

FIGURE 7.5 (a) Electron micrograph of a cross-sectioned stem of the aquatic macrophyte *Potamogeton*; (b) photograph of Cypress pneumatophores. Source: (a) From Jackson and Armstrong (1999). (b) From Wikipedia Commons.

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 aerenchymous 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 edaphic⁴ 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.

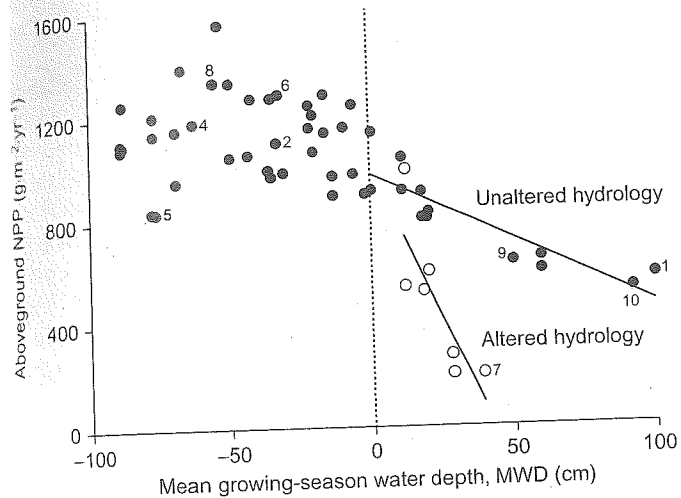


FIGURE 7.6 Water depth was negatively correlated with aboveground NPP for southern coastal wetlands. The effect of inundation was more pronounced when levees were built to maintain permanent flooding (plots shown in open circles). Source: From Megonigal et al. 1997. Used with permission of Springer.

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

I. PROCESSES AND REACTIONS

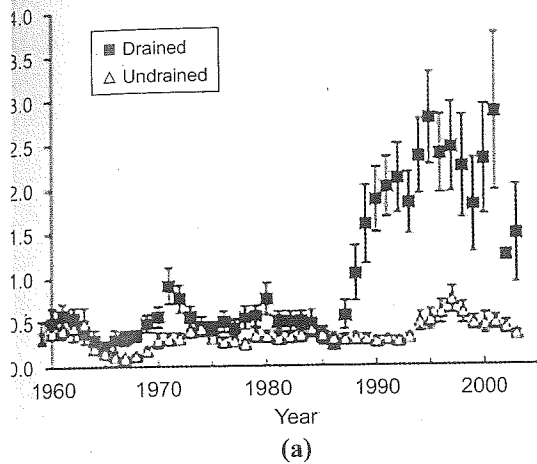
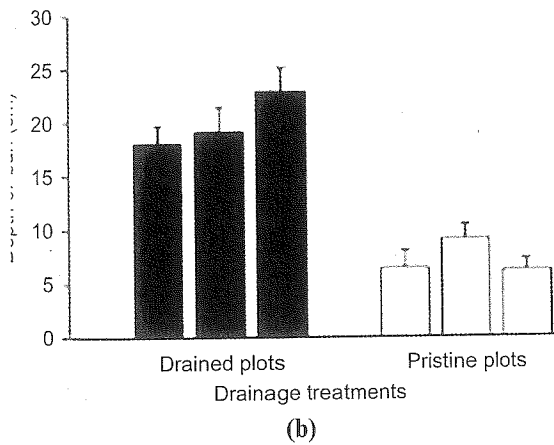


FIGURE 7.7 Drainage of a forested boreal fen in western Canada in 1986 doubled the rate of peat C accumulation through increases in tree biomass and detritus (indicated here by tree ring growth) (a), but also made the drained fen more susceptible to catastrophic losses of carbon in fire (b). In 2001, 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).



composition in both the oxic upper level and the lower level of the deposit. Through time, er 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 geochemically active *acrotelm*, the surface layer of peat above the lowest water table variation that experiences fluctuations between oxic and anoxic conditions, and the *catotelm*, underlying layers that are permanently saturated.

Peatland ecosystems can be perceived as a special category of wetland wherein plants mold 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 (Vosselink 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

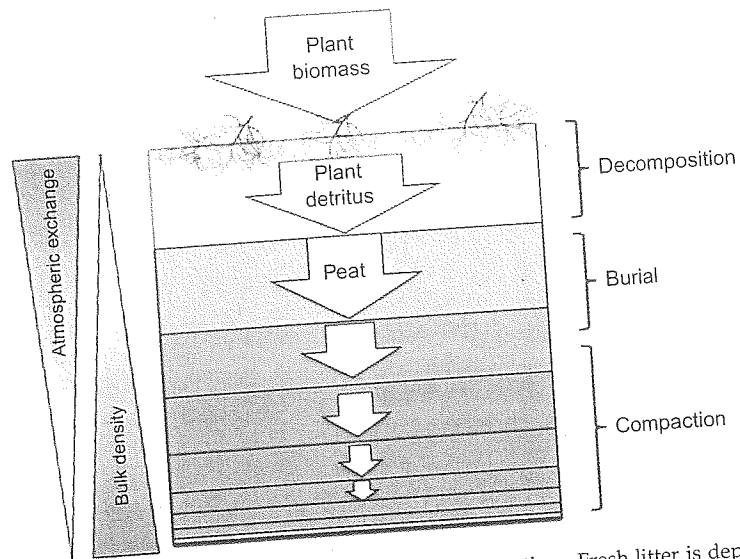


FIGURE 7.8 A model of peat accumulation and compaction over time. Fresh litter is deposited in the surface layers, where decomposition rates are highest due to oxygen diffusion and the supply of alternate electron acceptors. Organic matter that escapes decomposition is buried beneath new litter inputs 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 ($\text{g C m}^{-2} \text{ yr}^{-1}$)	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	<i>Picea</i> and <i>Sphagnum</i>	4790	11-61	Billings (1987)
Russia	Mires, bogs, and fens	3000-7000	12-80	Botch et al. (1995)
Manitoba	<i>Picea</i> and <i>Sphagnum</i>	2960-7939	13-26	Reader and Stewart (1972)
Western Canada	<i>Sphagnum</i> 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	<i>Eriophorum vaginatum</i>	7000	27	Viereck (1966)
Colorado	<i>Sphagnum</i> bogs	5300	30–32	Belyea and Warner (1996)
Russia	Siberian mires	8000–10,000	12.1–23.7	Turunen et al. (2001)
Canada	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)
Canada	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	<i>Sphagnum</i>	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)
Tropical Wetlands			70–387	
Louisiana	Salt marsh		200–300	Hatton et al. (1983)
Florida	<i>Cladium</i> swamp	25–30	70–105	Craft and Richardson (1993)

Continued

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	<i>Cladium sp.</i>		86-140	Reddy et al. (1993)
Florida Everglades	<i>Typha sp.</i>		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, Frohling 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

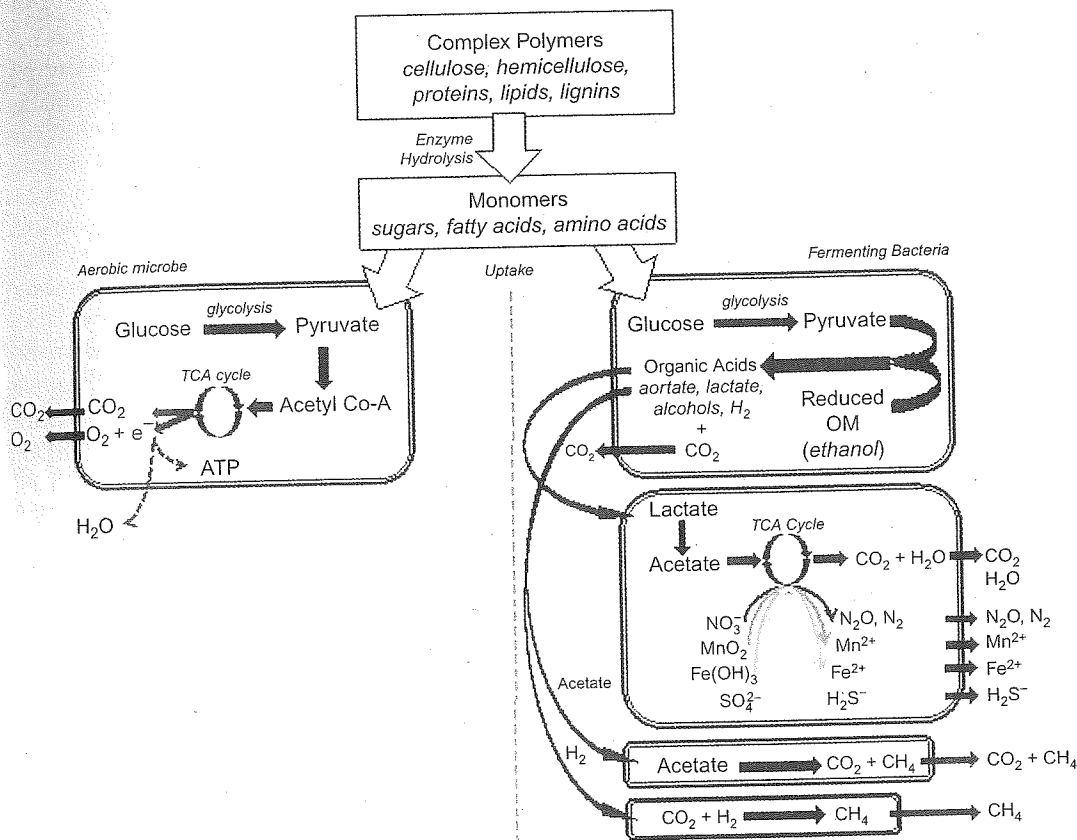


FIGURE 7.9 Contrasting the single aerobic respiration pathway with the multistage pathway involved in decomposition in the absence of oxygen. Source: Figure drawn with inspiration from Megonigal et al. (2003) and Reddy and DeLaune (2008).

completely degrade the resulting organic monomers to CO_2 using glycolysis followed by the Krebs 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 Krebs 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

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		E° (V)	Oxidation	E° (V)
Reduction				
(A)	$1/4\text{O}_2(\text{g}) + \text{H}^+ + \text{e}^- = 1/2\text{H}_2\text{O}$	+0.813	(L) $1/4\text{CH}_2\text{O} + 1/4\text{H}_2\text{O} = 1/4\text{CO}_2 + \text{H}^+ + \text{e}^-$	-0.485
(B)	$1/5\text{NO}_3^- + 6/5\text{H}^+ + \text{e}^- = 1/10\text{N}_2 + 3/5\text{H}_2\text{O}$	+0.749	(M) $1/2\text{CH}_4 + 1/2\text{H}_2\text{O} = 1/2\text{CH}_3\text{OH} + \text{H}^+ + \text{e}^-$	+0.170
(C)	$1/2\text{MnO}_2(\text{s}) + 1/2\text{HCO}_3 + 3/2\text{H}^+ + \text{e}^- = 1/2\text{MnCO}_3 + \text{H}_2\text{O}$	+0.526	(N) $1/8\text{HS}^- + 1/2\text{H}_2\text{O} = 1/8\text{SO}_4^{2-} + 9/8\text{H}^+ + \text{e}^-$	-0.222
(D)	$1/8\text{NO}_3^- + 5/4\text{H}^+ + \text{e}^- = 1/8\text{NH}_4^+ + 3/8\text{H}_2\text{O}$	+0.363	(O) $\text{FeCO}_3(\text{s}) + 2\text{H}_2\text{O} = \text{FeOOH}(\text{s}) + \text{HCO}_3(10^{-3}) + 2\text{H}^+ + \text{e}^-$	-0.047
(E)	$\text{FeOOH}(\text{s}) + \text{HCO}_3(10^{-3}) + 2\text{H}^+ + \text{e}^- = \text{FeCO}_3(\text{s}) + 2\text{H}_2\text{O}$	-0.047	(P) $1/8\text{NH}_4^+ + 3/8\text{H}_2\text{O} = 1/8\text{NO}_3^- + 5/4\text{H}^+ + \text{e}^-$	+0.364
(F)	$1/2\text{CH}_2\text{O} + \text{H}^+ + \text{e}^- = 1/2\text{CH}_3\text{OH}$	-0.178	(Q) $1/2\text{MnCO}_3(\text{s}) + \text{H}_2\text{O} = 1/2\text{MnO}_2(\text{s}) + 1/2\text{HCO}_3(10^{-3}) + 3/2\text{H}^+ + \text{e}^-$	+0.527
(G)	$1/8\text{SO}_4^{2-} + 9/8\text{H}^+ + \text{e}^- = 1/8\text{HS}^- + 1/2\text{H}_2\text{O}$	-0.222		
(H)	$1/8\text{CO}_2 + \text{H}^+ + \text{e}^- = 1/8\text{CH}_4 + 1/4\text{H}_2\text{O}$	-0.244		
(I)	$1/6\text{N}_2 + 4/3\text{H}^+ + \text{e}^- = 1/3\text{NH}_4$	-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).