

Biogeochemistry in anaerobic environments

- Sediments
 - Ocean, lakes, estuaries
- Soils
 - permanent or seasonal flooding
 - WFPS → anaerobic pockets
 - at depth: groundwater
- “anaerobic” = lacking oxygen
 - O_2 diffuses 10^4 times slower in water than air
 - O_2 gradients develop
 - other oxidizers necessary for metabolism

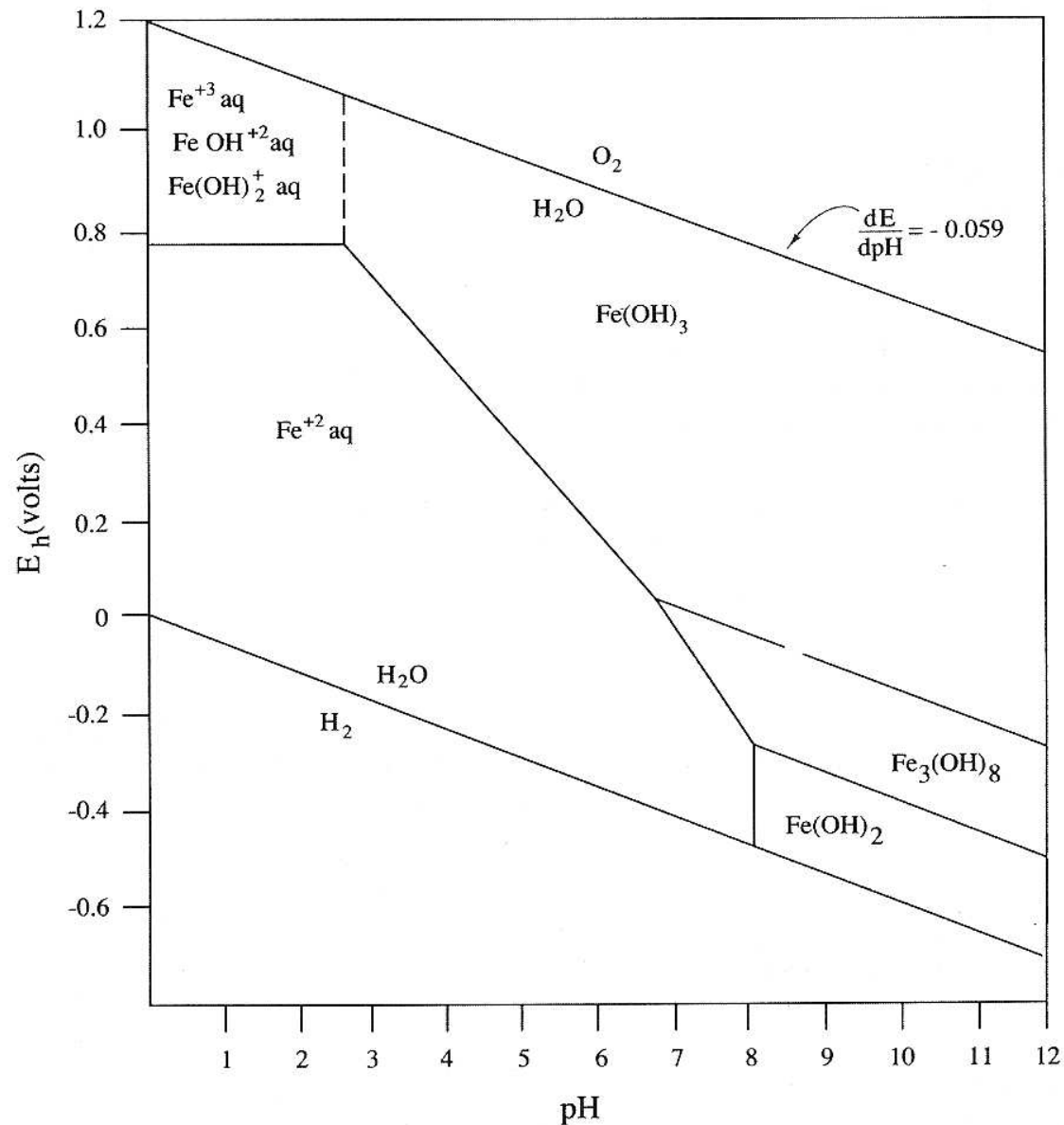


Figure 7.2 The stability of iron and iron hydroxides in soils relative to E_h and pH at 25°C. All conditions refer to 1 mM Fe^{2+} solution. Modified from Ponnampetuma et al. (1967).

- E_h and pH are environmental properties !!
- availability of organic matter determines *reducing power*
- E_h determines dominant microbial mechanism
- redox reactions influence pH

Table 1 Thermodynamic sequence for reduction of inorganic substances by organic matter^a.

Reaction	<i>Eh</i> (V)	ΔG^b
Reduction of O ₂ $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	0.812	-29.9
Reduction of NO ₃ ⁻ $NO_3^- + 6H^+ + 6e^- \rightleftharpoons N_2 + 3H_2O$	0.747	-28.4
Reduction of Mn ⁴⁺ to Mn ²⁺ $MnO_2 + 4H^+ + 2e^- \rightleftharpoons Mn^{2+} + 2H_2O$	0.526	-23.3
Reduction of Fe ³⁺ to Fe ²⁺ $Fe(OH)_3 + 3H^+ + e^- \rightleftharpoons Fe^{2+} + 3H_2O$	-0.047	-10.1
Reduction of SO ₄ ²⁻ to H ₂ S $SO_4^{2-} + 10H^+ + 8e^- \rightleftharpoons H_2S + 4H_2O$	-0.221	-5.9
Reduction of CO ₂ to CH ₄ $CO_2 + 8H^+ + 8e^- \rightleftharpoons CH_4 + 2H_2O$	-0.244	-5.6

Source: Schlesinger (1997).

^a Units are kcal mol⁻¹ e⁻¹ assuming coupling to the oxidation reaction $\frac{1}{4}CH_2O + \frac{1}{4}H_2O \rightarrow \frac{1}{4}CO_2 + H^+ + e^-$. ^b $\Delta G = -RT \ln(K)$; pH 7.0, 25 °C.

Anaerobic Metabolism: Linkages to Trace Gases and Aerobic Processes,
by Megonical et al., in *Biogeochemistry*, Ed. W.H. Schlesinger

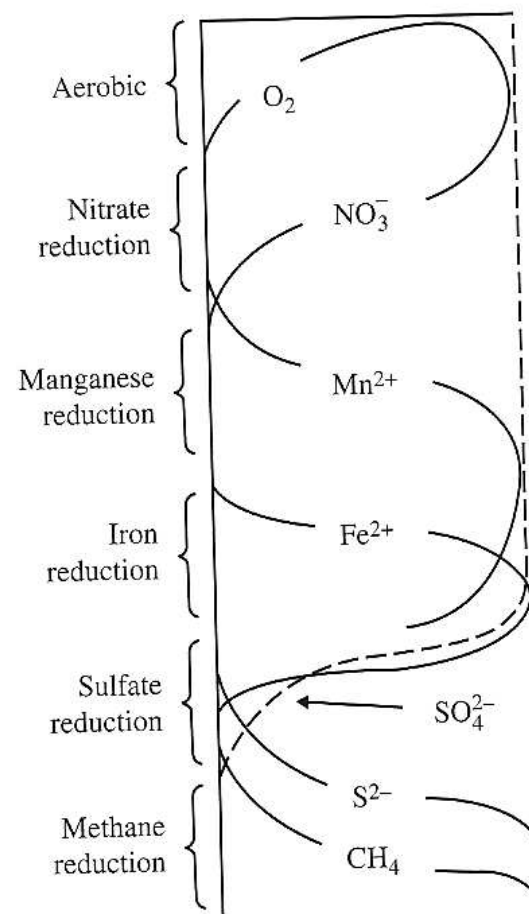


Figure 1 Vertical biogeochemical zones in sediments. The top is the sediment–water interface. Processes on the left represent the use of various electron acceptors (respirations) during the degradation of organic matter. Plots on the right represent the chemical profiles most widely used to delineate the vertical extent of each zone. Rotating the figure 90° to the left shows the sequence of electron acceptors used over time (*x*-axis) if a sample of oxic sediment were enclosed and allowed to become anaerobic over time.

Denitrification (dissimilatory)

- occurs at low $[O_2]$
- soils, oceans, sediments, etc.
- obligate anaerobes
 \emptyset nitrifiers themselves

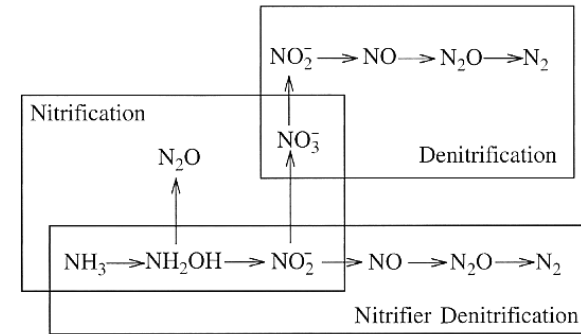
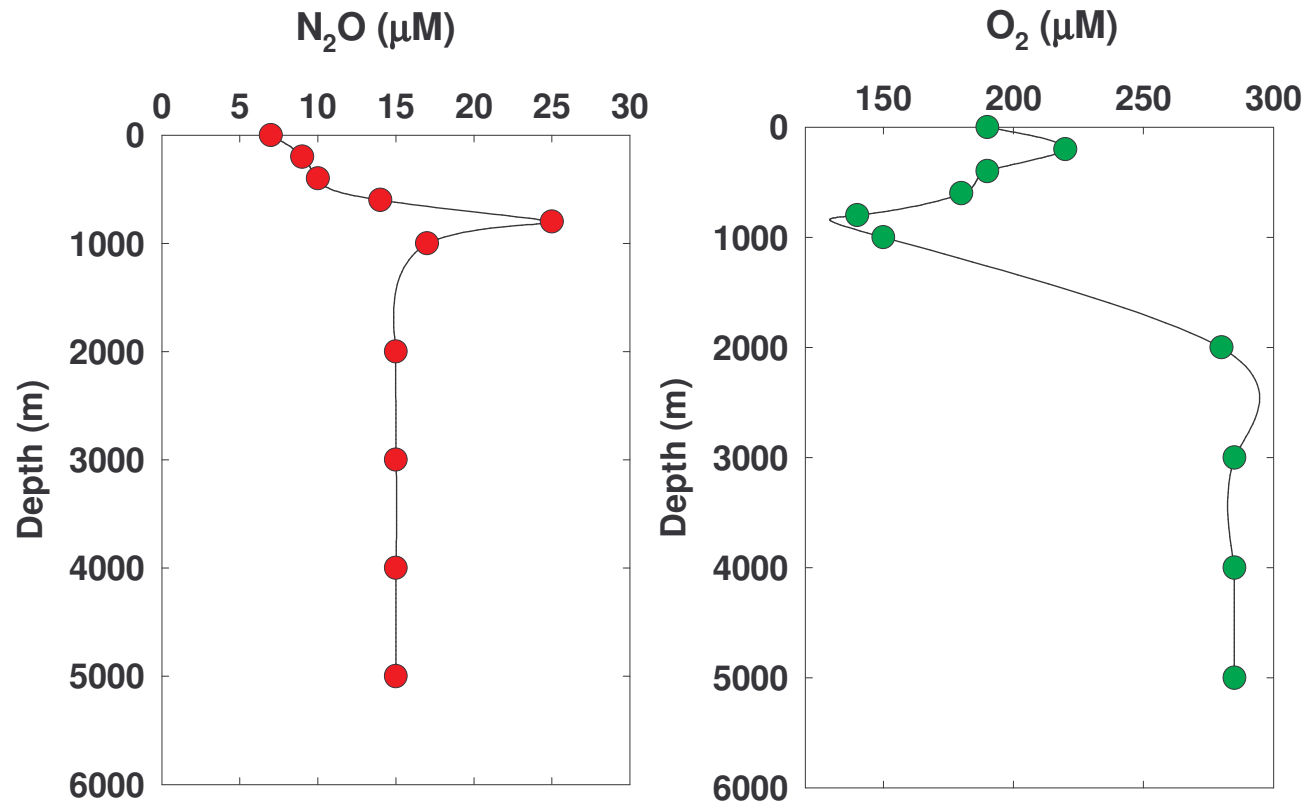


Figure 13 Relationships between three pathways of inorganic nitrogen oxidation and reduction (Wrage *et al.*, 2001) (reproduced by permission of Elsevier from *Soil Biol. Biochem.* **2001**, 33, 1723–1732).



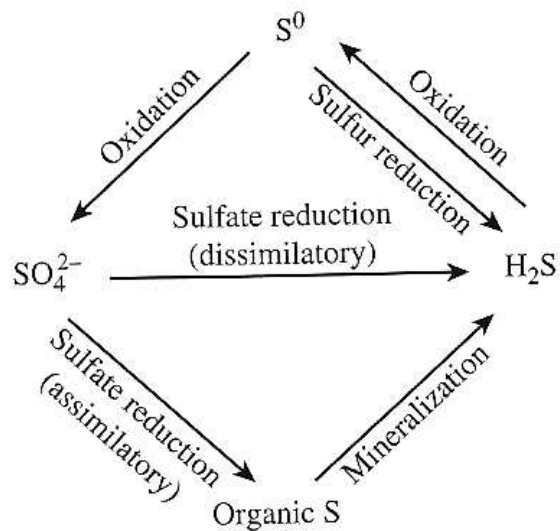


Figure 24 A simplified biological redox cycle for sulfur.

Anaerobic Metabolism: Linkages to Trace Gases and Aerobic Processes, by Megonical et al., in *Biogeochemistry*, Ed. W.H. Schlesinger

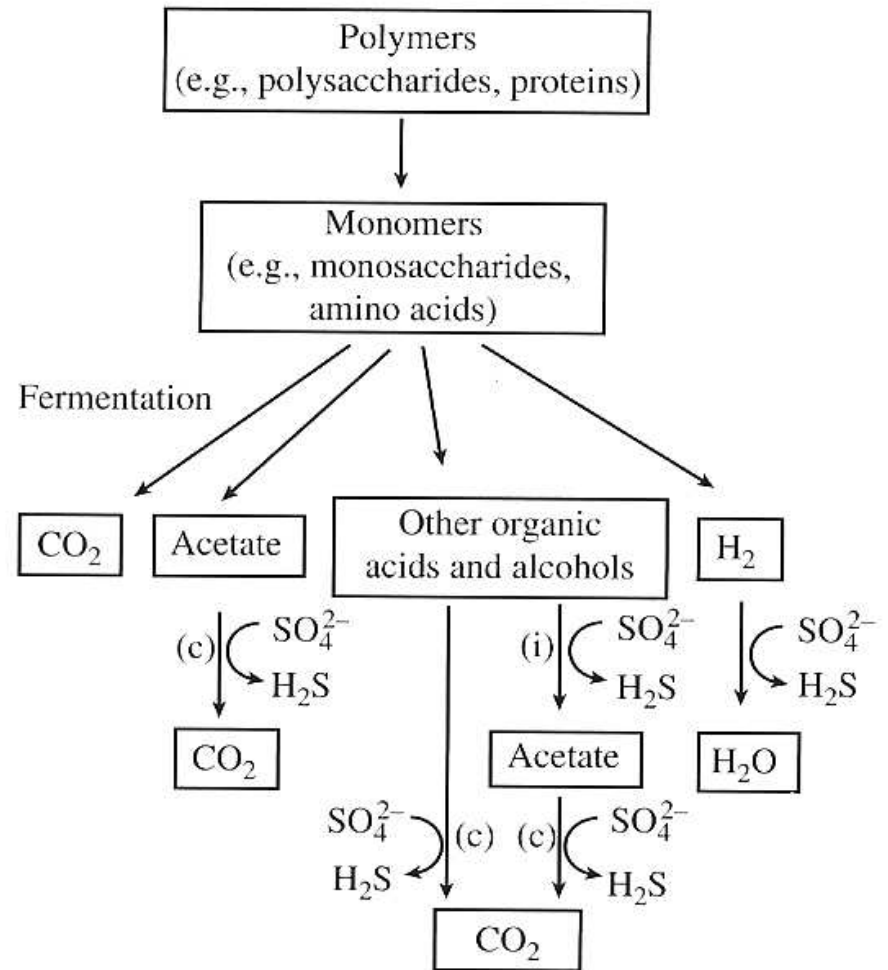


Figure 25 Anaerobic decomposition with sulfate reduction as the terminal step. Fermentation leads to several possible products including low molecular weight organic acids and alcohols and hydrogen and carbon dioxide. Incomplete oxidizers (i) produce acetate as an end product, whereas complete oxidizers (c) mineralize organic compounds, including acetate, to carbon dioxide.

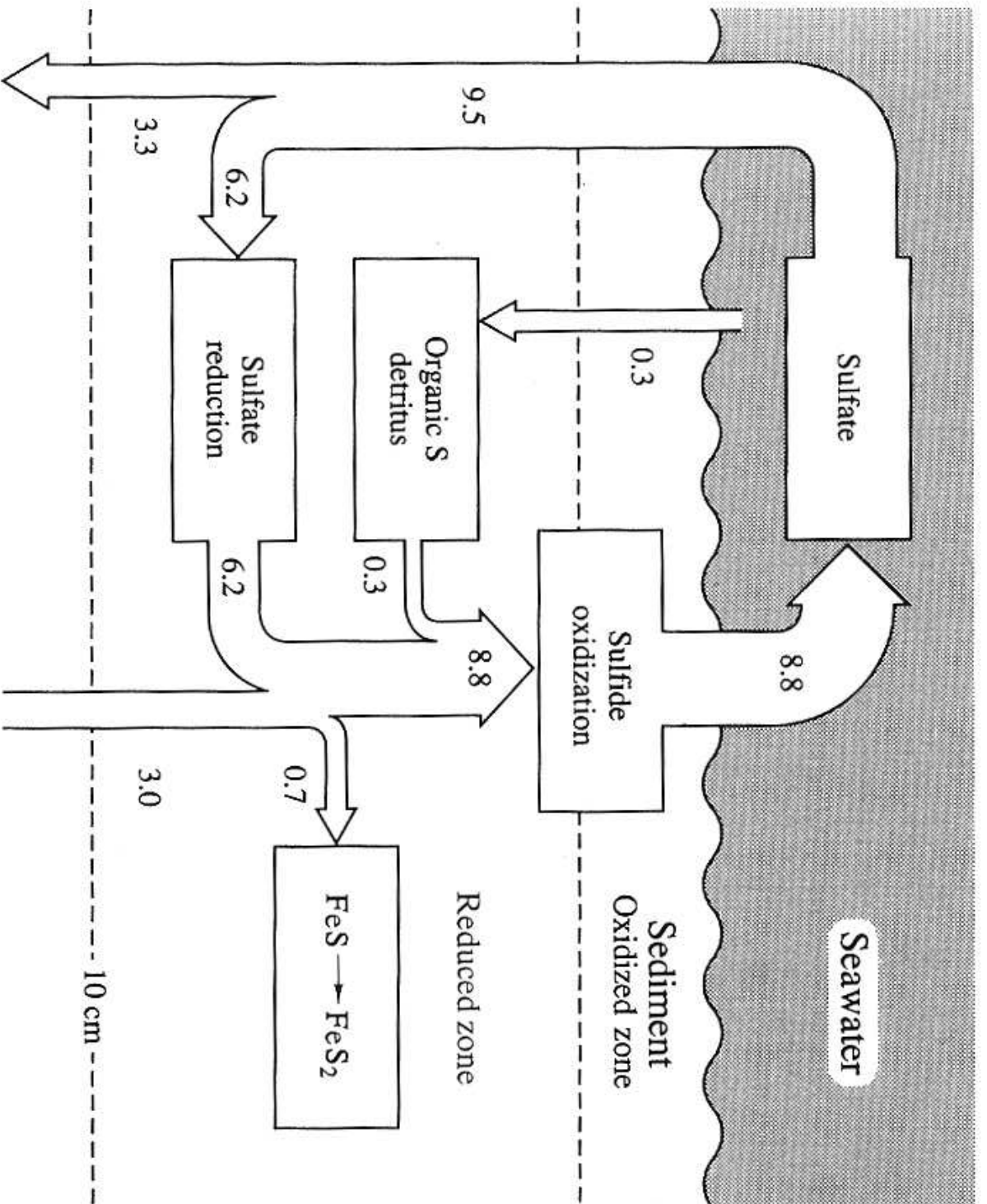


Figure 8.10 Transformations of sulfur in a coastal marine sediment. Note that of $6.2 \text{ g S m}^{-2} \text{ yr}^{-1}$ undergoing sulfate reduction, only $0.7 \text{ g S m}^{-2} \text{ yr}^{-1}$ is permanently stored in the sediment as pyrite or other reduced minerals. From Jørgensen (1977).

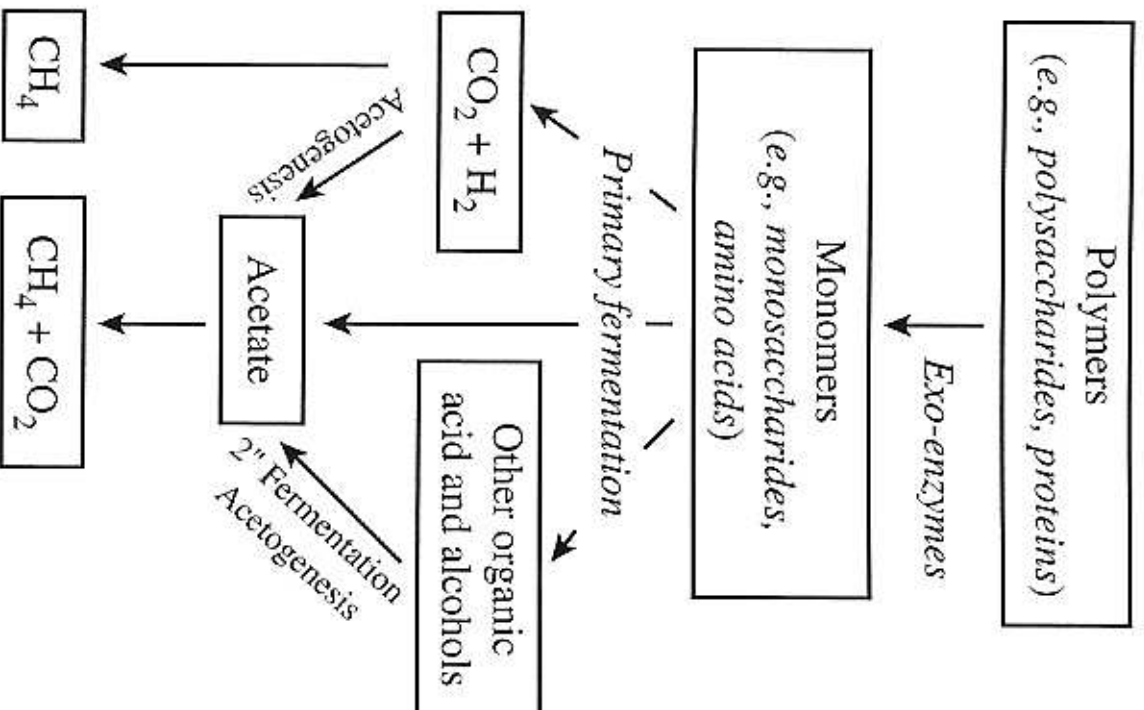


Figure 4 Metabolic scheme for the degradation of complex organic matter, culminating in methanogenesis. Polymers are cleaved via extracellular or cell-surface associated enzymes to monomers that are fermented to organic products, H₂ and CO₂. Methane is formed primarily from the oxidation of H₂ coupled to CO₂ reduction or by the fermentation of acetate. Acetate is formed by primary fermentation, acetogenesis from H₂/CO₂, and from secondary fermentation of primary fermentation products.

Table 4 Examples of reactions occurring in methanogenic environments illustrating the effect on energy yield of the consumption of fermentation products. Maintenance of low reactant concentrations allows secondary fermentation reactions that are endergonic under standard conditions to be exergonic (negative ΔG).

<i>Reaction</i>	<i>Free-energy change</i> (kJ)	
	$\Delta G^{0,a}$	ΔG^b
Glucose + 4H ₂ O → 2 acetate ⁻ + 2HCO ₃ ⁻ + 4H ⁺ + 4H ₂	- 207	- 319
Glucose + 2H ₂ O → butyrate ⁻ + 2HCO ₃ ⁻ + 3H ⁺ + 2H ₂	- 135	- 284
Butyrate ⁻ + 2H ₂ O → 2 acetate ⁻ + H ⁺ + 2H ₂	+48.2	- 17.6
Propionate ⁻ + 3H ₂ O → acetate ⁻ + HCO ₃ ⁻ + H ⁺ + H ₂	+76.2	- 5.5
2 Ethanol + 2H ₂ O → 2 acetate ⁻ + 2H ⁺ + 4H ₂	+19.4	- 37
Benzoate + 6H ₂ O → 3 acetate ⁻ + 2H ⁺ + CO ₂ + 3H ₂	+47	- 18

Source: Zinder (1984).

^a Standard conditions: solutes, 1 M; gases, 1 atm. ^b Concentrations of reactants typical of anaerobic habitats: fatty acids, 1 mM; glucose, 10 μM; CH₄, 0.6 atm; H₂, 10⁻⁴ atm; HCO₃⁻; 20 mM.

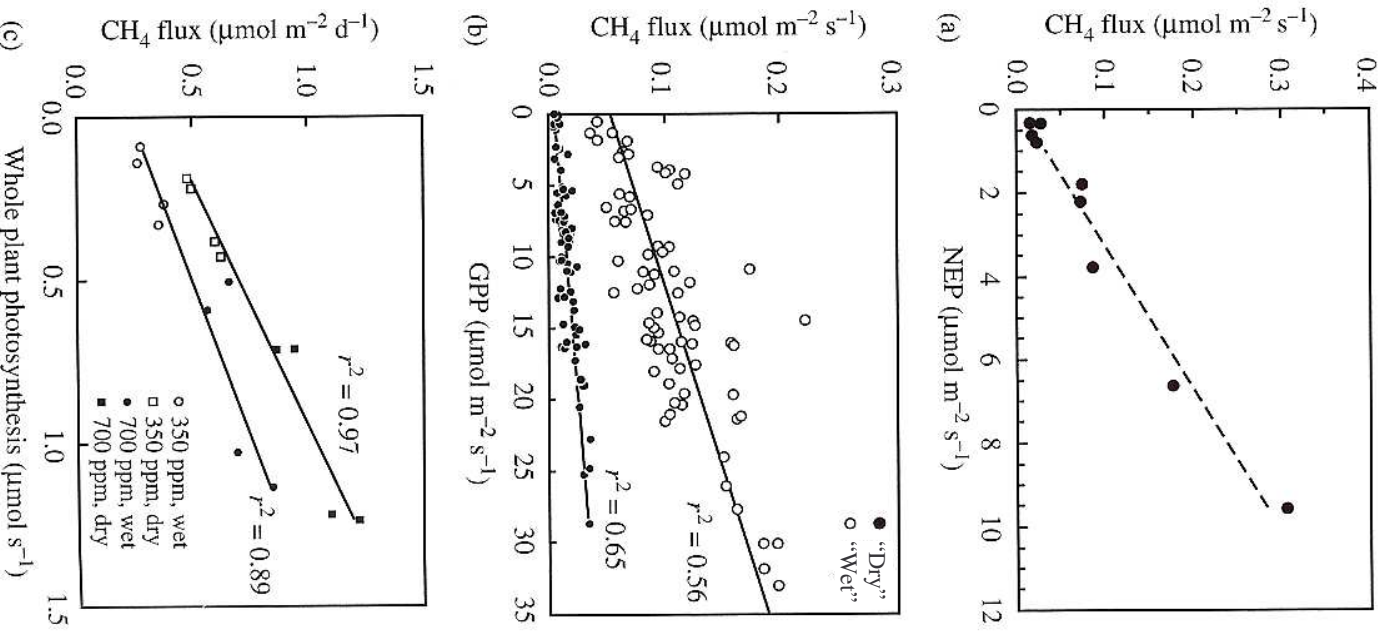


Figure 6 The relationship between wetland CH_4 emissions and various measures of primary productivity: (a) emissions versus net ecosystem production (NEP) in North-American ecosystems ranging from the subtropics to the subarctic; (b) emissions versus GPP in fen peatland mesocosms with high or low water table depths; and (c) emissions versus whole-plant net photosynthesis in marsh microcosms exposed to elevated and ambient concentrations of atmospheric CO_2 , (after Whiting and Chanton, (1993); Uptegraff *et al.*, (2001); and Vann and Megonigal (2003), respectively).

Table 6 Selected estimates of the proportion of SO_4^{2-} reduction in marine sediments that is mediated by anaerobic CH_4 oxidation.

<i>Site</i>	<i>Peak contribution to SO_4^{2-} reduction (%)</i>	<i>Depth-integrated contribution to SO_4^{2-} reduction (%)</i>	<i>Citation</i>
Aarhus Bay, Denmark	47–52	9	Thomsen <i>et al.</i> (2001)
Kattegat, Denmark	61	10	Iverson and Jørgensen (1985)
Skagerrak	89	10	Iverson and Jørgensen (1985)
Upwelling Zone, Namibia	100		Niewöhner <i>et al.</i> (1998)
Amazon Fan Sediment	50–85		Burns (1998)
Norsminde Fjorde	10–30		Hansen <i>et al.</i> (1998)
Big Soda Lake, Nevada		2	Iverson <i>et al.</i> (1987)
Kysing Fjord		<0.1	Iverson and Blackburn (1981)
Hydrate Ridge, Oregon ^a	100	100	Boetius <i>et al.</i> (2000b)

^a Inferred by comparing SRR above decomposing CH_4 hydrates to nearby nonhydrate sites.

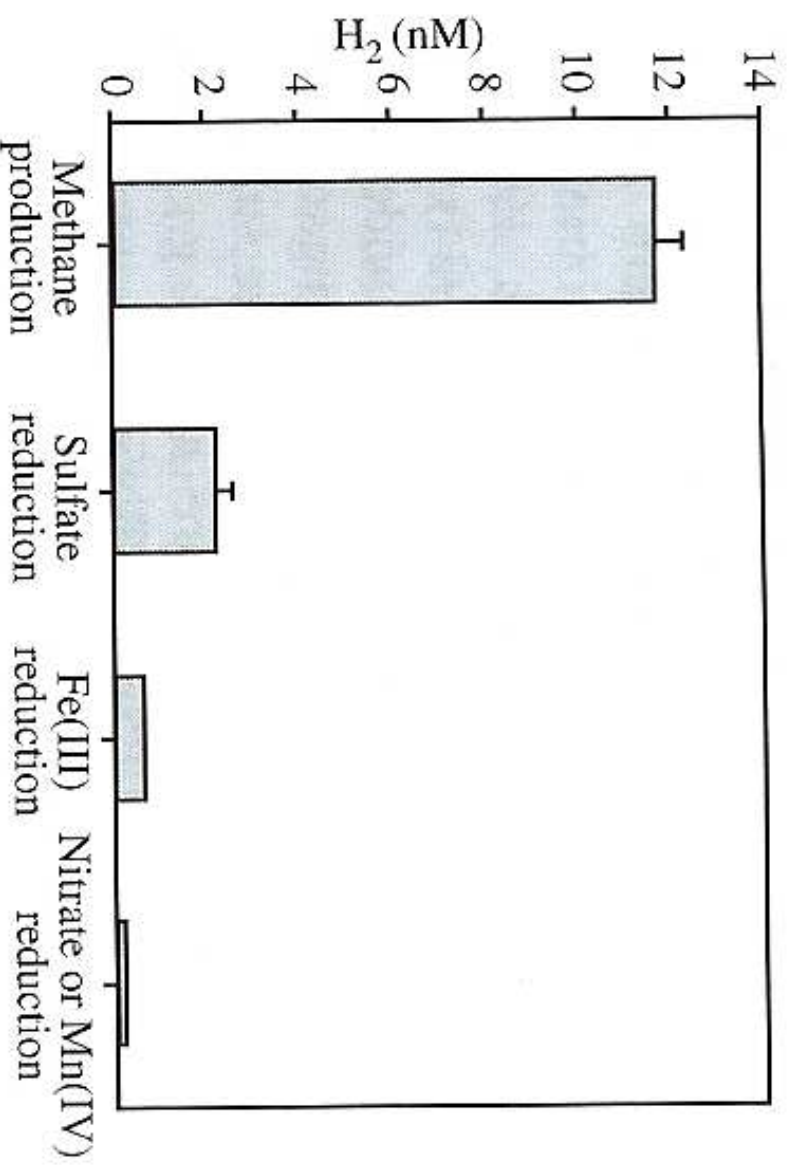


Figure 27 Steady-state H₂ concentrations in sediments with different dominant terminal electron accepting processes (Lovely and Goodwin, 1988) (reproduced by permission of Elsevier from *Geochim. Cosmochim. Acta.* **1988**, 52, 2993–3003).