pathways. In addition to using nitrate to acquire energy through dissimilatory reactions, all microbes require N assimilation into biomass (*black arrow*). *Source: From Burgin and Hamilton (2007). Used with permission of Ecological Society of America.*

energy yield of competing reactions resulting from the relative concentration of chemical substrates (e.g., heterotrophic pathways will likely dominate when suitable organic molecules are available).

Iron and Manganese Reduction

Manganese reduction, although thermodynamically favorable in many anoxic environments, is only locally important because Mn^{4+} is rarely found at high concentrations. The product of the reaction, soluble Mn^{2+}, is toxic to many plants and can affect productivity or species composition. In contrast, Fe reduction is a dominant metabolic pathway in many wetlands (e.g., Figure 7.11). In many cases there appears to be some overlap between the zone of denitrification and the zone of Mn reduction in sediments (e.g., Klinkhammer 1980, Kerner 1993; Figure 7.10), and most of the microbes in this zone are facultative anaerobes that can tolerate periods of oxic conditions (Chapter 6). In contrast, there is little overlap between the zone of Mn reduction and that of Fe reduction because soil bacteria show an enzymatic preference for Mn^{4+}, and Fe^{3+} reduction will not begin until Mn^{4+} is completely depleted (Lovley and Phillips 1988). Below the zone of Mn^{4+} reduction most redox reactions are performed by obligate anaerobes. Our earlier emphasis on the redox state of iron (refer to Figure 7.14) reflects the widespread use of Fe as an index of the transition from mildly oxidizing to strongly reducing conditions.

Certain types of bacteria (e.g., *Shewanella putrefaciens*) can couple the reduction of Mn and Fe directly to the oxidation of simple organic substances (Lovley and Phillips 1988, Lovley 1991, Caccavo et al. 1994), but usually these reactions are catalyzed by a suite of coexisting bacteria—with some species using fermentation to obtain metabolic energy (Eqs. 1 and 3 in Table 7.6), while others oxidize hydrogen, using Mn^{4+} and Fe^{3+} as electron acceptors (Eqs. 2 and 4 in Table 7.6) (Lovley and Phillips 1988, Weber et al. 2006). Below the depth of iron reduction, the redox potential progressively drops as sulfate reduction and then methanogenesis become the dominant terminal decomposition pathways (Lovley and Phillips 1987).

TABLE 7.6 Chemical Reactions and Associated Free Energy Yield (per mol of organic matter or hydrogen compound) for Fe and Mn Reduction Pathways

Reaction		$-\Delta G^{\circ}$ (kJ mol^{-1})	Organisms catalyzing these reaction
$2\,MnO_2 + (CH_2O) + 2\,H^+$	$\rightarrow MnCO_3 + Mn^{2+} + 2\,H_2O$	94.5	Members of the genus *Bacillus*, *Micrococcus*, and *Pseudomonas*
$2\,Mn^{3+} + H_2$	$\rightarrow 2\,Mn^{2+} + 2\,H^+$	285.3	Members of the genus *Shewanella*
$4\,FeOOH + (CH_2O) + 6\,H^+$	$\rightarrow FeCO_3 + 3\,Fe^{2+} + 6\,H_2O$	24.3	Members of the genus *Bacillus*
$2\,Fe^{3+} + H_2$	$\rightarrow 2\,Fe^{2+} + 2\,H^+$	148.5	Members of the genus *Pseudomonas* and *Shewanella*

Source: From Zehnder and Stumm (1988), Lovley (1991).

Sulfate Reduction

In Chapter 6 we examined the reduction of sulfate that accompanied the uptake, or assimilation, of sulfur by soil microbes and plants. In contrast, dissimilatory sulfate reduction in anaerobic soils is analogous to denitrification in which SO_4^{2-} acts as an electron acceptor during the oxidation of organic matter by bacteria (Table 7.7). This metabolic pathway evolved at least 2 bya (Chapter 2), and before widespread human air pollution the release of biogenic gases from wetlands was a dominant source of sulfur gases in the atmosphere (Chapter 13). Sulfate-reducing bacteria produce a variety of sulfur gases including hydrogen sulfide, H_2S; dimethylsulfide, $(CH_3)_2\,S$); and carbonyl sulfide, COS (Conrad, 1996). In brackish or saline waters, sulfate is typically the dominant electron acceptor and sulfate reduction can be an important fate for organic matter (e.g., Howarth 1984, Neubauer et al. 2005).

Although the production of reduced-sulfur gases in wetlands may be high, the escape of H_2S from wetland soils is often much less than the rate of sulfate reduction at depth as a result of reactions between H_2S and other soil constituents (e.g., NO_3, Table 7.5). Hydrogen sulfide

TABLE 7.7 Chemical Reactions and Associated Free Energy Yield (per mol of organic matter or H_2 compound) for Sulfate Reduction Pathways

Reaction		$-\Delta G^{\circ}$ (kJ mol^{-1})	Organisms catalyzing these reactions
$1/2\,SO_4^{2-} + (CH_2O) + 1/2\,H^+$	$\rightarrow 1/2\,HS^- + CO_2 + H_2O$	18.0	*Desulfobacter sp., Desulfovibrio sp., Desulfonema sp.*, etc.
$S^0 + (CH_2O) + H_2O$	$\rightarrow HS^- + H^+$	12.0	*Desulfomonas acetoxidans, Campylobacter sp. Thermoproteus tenax, Pyrobaculum islandicum*
$S^0 + H_2$	$\rightarrow HS^- + H^+$	14.0	*Thermoproteus sp., Thermodiscus sp., Pyrodictum sp.*, various bacteria

Source: Adapted from Zehnder and Stumm (1988).

can also react abiotically with Fe^{2+} to precipitate FeS, which gives the characteristic black color to anaerobic soils. FeS may be subsequently converted to pyrite in the reaction

$$FeS + H_2S \rightarrow FeS_2 + 2H^+ + 2e^-. \tag{7.19}$$
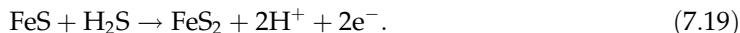
When H_2S diffuses upward through the zone of oxidized Fe^{3+}, pyrite (FeS_2) is precipitated following

$$2Fe(OH)_3 + 2H_2S + 2H^+ \rightarrow FeS_2 + 6H_2O + Fe^{2+}. \tag{7.20}$$
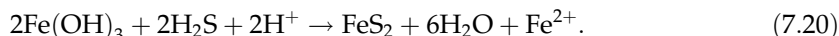
Thus, not all the reduced iron in wetland soils is formed directly by iron-reducing bacteria. In some cases the indirect pathways (Eqs. 7.19 and 7.20) may account for most of the total (Canfield 1989a, Jacobson 1994).

This effective sink for reduced sulfur initially led many researchers to believe that sulfate reduction was not a particularly important pathway for organic matter decomposition in wetland ecosystems since the emission of reduced sulfur gases from wetlands was too low to account for a large proportion of organic matter decomposition. However, Howarth and Teal (1980) used an elegant $^{34}SO_4^{2-}$ isotope tracer experiment to demonstrate that sulfate reduction was responsible for the majority of organic matter decomposition in the salt marsh surrounding Sapelo Island, Georgia, and that nearly all of the ^{34}S introduced to the marsh as sulfate was rapidly reduced and subsequently sequestered in the sediments as $Fe^{34}S_2$.

A low iron content limits the accumulation of iron sulfides in many wetland sediments (Rabenhorst and Haering 1989, Berner 1983, Giblin 1988). During periods of low water, specialized bacteria may reoxidize the iron sulfides (Ghiorse 1984), releasing SO_4^{2-} that can diffuse to the zone of sulfate-reducing bacteria. Thus, high rates of sulfate reduction may be maintained in soils and sediments that have relatively low SO_4^{2-} concentrations, owing to the recycling of sulfur between oxidized and reduced forms (Marnette et al. 1992, Urban et al. 1989b, Wieder et al. 1990).

Hydrogen sulfide also reacts with organic matter to form carbon-bonded sulfur that accumulates in peat (Casagrande et al. 1979, Anderson and Schiff 1987). In many areas, the majority of the sulfur in wetland soils is carbon-bonded and only small amounts are found in reduced inorganic forms—that is, H_2S, FeS, and FeS_2 (Spratt and Morgan 1990, Wieder and Lang 1988). Carbon-bonded forms—from the original plant debris, from the reaction of H_2S with organic matter, and from the direct immobilization of SO_4 by soil microbes—are relatively stable (Rudd et al. 1986, Wieder and Lang 1988). Carbon-bonded sulfur accounts for a large fraction of the sulfur in many coals (Casagrande and Siefert 1977, Altschuler et al. 1983) and thus for the sulfuric acid content of acid rain and coal-mining effluents. Organic sediments and coals containing carbon-bonded sulfur that is the result of dissimilatory sulfate reduction show negative value for $\delta^{34}S$ as a result of bacterial discrimination against the rare heavy isotope $^{34}SO_4^{2-}$ in favor of $^{32}SO_4^{2-}$ during sulfate reduction (Chambers and Trudinger 1979, Hackley and Anderson 1986).

Because H_2S can react with various soil constituents and is oxidized by sulfur bacteria as it passes through the overlying sediments and water (Eq. 2.13), many biogeochemists once believed that various organic sulfur gases might be the dominant forms escaping from wetland soils. Most studies, however, have found that H_2S accounts for a large fraction of the emission

from wetland soils (Adams et al. 1981, Kelly 1990). Castro and Dierberg (1987) reported a flux of H_2S containing 1 to 110 mg S m^{-2} yr^{-1} from various wetlands in Florida. Nriagu et al. (1987) reported a total flux of sulfur gases ranging from 25 to 184 mg m^{-2} yr^{-1} from swamps in Ontario and found that the sulfate in rainfall in the surrounding region had a lower δ^{34}S value during the summer than during the winter. Presumably a portion of the SO_4^{2-} content in this ^{34}S-depleted rain is derived from the oxidation of sulfur gases released to the atmosphere by sulfate reduction in local wetlands.

Methanogenesis

Methanogenesis is the final step in anaerobic degradation of carbon. This is the metabolism that degrades carbon when all alternative electron acceptors have been exhausted. Despite its extremely low energy yield (refer to Table 7.3), methanogenesis is a dominant pathway for organic matter decomposition in many wetlands due to the lack of oxidants typical of water-logged soils. Methane can be produced from two different pathways in flooded sediments, both of which are accomplished by methanogens, a diverse group of strict anaerobes in the archaea (Zehnder and Stumm 1988). When organic matter fermentation produces organic acids at concentrations in excess of the availability of alternative electron donors (NO_3^-, Fe^{3+}, SO_4^{2-}), then methanogens can split acetate to produce methane in a process called acetoclastic methanogenesis or acetate fermentation (refer to Table 7.8, Reaction 1). The energy yield of acetoclastic methanogenesis is very low compared to other anaerobic metabolic pathways (Table 7.4), and the product of this reaction produces a δ^{13}C of -50 to -65‰ in CH_4 (Woltemate et al. 1984, Whiticar et al. 1986, Cicerone et al. 1992). Acetoclastic methanogenesis is performed by only two genera of methanogens: the *Methanosarcina* and *Methanosaeta* (Megonigal et al. 2003).

When acetate is unavailable, a much wider variety of methanogens can perform hydrogen fermentation coupled to CO_2 reduction (Table 7.8, Reaction 2), in which the hydrogen serves as a source of electrons and energy while the CO_2 serves as the source of C and as an electron acceptor. Methanogenesis by CO_2 reduction accounts for the limited release of H_2 gas from wetland soil (Conrad 1996). This methane is even more highly depleted in ^{13}C than that produced from acetoclastic methanogenesis, with δ^{13}C of -60 to -100‰ (Whiticar et al. 1986).

TABLE 7.8   Chemical Reactions and Associated Free Energy Yield (per mol of organic matter or H_2) for the Methane-Producing Pathways of Acetate Splitting and CO_2 Reduction (or hydrogen fermentation)

Reaction		$-\Delta G°$ (kJ mol^{-1})	Organisms catalyzing these reactions
Acetate splitting **(1)** CH_3COOH	$\rightarrow CH_4 + CO_2$	28	Some methanogens (*M. barkeri*, *M. mazei*, *M. söhngenii*)
CO_2 reduction **(2)** $CO_2 + 4 H_2$	$\rightarrow CH_4 + H_2O$	17.4	Most methane bacteria

Source: Adapted from Zehnder and Stumm (1988).

Methanogenesis is often limited by the supply of fermentation products (H_2 or acetate), and can be stimulated through experimental additions of either organic matter or hydrogen (Coles and Yavitt 2002). Thus, methanogenesis generally declines with depth below the oxic-anoxic interface in wetland sediments (Megonigal and Schlesinger 1997), and with greater depth, methane production is increasingly from CO_2 reduction (Hornibrook et al. 2000). Methanogenic bacteria can use only certain organic substrates for acetate splitting and in many cases there is evidence that sulfate-reducing bacteria are more effective competitors for the same compounds (Kristjansson et al. 1982, Schonheit et al. 1982).

Sulfate-reducing bacteria also use H_2 as a source of electrons, and they are more efficient in the uptake of H_2 than methanogens engaging in CO_2 reduction (Kristjansson et al. 1982, Achtnich et al. 1995). Thus in most environments there is little to no overlap between the zone of methanogenesis and the zone of sulfate reduction in sediments (Lovley and Phillips 1986, Kuivila et al. 1989). Methanogenesis in marine sediments is inhibited by the high concentrations of SO_4 in seawater, and where methanogenesis occurs in marine environments CO_2 reduction is much more important than acetate splitting because acetate is entirely depleted within the zone of sulfate-reducing bacteria (Chapter 9). Because sulfate reduction provides a higher energy alternative, sulfate inputs to freshwater wetlands via acid deposition appear to suppress CH_4 flux (Dise and Verry 2001, Gauci et al. 2004, Gauci and Chapman 2006).

Methane flux varies widely across wetland ecosystem types, making global extrapolations challenging. Current estimates suggest that approximately 3% of wetlands' net annual ecosystem production is released to the atmosphere as CH_4 (an estimated 150 Tg CH_4 annually) (Dlugokencky et al. 2011; refer to Table 11.2). These scaling exercises also suggest that much of the interannual variation in global CH_4 fluxes could be explained by annual variation in wetland emissions (Bousquet et al. 2006). The flux of methane from wetland ecosystems results from the net effects of methanogenesis and methanotrophy. Methanogenesis is limited by the supply of labile organic matter (Bridgham and Richardson 1992, Cicerone et al. 1992, Valentine et al. 1994, Van der Gon Denier and Neue 1995), and CH_4 flux shows a direct correlation to net ecosystem production across a variety of wetland ecosystems (Whiting and Chanton 1993, Updegraff et al. 2001, Vann and Megonigal 2003; Figure 7.17).

The positive association between plant productivity and methane flux may be due at least in part to the facilitated gas exchange provided by many wetland plants (Sebacher et al. 1985, Chanton and Dacey 1991, Yavitt and Knapp 1995). Many wetland plants, including rice, have hollow stems composed of aerenchymous tissue, which allows O_2 to reach the roots. These hollow stems inadvertently act as a conduit for CH_4 transport to the surface (Kludze et al. 1993). When oxic soil layers overlay zones of highly reduced anoxic sediments, much of the CH_4 that diffuses to the sediment surface will be oxidized. Higher methane fluxes typically occur when water tables are higher and a greater proportion of sediment pore spaces are filled with water. Under these conditions obligate anaerobic methanogens can operate in shallower sediments, where high-quality organic matter is concentrated and there is less habitat available for methanotrophs and thus a greater chance for CH_4 escape to the atmosphere (Sebacher et al. 1986, Moore and Knowles 1989, Shannon and White 1994, von Fischer et al. 2010). In flooded soils CH_4 flux also increases with soil temperature (Roulet et al. 1992, Bartlett and Harriss 1993).
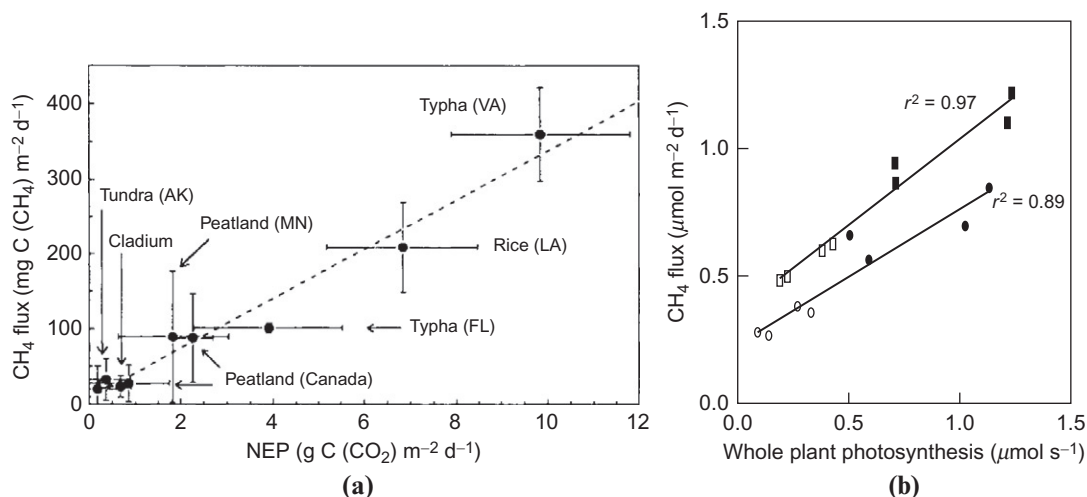
FIGURE 7.17   The relationship between wetland CH_4 emissions and various measures of primary productivity. (a) Emissions versus NEP in North American ecosystems ranging from the subtropics to the subarctic; here the slope is 0.033 g methane C/g CO_2. (b) Emissions versus whole-plant net photosynthesis in marsh microcosms planted with the emergent macrophyte *Orantium aquaticum* that were exposed to elevated and ambient concentrations of atmospheric CO_2. *Source: Figure (a) from Whiting and Chanton (1993); figure (b) from Vann and Megonigal (2003). Used with permission of Nature Publishing Group and Springer.*

Aerobic Oxidation of CH_4

Methanotrophs tend to outcompete nitrifiers for O_2 when CH_4 is abundant since more energy can be released from oxidizing methane than from oxidizing NH_4. Thus much of the methane produced at depth is oxidized to CO_2 before it is released from wetland sediments (Figure 7.18). When CH_4 concentrations are very high at depth—high enough to exceed the hydrostatic pressure of the overlying water—then CH_4-rich gas bubbles can escape to the surface in the process of *ebullition* (Figure 7.18). Effectively bypassing the methanotrophs, ebullition can account for a large fraction of the methane flux to the atmosphere (Fechner Levy and Hemond 1996, Neue et al. 1997, Baird et al. 2004, Goodrich et al. 2011, Comas and Wright 2012). Bubbles escaping by ebullition may be nearly pure CH_4, whereas bubbles emerging from vegetation are often diluted with N_2 from the atmosphere (Chanton and Dacey 1991). The effect of plant-facilitated gas exchange on methane transport and oxidation is complex because, by oxidizing their rhizosphere, aerenchymous plants create a larger volume of oxidized soil where methanotrophs can oxidize CH_4 at the same time that aerenchymous tissues can facilitate CH_4 escape through direct transport (Laanbroek 2010).

Anaerobic Oxidation of CH_4

It has been known for some time that in marine sediments anaerobic methane oxidation (AMO) by sulfate-reducing bacteria can be a major sink for methane (Reeburgh 1983, Henrichs and Reeburgh 1987, Blair and Aller 1995):
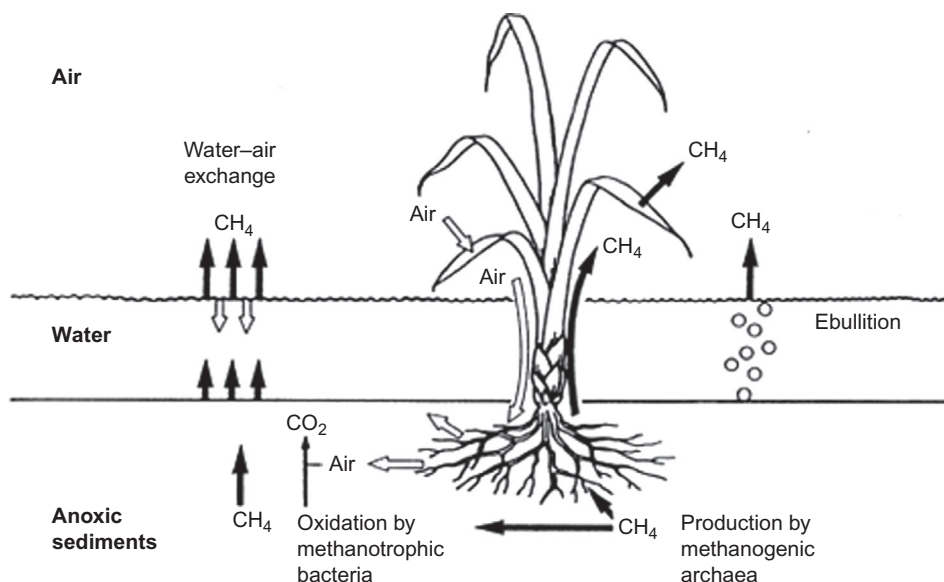
$$CH_4 + SO_4^{2-} \rightarrow HS^- + HCO_3^- + H_2O, \tag{7.21}$$
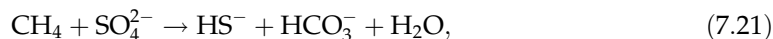
FIGURE 7.18   Processes of methane production, oxidation, and escape from wetland soils. *Source: From Schutz et al. (1991).*

and it has been suggested that AMO may be an important mechanism regulating methane emissions in freshwater wetlands as well (Smemo and Yavitt 2011). Either sulfate reduction or nitrate reduction may be coupled to anaerobic methane oxidation through close associations between methanogens and sulfate-reducing or denitrifying microbes (Conrad 1996, Boetius et al. 2000, Raghoebarsing et al. 2006).

Due to both anaerobic and aerobic methane oxidation, the net ecosystem fluxes of CH_4 from wetlands are often far lower than gross rates of methanogenesis. Reeburgh et al. (1993) have estimated that the global rate of methane production in wetlands is about 20% larger than the net release of methane from wetland soils. To understand the relative importance of methane consumption, investigators note that methane-oxidizing bacteria alter the $\delta^{13}C$ of CH_4 escaping to the atmosphere, and comparisons of the isotopic ratio of CH_4 in sediments and surface collections can indicate the importance of oxidation (Happell et al. 1993). In the Florida Everglades, for example, more than 90% of methane production is consumed by methanotrophs before it diffuses to the atmosphere (King et al. 1990).

The flux of methane from wetlands shows great spatial variability as a result of differences in soil properties, topography, and vegetation (Bartlett and Harriss 1993, Bubier 1995, Zou et al. 2005, Keller and Bridgham 2007, Levy et al. 2012, Morse et al. 2012), making global extrapolations difficult. Methane fluxes may increase with increasing temperatures if wetland sediments remain saturated (Christensen et al. 2003). In contrast, for wetlands that dry during the warmest months of the year, wetlands may shift from being net CH_4 sources during wet seasons to net CH_4 sinks as temperatures rise (Harriss et al. 1982). In an early comprehensive synthesis of wetland methane efflux studies, Bartlett and Harris (1993) reported that tropical wetlands were responsible for >60% of total global wetland CH_4 emissions while northern wetlands (north of 45° N) were responsible for nearly one-third of global emissions (Table 7.9).

TABLE 7.9   Compiled Estimates of Global Emissions of CH_4 from Natural Wetlands

Authors	Method	Global emissions from wetlands (Tg CH_4 yr^{-1})	Global natural emissions (Tg CH_4 yr^{-1})	Percent of natural sources
Matthews and Fung (1987)	Upscaling from field estimates	110	—	—
Aselmann and Crutzen (1989)	Upscaling from field estimates	40–160	—	—
Hein et al. (1997)	Global inverse modeling	231	—	—
Houweling et al. (2000b)	Global inverse modeling	163	222	73
Wuebbles and Hayhoe (2002)		100	145	69
Wang et al. (2004)	Global inverse modeling	176	200	88
Fletcher et al. (2004)	Global inverse modeling	231	260	89
Chen and Prinn (2006)	Global inverse modeling	145	168	86
Our synthesis: Table 11.2	Data synthesis	143	258	55

Although the range of measured rates of CH_4 emissions overlaps considerably across latitudes, the longer growing seasons and greater spatial extent of tropical wetlands explain their greater contribution to global atmospheric CH_4 (Figure 7.19; Bartlett and Harriss 1993). Net regional losses from wetlands are partially balanced by the consumption of atmospheric methane in adjacent upland soils, where it is consumed by methane-oxidizing bacteria (Whalen and Reeburgh 1990, Le Mer and Roger 2001; see also Chapter 11). Efforts over the last two decades to constrain the global estimates of CH_4 emissions from natural wetlands
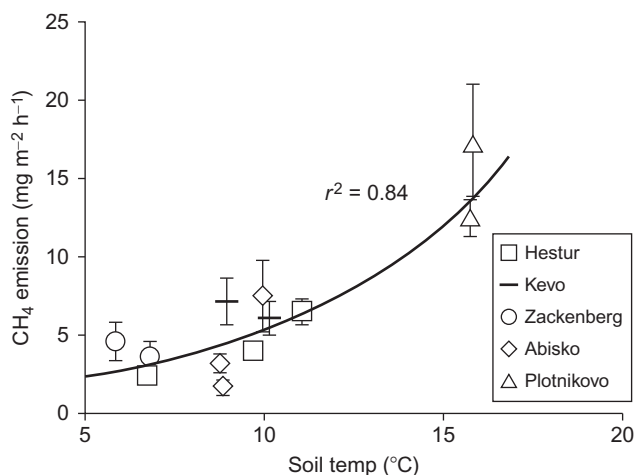

FIGURE 7.19   The relationship between mean seasonal soil temperature (at 5-cm depth) and mean seasonal CH_4 flux (measured at least 8 times throughout the growing season at each site) at the measurement site during all years. *Source: From Christensen et al. (2003). Used with permission of American Geophysical Union.*

have suggested that wetlands may produce 100 to 231 Tg CH_4 yr^{-1}, or 55 to 89% of the total annual flux of CH_4 from natural sources (refer to Table 11.2).

Microbial Consortia

The large differences in free energy yield between the various terminal decomposition pathways in wetlands can be used to predict the dominant metabolic processes under many environmental conditions. When NO_3^- or oxidized Fe or Mn is available in anoxic sediments, sulfate reduction is generally suppressed. Similarly, methanogenesis is suppressed by the provision of SO_4. Indeed, it has been suggested that sulfate delivered by acid rain could be suppressing current global CH_4 emissions by as much as 8% (Vile et al. 2003, Gauci et al. 2004, Weston et al. 2006). Most of our theoretical understanding of anaerobic metabolism is based on using the measured free energy yields from pure culture laboratory studies. A variety of recent studies have demonstrated that consortia of co-occurring microbial species can collectively perform chemical reactions that would not be predicted from studies of individual species (Lovley and Phillips 1988; Boetius et al. 2000; Raghoebarsing et al. 2005, 2006).

WETLANDS AND WATER QUALITY

Thus far we have primarily focused on the retention of C in solid organic matter within wetland sediments and the gaseous loss of C as CO_2 or CH_4. Hydrologic losses of dissolved organic carbon (DOC) from wetlands represent a major export term and an important source of organic carbon and nutrients for many rivers and coastal estuaries. Water in contact with peat leaches DOC from the peat matrix (Dalva and Moore 1991), and concentrations of DOC in peatland soils and overlying surface waters typically range from 20 to 100 mg C L^{-1}, with the vast majority of the DOC characterized as humic substances (Thurman 1985). Higher water tables tend to increase the rate of DOC production and, for wetlands that are hydrologically connected to downstream ecosystems or groundwaters, will increase rates of DOC loss (Blodau et al. 2004). Much of the variation in DOC fluxes between rivers can be explained by differences in the wetland area of their watersheds (Dalva and Moore 1991, Dillon and Molot 1997, Gergel et al. 1999, Pellerin et al. 2004, Johnston et al. 2008).

Without oxygen, decomposition is slow in saturated sediments, maintaining nutrient limitation of biomass growth in many wetlands and leading to the gradual buildup of soil organic matter. Wetlands can thus sequester large quantities of nutrients and trace elements delivered from their catchments, incorporating these elements into plant biomass and eventually into soil organic matter. In addition to retaining elements in tissues and soils, wetland sediments provide ideal conditions for denitrifers and possess a great capacity to remove excess NO_3 and convert inorganic phosphorus and other trace elements into organic molecules (e.g., Johnston et al. 1990, Emmett et al. 1994, Zedler and Kercher 2005, Fergus et al. 2011). In addition to sequestering trace elements, microbes in wetland sediments are responsible for the methylation of a wide variety of metals, some of which are toxic to biota and more rapidly assimilated in the methyl form (Chapter 13).

WETLANDS AND GLOBAL CHANGE

The areal extent of wetlands has declined through human history as wetlands have been drained, filled, or cultivated for agricultural or urban development. Although it is impossible to determine the global extent of wetlands that have been lost through direct human intervention, recent estimates suggest that 50% of all terrestrial wetlands have been destroyed by human activities in the United States, with higher rates for the developed regions of Canada, Europe, Australia, and Asia (Mitsch and Gosselink 2007).

Global Wetland Loss

Climate change is likely to accelerate the rate of wetland loss, as wetlands are particularly vulnerable to altered patterns of precipitation and evaporation on the world's continents (Chapter 10). It is difficult to anticipate the net effect of wetland loss on the global C cycle (Avis et al. 2011). Less frequent inundation is likely to foster oxidation of soil organic matter, but the loss of organic matter may be coupled with enhanced NPP (Megonigal et al. 1997, Choi et al. 2007) and reduced CH_4 emissions (Bousquet et al. 2006, Ringeval et al. 2010).

Sea Level Rise and Saltwater Intrusion

In some regions freshwater wetlands may become brackish or saline as a result of saltwater intrusion into coastal wetlands or through drought-induced evaporative concentration of salts. The resulting changes in ionic strength have been shown to drive "internal eutrophication," as PO_4^{3-} formerly bound to anion adsorption sites is displaced by Cl^- and SO_4^{2-} ions and reduced S compounds bind with Fe, reducing the efficiency of $Fe-PO_4$ binding (Caraco et al. 1989, Lamers et al. 1998, Beltman et al. 2000). The provision of the important electron acceptor SO_4^{2-}, a dominant constituent of seawater, alters the availability of electron acceptors in waterlogged soils, enhancing organic matter decomposition (through sulfate reduction), increasing concentrations of HS^-, and potentially suppressing methanogenesis and denitrification (Lamers et al. 1998, Weston et al. 2006, Sutton-Grier et al. 2011).

Rising Temperatures

Predicting the effect of rising temperatures on wetland biogeochemistry is difficult because it requires reconciling sometimes opposite direct effects and complex positive and negative feedbacks. For instance, higher temperatures will lead to a lower oxygen-holding capacity of water, perhaps further reducing the zones of aerobic respiration in many wetlands and slowing organic matter decomposition. At the same time, both methanogenesis and CO_2 production increase in wetland sediments at higher temperatures (Avery et al. 2002). The effect of warmer temperatures on plant evapotranspiration and the resulting changes in wetland hydroperiods will likely have the greatest impact on wetland processes globally.

Of particular concern is the potential for a loss of high-latitude wetlands due to permafrost thaw (Limpens et al. 2008, Schuur et al. 2008, Tarnocai et al. 2009, McGuire et al. 2010, Koven et al. 2011, Shaver et al. 2011). More than 50% of all wetlands are located at high latitudes (refer to Figure 7.1), and recent estimates suggest that as much as 1672 Pg of soil C is held within the

northern permafrost region, of which about 88% occurs in perennially frozen soils (Tarnocai et al. 2009). The hydrology of many boreal wetlands is constrained by permafrost barriers to drainage; thus permafrost melting may lead to wetland drainage, with the potential for positive feedbacks to climate change through the decomposition of previously saturated organic matter (Avis et al. 2011) and the hydrologic export of large amounts of DOC (Guo et al. 2007, Olefeldt and Roulet 2012).

The abundance of stored soil organic matter in peatland ecosystems results from inefficient decomposition over long periods of time rather than high rates of organic matter production. Peat decomposition will increase as water tables drop (Yu et al. 2003, Fenner and Freeman 2011); thus drier arctic climates will lead to lower water table elevations and increased rates of organic matter oxidation. Changes in the flux of methane to the atmosphere may occur if global warming causes changes in the saturation of peatlands, particularly at northern latitudes. If these soils become warm and dry, the flux of methane may be lower while the flux of CO_2 to the atmosphere may increase (Freeman et al. 1993; Moore and Roulet 1993; Funk et al. 1994). The potential for catastrophic carbon losses from peatlands in a warming climate is of concern. Drainage of wetlands (either intentionally or as a result of a drier climate) can make wetlands more susceptible to wildfire and can support fires that burn more deeply into peat or spread over a greater spatial extent (Grosse et al. 2011). Recent peatland fires in Alaska (Mack et al. 2011) and Canada (Turetsky et al. 2011) each removed centuries of accumulated peat.

Elevated CO_2

Based on lab and field experiments, elevated CO_2 has less consistent effects on total aboveground plant biomass in wetlands than it does on upland ecosystems. Several experimental CO_2 enrichments in peatlands have shown that higher atmospheric CO_2 increases vascular plant biomass, but the effect is considerably offset by accompanying losses of peat-building bryophytes (especially *Sphagnum*) (Berendse et al. 2001, Freeman et al. 2001a). In brackish coastal marshes, Langley and Megonigal (2010) found that the vascular plant biomass response to CO_2 was constrained by low nutrient availability, and the low nutrient turnover in many wetlands may substantially limit their ability to sequester additional C in biomass in response to elevated CO_2. Both field and laboratory evidence suggests that elevated CO_2 leads to enhanced organic matter exudation by wetland plants that can exacerbate wetland DOC losses (Freeman et al. 2001a), promote organic matter oxidation (Wolf et al. 2007), and increase CH_4 production (Vann and Megonigal 2003, van Groenigen et al. 2011).

The flux of methane from natural wetlands accounts for ~140 Tg of CH_4 annually, which is a large portion of the total global flux to the atmosphere (Chapter 11). With the atmospheric concentration increasing at about 1% yr^{-1}, various workers have asked whether changes in ecosystem processes within wetlands or changes in the spatial extent of wetlands might be responsible. Certainly, global methanogenesis has increased with the increasing cultivation of rice, which now accounts for ~25% of the global production of methane from wetlands (Hein et al. 1997, Houweling et al. 2000a, Wuebbles and Hayhoe 2002, Fletcher et al. 2004, Wang et al. 2004). Because CH_4 production has been found to be highly correlated with NEP in a number of studies (refer to Figure 7.17), there is concern that as rising atmospheric

CO_2 stimulates the growth of wetland plants it may simultaneously provide a greater supply of organic substances for methane-producing bacteria (Megonigal and Schlesinger 1997, Vann and Megonigal 2003, Fenner et al. 2007). A meta-analysis of CO_2-enrichment experiments in 16 studies of natural wetlands and 21 studies in rice paddies found that increased CO_2 stimulated CH_4 emissions in wetlands by 13.2% and in rice paddies by 43.4% (van Groenigen et al. 2011), suggesting that enhanced production of CH_4 may offset C sequestration in wetlands exposed to elevated CO_2. Collectively, elevated CO_2 research in wetlands provides little evidence for increasing plant biomass in response to rising CO_2, and it raises concerns that increased CO_2 may stimulate enhanced rates of soil organic matter oxidation and CH_4 production.

SUMMARY

Wetlands occupy a small (and shrinking) proportion of the continental land surface, but play a critical role in global biogeochemistry by storing as much as 50% of soil organic matter, producing more than 20% of CH_4, and by substantially reducing the inorganic nutrient export to river networks and the sea. The unique role of wetlands in local to global biogeochemical cycling results from the tendency for wetlands to have waterlogged, anoxic soils for some or all of each year. The limited availability of oxygen to wetland heterotrophs impedes decomposition, slows nutrient turnover, and allows a variety of alternative metabolic pathways to dominate ecosystem C cycling and to link the cycling of C with that of nitrate, manganese, iron, sulfate, and hydrogen through microbial energetics.

Recommended Readings

Reddy, K.R., and R.D. DeLaune. 2008. *Biogeochemistry of Wetlands: Science and Applications*. Taylor and Francis.

Megonigal, J.P., M.E. Hines, and P.T. Visscher. 2003. Anaerobic metabolism: Linkages to trace gases and aerobic processes, pp. 317–324. In W.H. Schlesinger, editor. *Biogeochemistry*. Elsevier-Pergamon.

Stumm, W., and J.J. Morgan. 1996. *Aquatic Chemistry* (third ed.). Wiley.

Wetzel R.G. 2001. *Limnology* (third ed.). Academic Press.

Zehnder, A.J.B. 1988. *Biology of Anaerobic Microorganisms*. Wiley.

PROBLEMS

1. Calculate the oxygen concentration at which the actual free energy yield of denitrification is equivalent to aerobic respiration, assuming starting conditions of NO_3 of 0.1 mg N L^{-1}, DOC concentrations at 5 mg CL^{-1}, at a pH of 7, and standard atmospheric pressure. Now repeat your analysis, assuming that NO_3 concentrations elevated by fertilizer or acid rain inputs to be 5 mg L^{-1}.

2. Use the following equation to predict C losses from a 1-ha plot in the Siberian permafrost under two contrasting summer thaw conditions.

$$C_t = C_0(1 - e^{-kt}),$$

   where C_t is the cumulative C release over time, C_0 is the proportion of C in the permafrost that is susceptible to microbial decomposition after thaw, k is the inverse of the turnover time for decomposition, and t is the length of the study period. Assume that bulk soil in the plot has a density of 1 g cm^{-3}, C content is 15 mg g^{-1}, of which 10% is susceptible to decomposition, Q_{10} is 1.9, and base respiration rate is 2.5 mg C $gsoil^{-1}$. Use this information to estimate the rate of C loss over 30 days in a cool growing season (average temperature of 5°C) versus a warm growing season (average temperature of 10°C). Assume that in the cooler year permafrost thaws to a depth of 10 cm and in the warmer year it thaws to a depth of 20 cm. Repeat your analyses for a longer and warmer growing season (average temperature of 10°C with a growing season of 45 days). Relevant numbers for this problem are derived from Dutta et al. (2006).

3. Both acid rain and saltwater intrusion are expected to reduce the production of methane from affected wetlands through the provision of SO_4^{2-} ions. Use free energy calculations to demonstrate how the free energy yield of sulfate reduction changes as you increase soil solution SO_4^{2-} concentrations from 10 to 2701 mg SO_4^{2-} per liter (freshwater to full-strength seawater). Graph your results. For comparison, show the free energy yield for methanogenesis and denitrification on the same plot. Assume that the sediments are anoxic, the pH $= 7$, and organic carbon is in excess of potential demand. Compare this free energy to methanogenesis and denitrification under the same conditions (assuming NO_3 of 1.0 mg N L^{-1}. At what sulfate concentration should sulfate reducers outcompete methanogens? Denitrifiers?

4. Use the relationship between plant photosynthesis and CH_4 flux from Figure 7.17(b) under ambient and elevated CO_2 treatments to calculate how much of the enhancement of plant C fixation into biomass resulting from elevated CO_2 is offset by CH_4 emissions. Assume that 50% of C fixed in photosynthesis is incorporated into biomass and that methane has a greenhouse warming potential 25× that of CO_2 (IPCC 2007). Does the offset differ between flooded and unflooded treatments? [*Hint:* To turn a graph into datapoints in a spreadsheet you can either use a ruler or, for a more elegant solution, go to the original source of the graph (Vann and Megonigal 2003), select and save the relevant figure as an image, and then use the free program "data thief" (*www.datathief.org*) to extract the datapoints.]