Nutrient Cycling in Aquatic Ecosystems: 1. Wetlands, Lakes and Estuaries

Introduction: The importance of theses aquatic ecosystems

Redox potentials and key biogeochemical reactions
  - Redox potential
  - Denitrification
  - Sulfate reduction
  - Methanogenesis
  - Biomethylations

Characteristics of biogeochemistry in wetlands and lakes
  - Primary production
  - Sources of nutrients

Characteristics of biogeochemistry in estuaries and salt marshes

The issue of eutrophication in aquatic ecosystems

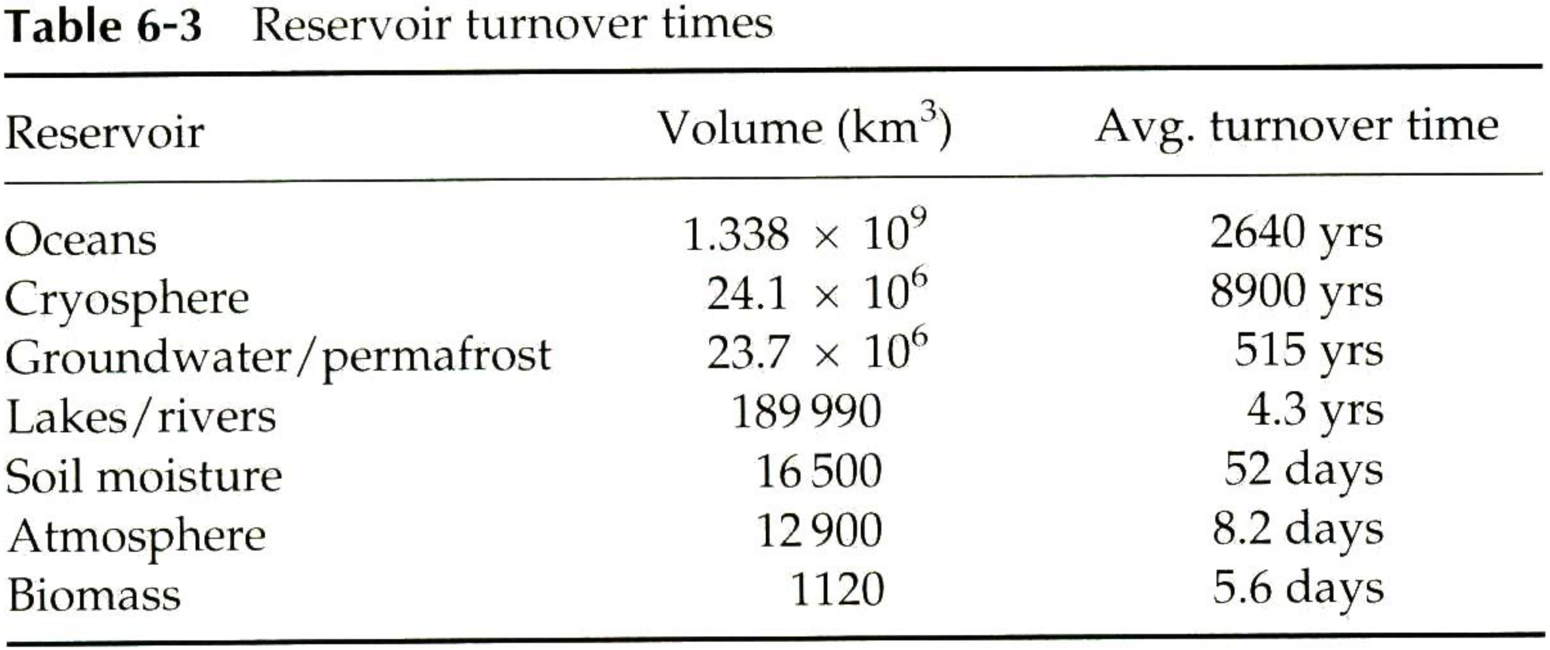

Table 6-3 Reservoir turnover times

Reservoir	Volume (km^3)	Avg. turnover time
Oceans	1.338×10^9	2640 yrs
Cryosphere	24.1×10^6	8900 yrs
Groundwater/permafrost	23.7×10^6	515 yrs
Lakes/rivers	189 990	4.3 yrs
Soil moisture	16 500	52 days
Atmosphere	12 900	8.2 days
Biomass	1120	5.6 days

From: Jacobson, Charlson, Rodhe & Orians 2000. Earth Syst. Sci.

The value of the world's ecosystem services (1994 US $)

(by Robert Costanza (U. Maryland) et al. NATURE, Vol 387 page 253-260)

Biome	%globe	%land	$/ha/Yr	NPP$_{gC/m^2/y}$
Marine	70.3	\	577	69
Open ocean	64.3	\	252	57
Coastal	6.0	\	4,052	162
Estuaries	0.3	\	22,832	810
Coral reefs	0.1	\	6,075	900
Terrestrial	29.7	100.0	804	324
Tropical forest	3.7	12.4	2,007	900
Temperate/boreal	5.7	19.3	302	500
Grass/rangelands	7.6	25.4	232	280
Wetlands	0.6	2.2	14,785	1,125
Tidal marsh	0.3	1.1	9,990	1,150
Swamps	0.3	1.1	19,580	1,100
Lakes/rivers	0.4	1.3	8,498	225
Desert	3.7	12.6	\	32
Tundra	1.4	4.8	\	65
Ice/rock	3.2	10.7	\	1.5
Cropland	2.7	9.1	92	290
Total	100.0	\	\	

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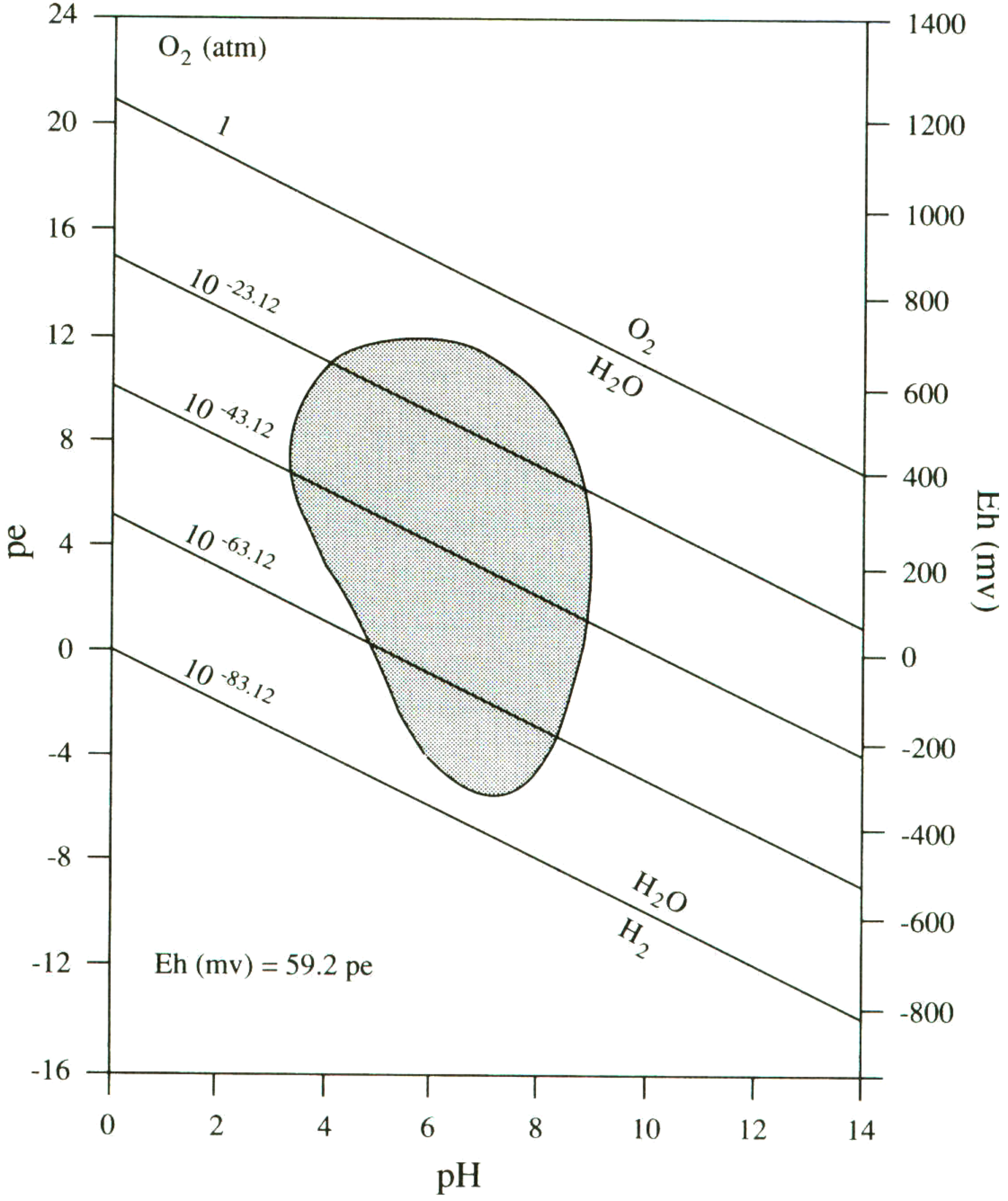
Redox potential is used to express the tendency of an environment to receive or supply electrons.

Aerobic (having free O_2) systems are said to have a high redox potential because O_2 is available as an electron acceptor. Hydrogen electrode is used as a standard reference for redox potential measurements.

Redox potential is expressed as the voltage required to prevent the follow of electrons using a standard hydrogen electrode as the reference.



O_2 (atm)
1
$10^{-23.12}$
$10^{-43.12}$
$10^{-63.12}$
$10^{-83.12}$
O_2
H_2O
H_2O
H_2
Eh (mv) = 59.2 pe
pe
24
20
16
12
8
4
0
-4
-8
-12
-16
Eh (mv)
1400
1200
1000
800
600
400
200
0
-200
-400
-600
-800
pH
0
2
4
6
8
10
12
14

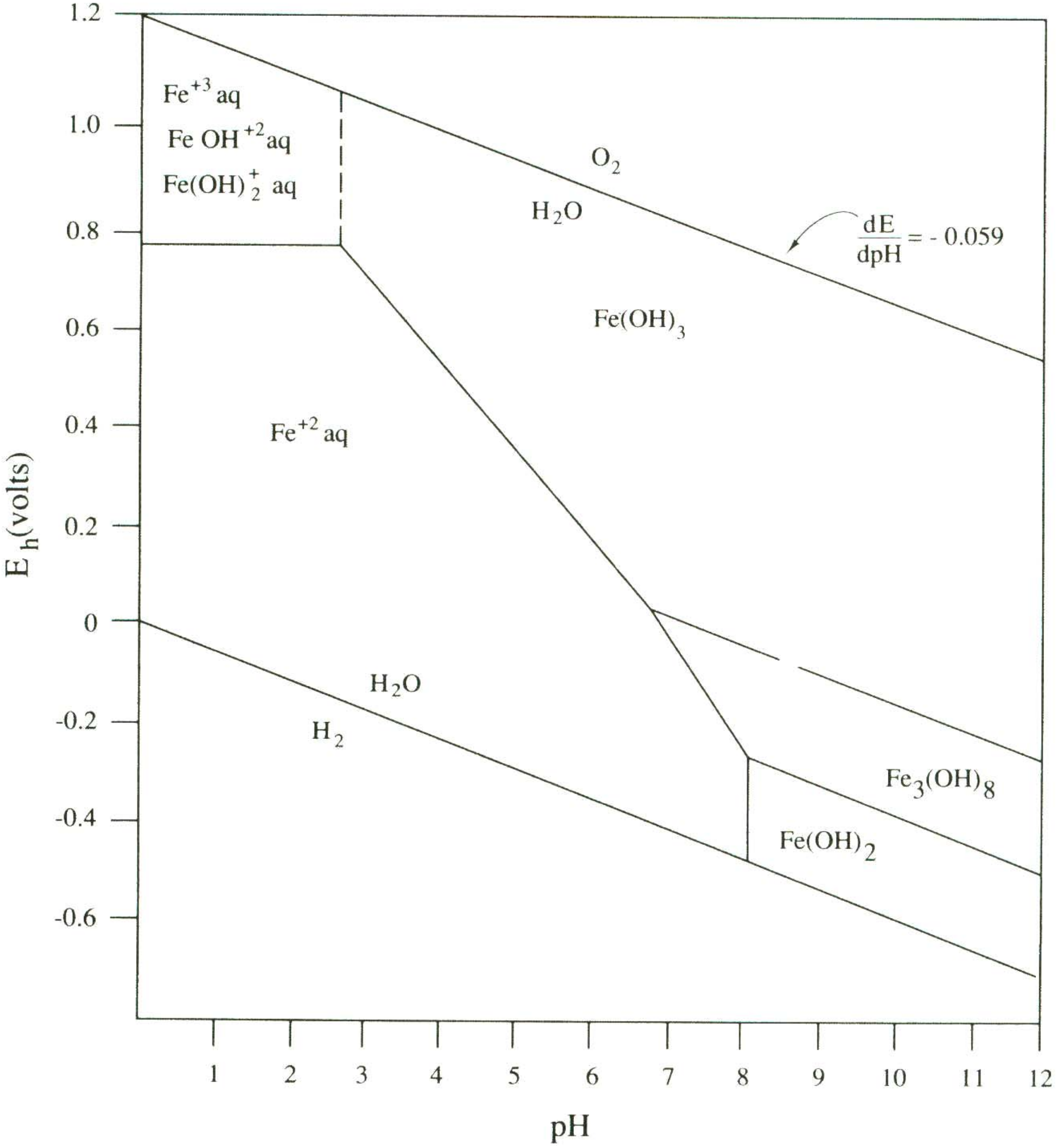


Figure 7.15 The stability of iron and iron hydroxides in soils relative to E_h and pH at 25°C. ll conditions refer to 1 m*M* Fe^{2+} solution. Modified from Ponnamperuma et al. (1967).

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).

Denitrification

Denitrification is a series of microbial processes starting from nitrate (NO_3^-) and ending with N_2:

$$NO_3^- \text{ ----> } NO_2^- \text{ ----> } (NO_x) \text{ ----> } N_2$$

Denitrifying microbes use NO_3^- or NO_2^- as electron acceptors.

Denitrification only occurs under anaerobic condition.

Denitrification needs reducing substrates as energy source.

The enzyme system of denitrifiers is totally inhibited by free oxygen, but not ammonia. **Denitrification is the process of returning reactive nitrogen back to the atmosphere.**

Acetylene can block the N_2O (nitrous oxide) reductase (Balderson et al.1976), so now this is used for measuring denitrification rate, since N_2 is very hard to measure due to the high background in the air. When adding 0.01 atm acetylene gas to the incubation atmosphere, the final product of denitrification is N_2O.

Sulfate Reduction:

$$SO_4^{2-} \text{--->} SO_3^{2-} \text{--->} S^0 \text{--->} H_2S$$

Sulfate reduction occurs at wide range of pH values, pressure, temperature and salinity. Sulfate reduction is inhibited by oxygen, nitrate, ferric (Fe^{3+}) ions. H_2S is very toxic to aerobes and plant roots.

Sulfate reduction is carried out by bacteria using organic substrates as reducing agents and sulfate as the electron acceptor.

Sulfur oxidation is a series of reverse reaction of the above equations when there is a switch of Redox due to a change of water levels.

Methanogenesis:

$$HCO_3^- + H^+ + 4H_2 \text{ ----> } CH_4 + 3H_2O$$

Methanogenic bacteria require strictly anaerobic condition and redox potentials between -350 and -450 mV, or highly reducing environment.

Methanotrophy:

$$CH_4 + 2O_2 \text{ -----> } CO_2 + 2H_2O$$

All methanotrophic bacteria require free oxygen for them to effectively oxidize methane.

Based on the two processes above, natural methane input to the atmosphere is a result of the net balance between total methanogenic activities and total methanotrophic activities.

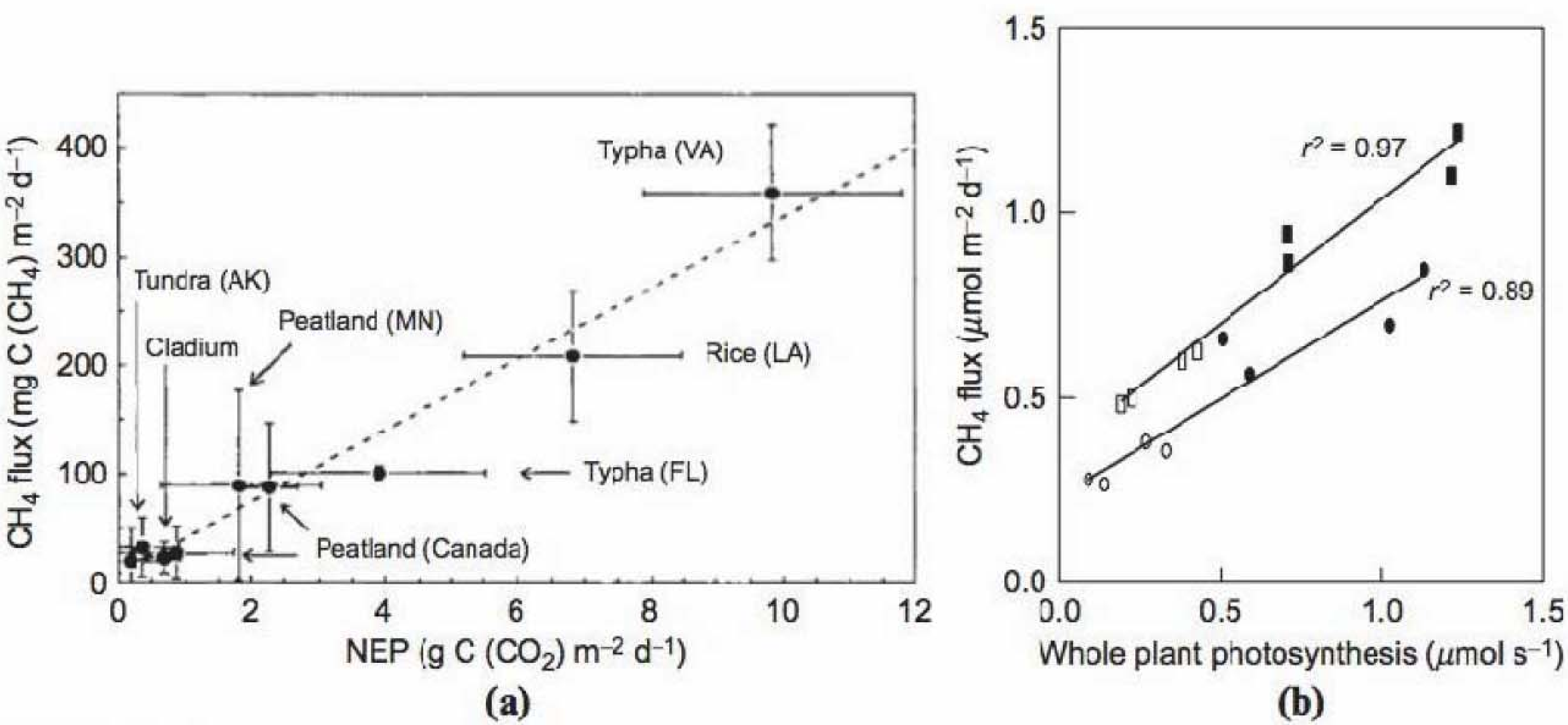


FIGURE 7.17 The relationship between wetland CH_4 emissions and various measures of primary productivity. (a) Emissions versus NEP in North American ecosystems ranging from the subtropics to the subarctic; here the slope is 0.033 g methane C/g CO_2. (b) Emissions versus whole-plant net photosynthesis 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.*

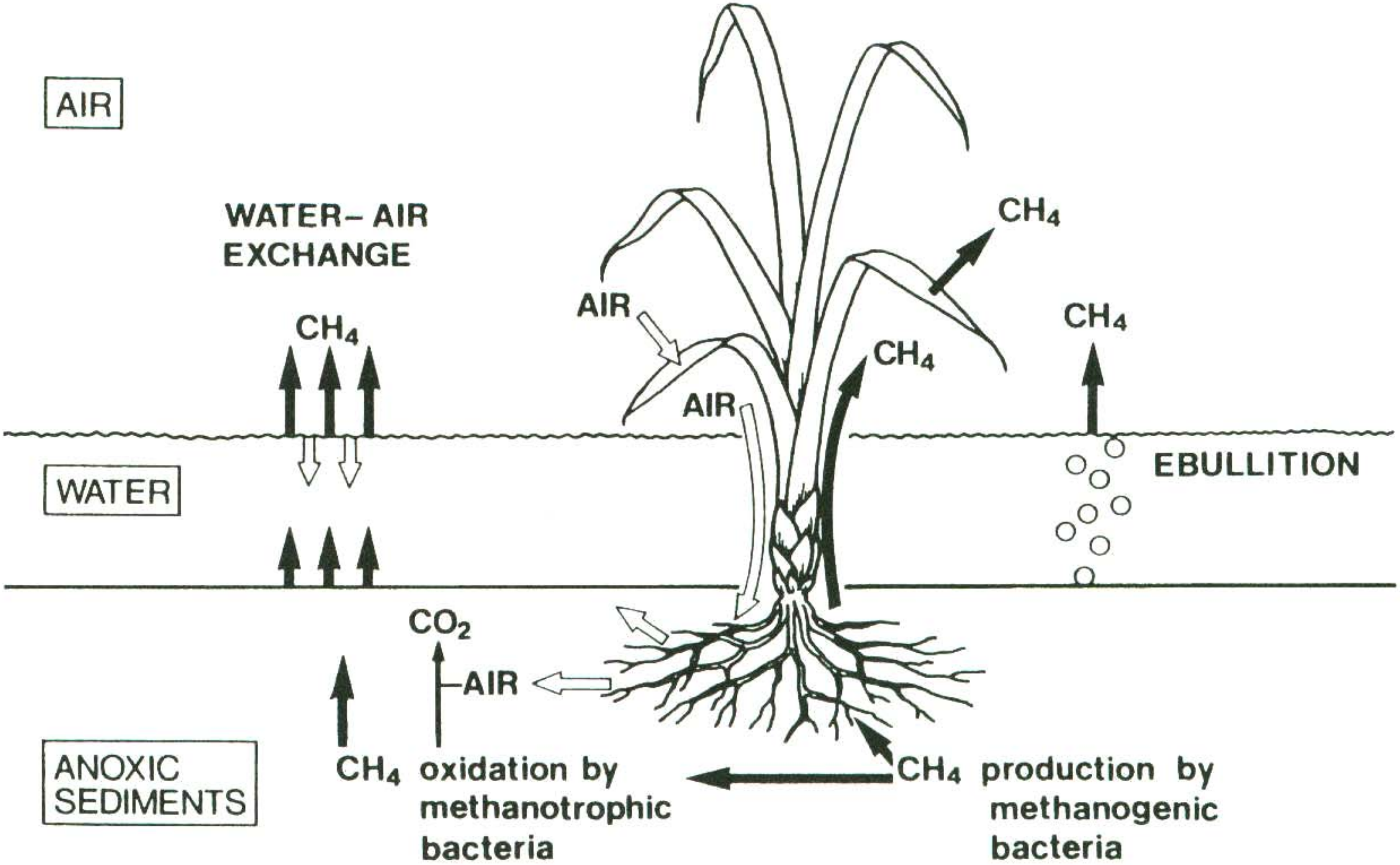


Figure 7.18 Processes of methane production, oxidation, and escape from wetland soils. From Schütz et al. (1991).

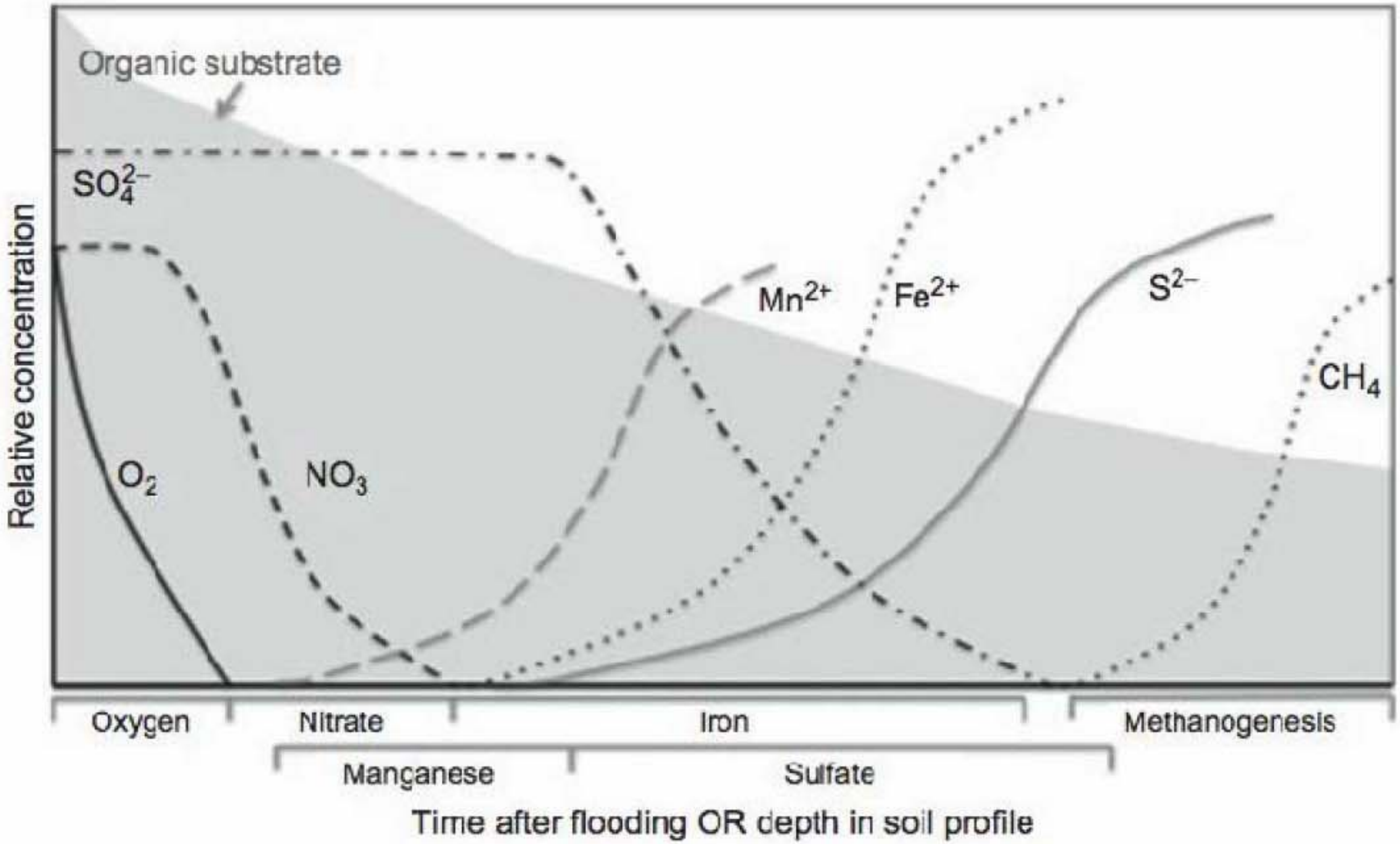


FIGURE 7.10 The concentrations of reactants and products of terminal decomposition pathways are shown for a wetland sediment over time following flooding. Rotating the figure 90° to the right shows the pattern of substrate concentrations (and the order of metabolic pathways) with depth in a soil profile.

Biomethylation

Microbial methylation of metals in the aquatic environment is an important process in biogeochemical cycling of metal ions, especially mercury:

$$Hg^{2+} \rightarrow HgCH_3$$

Methanogenic bacteria participate in methylation process. Methylmercury bioaccumulates in aquatic organisms, which transfers mercury in the food chain. For methylation to occur, anaerobic condition and low pH are required.

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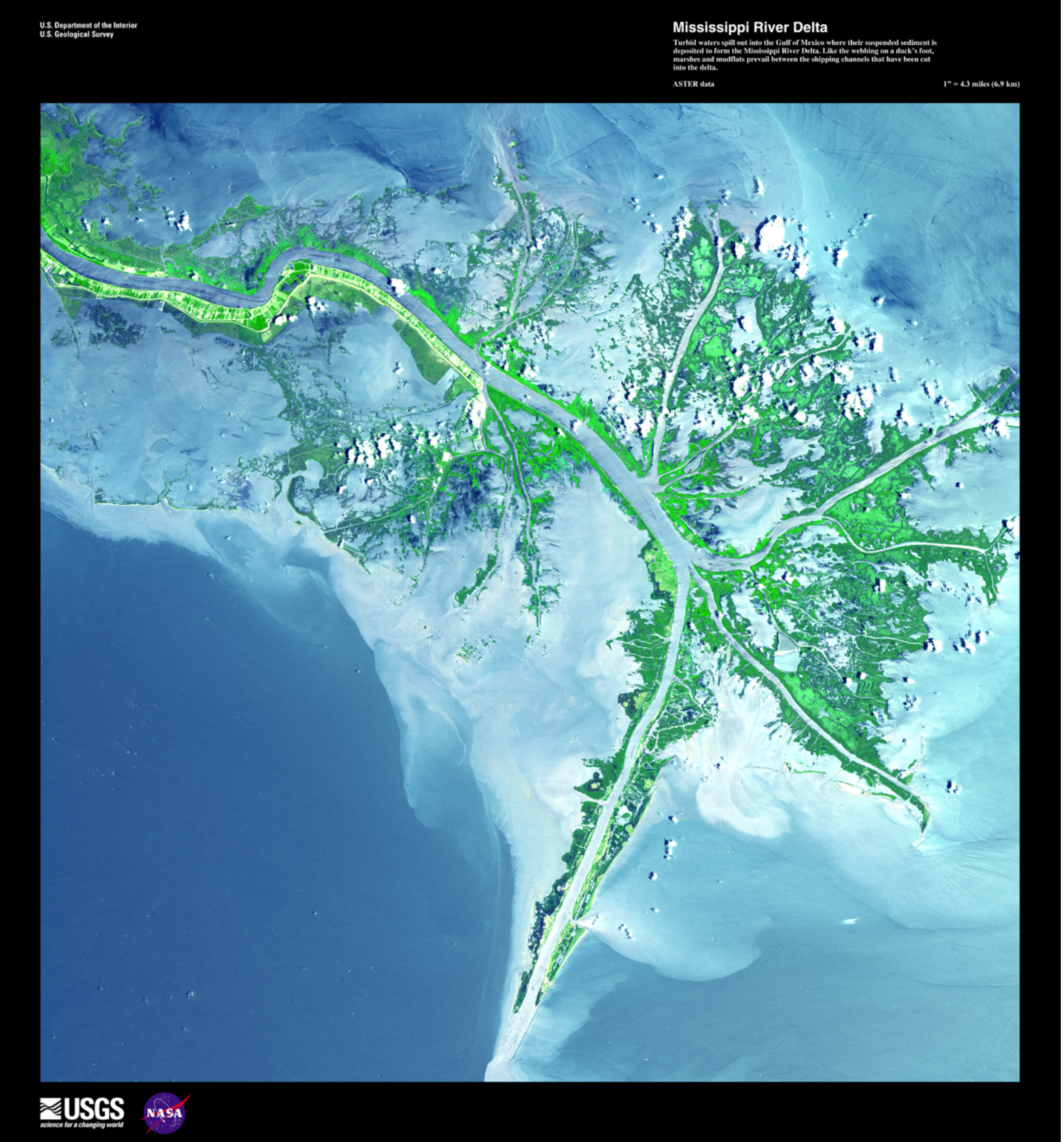
- **Sources of nutrients**



U.S. Department of the Interior
U.S. Geological Survey

Mississippi River Delta

Turbid waters spill out into the Gulf of Mexico where their suspended sediment is deposited to form the Mississippi River Delta. Like the webbing on a duck's foot, marshes and mudflats prevail between the shipping channels that have been cut into the delta.

ASTER data

1" = 4.3 miles (6.9 km)

Mississippi River Delta
Image taken 5/24/2001 by ASTER on Landsat-7.

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U.S. Department of the Interior
U.S. Geological Survey

Delta Region, Netherlands

Along the southern coast of the Netherlands, sediment-laden rivers have created a massive delta of islands and waterways in the gaps between coastal dunes. After unusually severe spring tides devastated this region in 1953, the Dutch built an elaborate system of dikes, canals, dams, bridges, and locks to hold back the North Sea.

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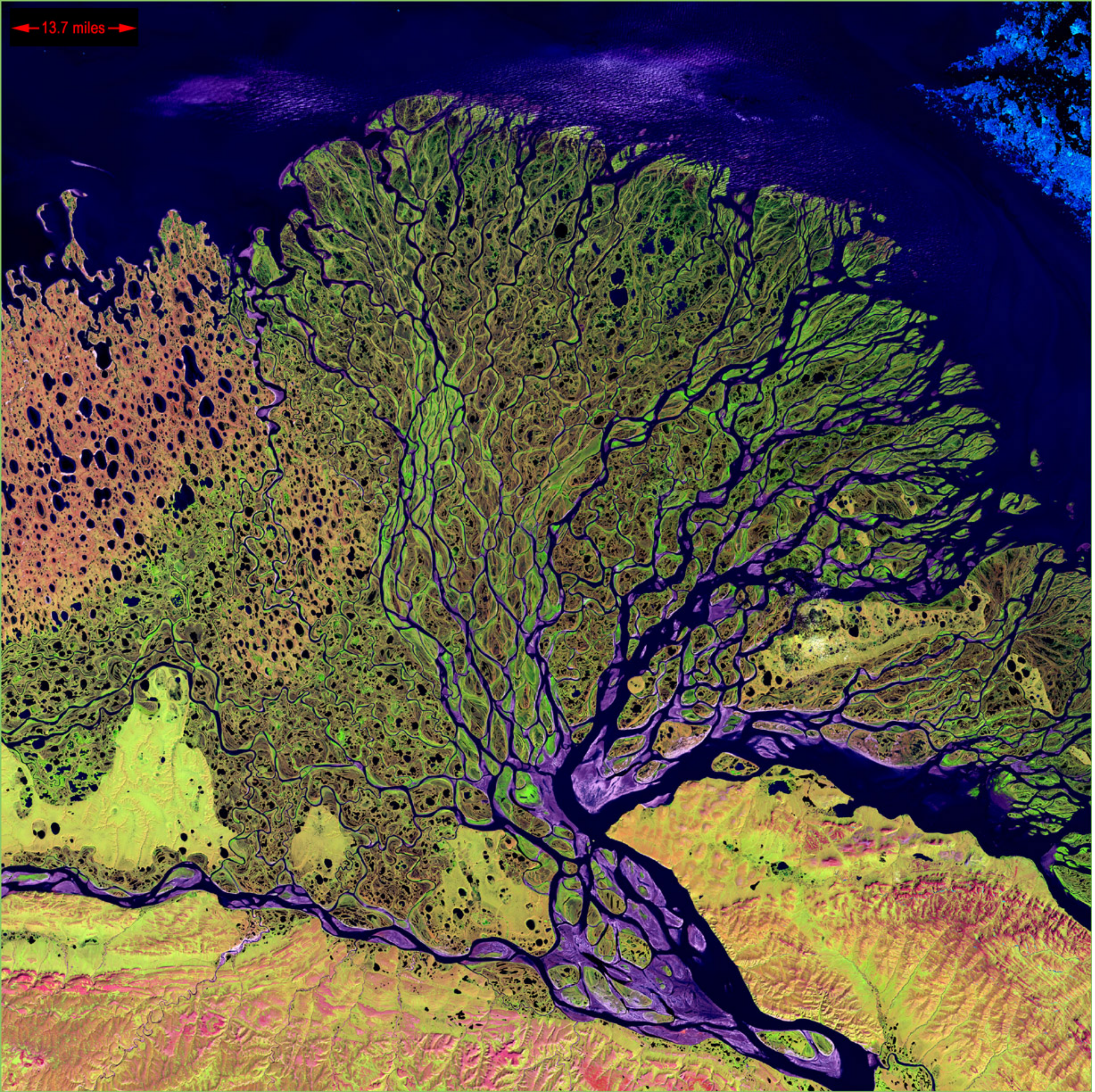


Lena Delta
Image taken 7/27/2000

The Lena River, some 2,800 miles (4,400 km) long, is one of the largest rivers in the world. The Lena Delta Reserve is the most extensive protected wilderness area in Russia. It is an important refuge and breeding grounds for many species of Siberian wildlife.

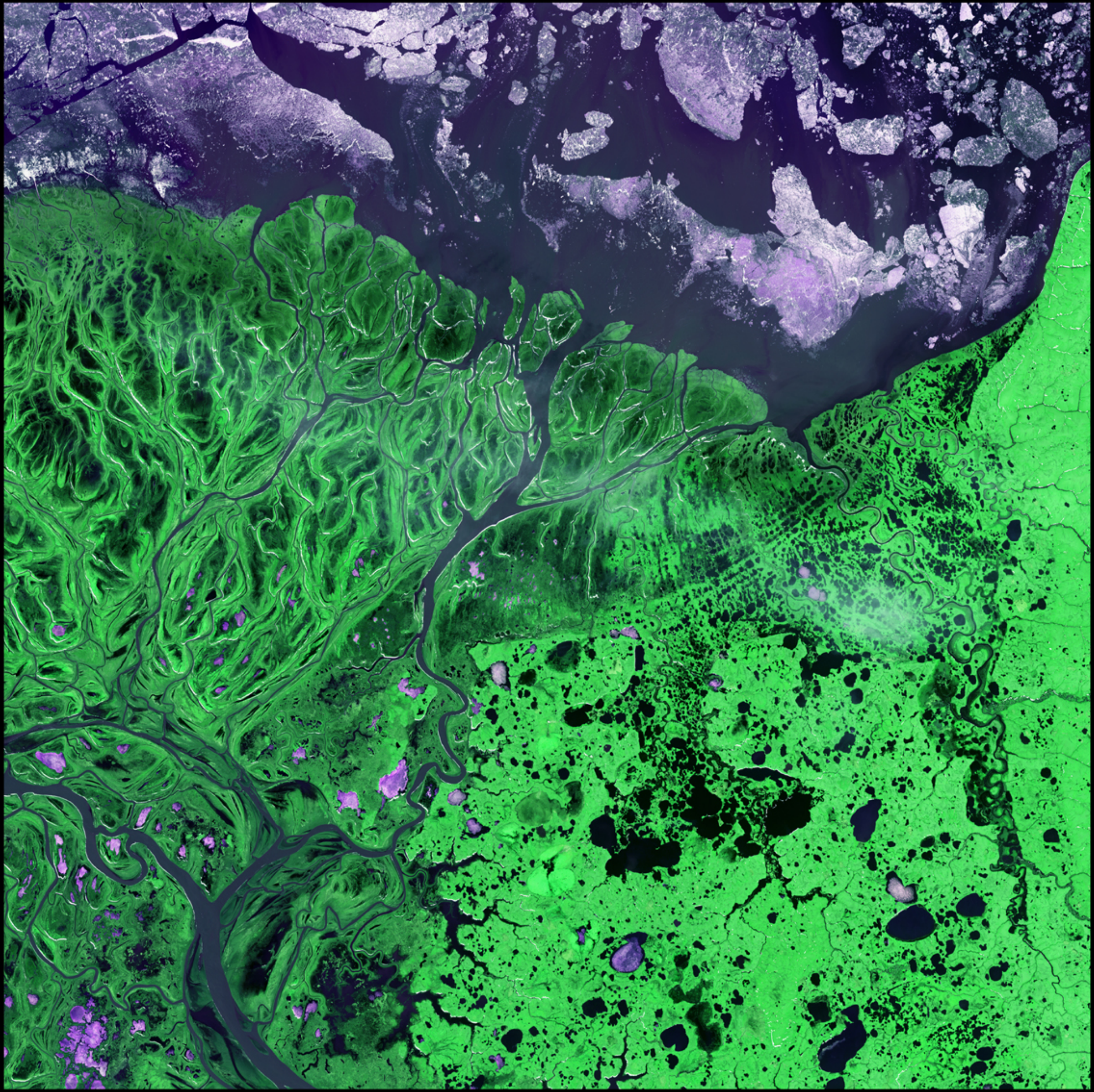
U.S. Department of the Interior
U.S. Geological Survey

The Yukon Delta

An intricate maze of small lakes and waterways define the Yukon Delta at the confluence of Alaska's Yukon and Kuskokwim Rivers with the frigid Bering Sea. Wildlife abounds on the delta and offshore where sheets of sea ice form during the coldest months of the year.

ASTER data

1" = 4.3 miles (6.9 km)



USGS science for a changing world

The Yukon Delta
Image taken 5/26/2002

An intricate maze of small lakes and waterways define the Yukon Delta at the confluence of Alaska's Ukon and Kuskokwim Rivers with the frigid Bering Sea. Wildlife abounds on the delta and offshore where sheets of sea ice form during the coldest months of the year.

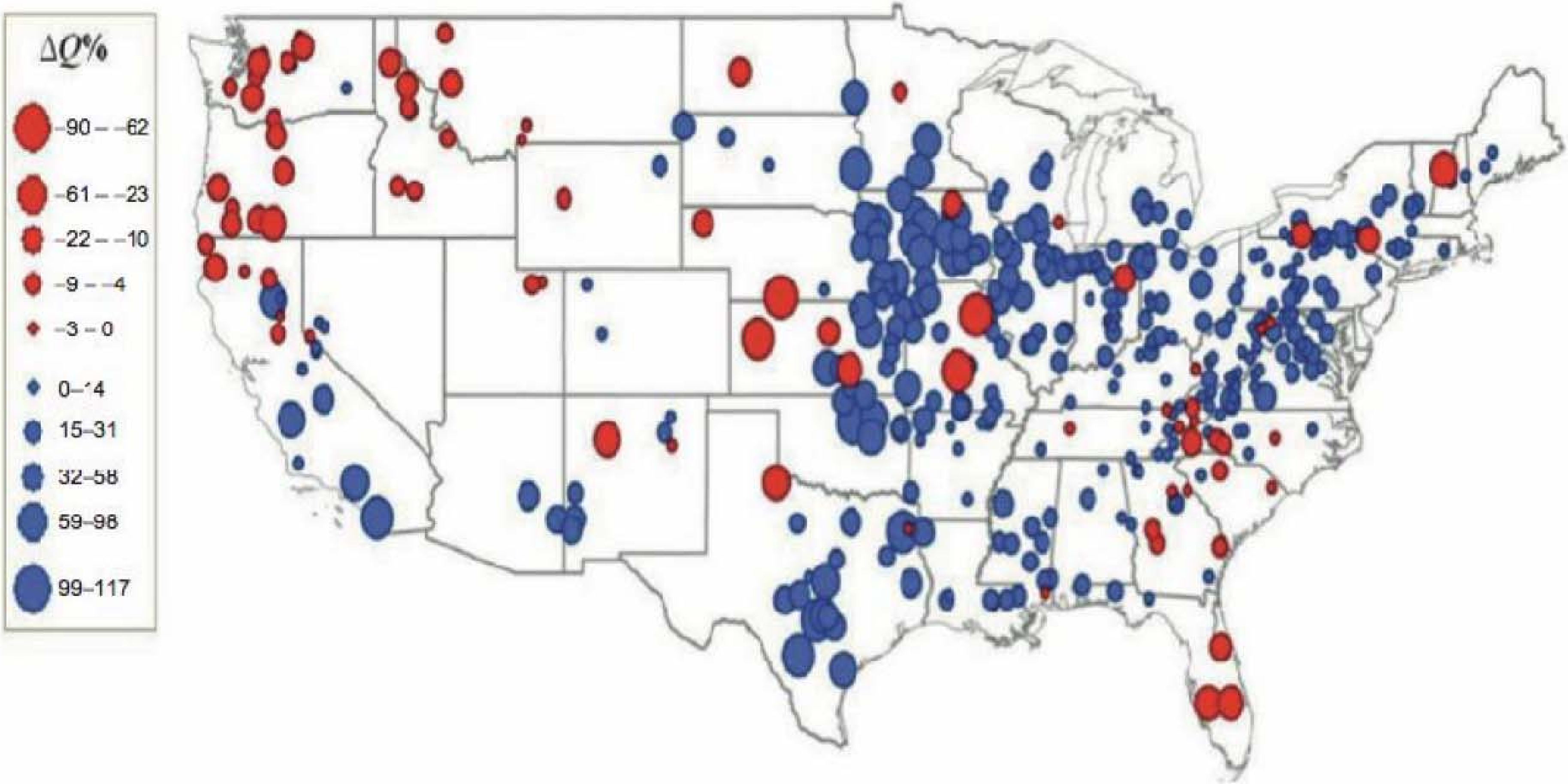


FIGURE 8.40 Spatial distribution of the change in stream flow (Q) recorded for 413 U.S. watersheds between the periods 1948–1970 and 1971–2003. *Source: From Wang and Hejazi 2011. Used with permission of the American Geophysical Union.*

The productivity of the biosphere

(From Whittaker and Likens, 1973)

Biome	Area	%globe	% Land	NPP g C/m^2 /y
Marine	36,302	70.3	\	69
Open ocean	33,200	64.3	\	57
Coastal	3,102	6.0	\	162
Estuaries	180	0.3	\	810
Coral reefs	62	0.1	\	900
Terrestrial	15,323	29.7	100	324
Tropical forest	1,900	3.7	12.4	900
Temperate/boreal	2,955	5.7	19.3	500
Grass/rangelands	3,898	7.6	25.4	280
Wetlands	330	0.6	2.2	1,125
Lakes/rivers	200	0.4	1.3	225
Desert	1,925	3.7	12.6	32
Tundra	743	1.4	4.8	65
Ice/rock	1,640	3.2	10.7	1.5
Cropland	1,400	2.7	9.1	290
Total	51,625	100.0		

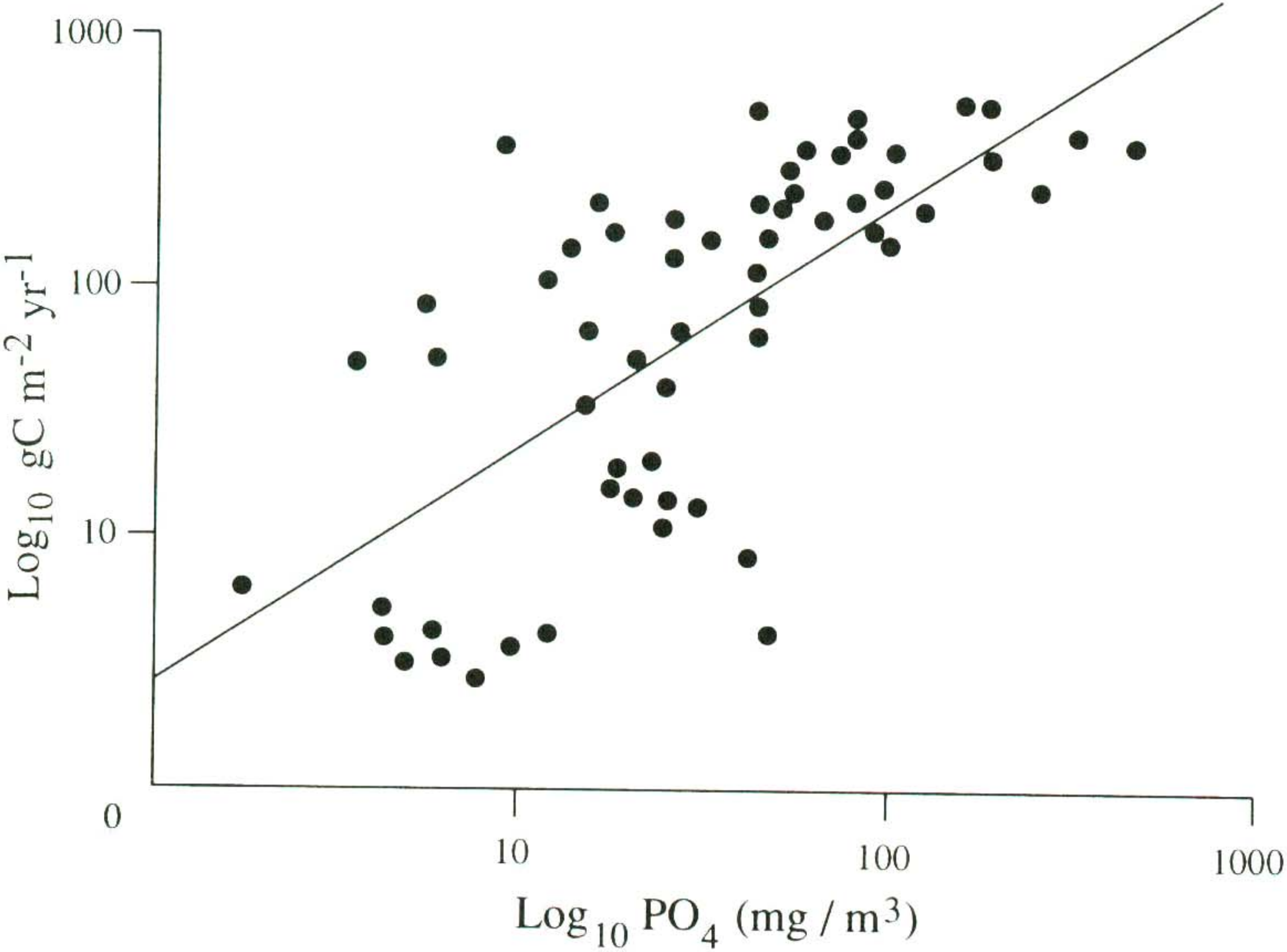
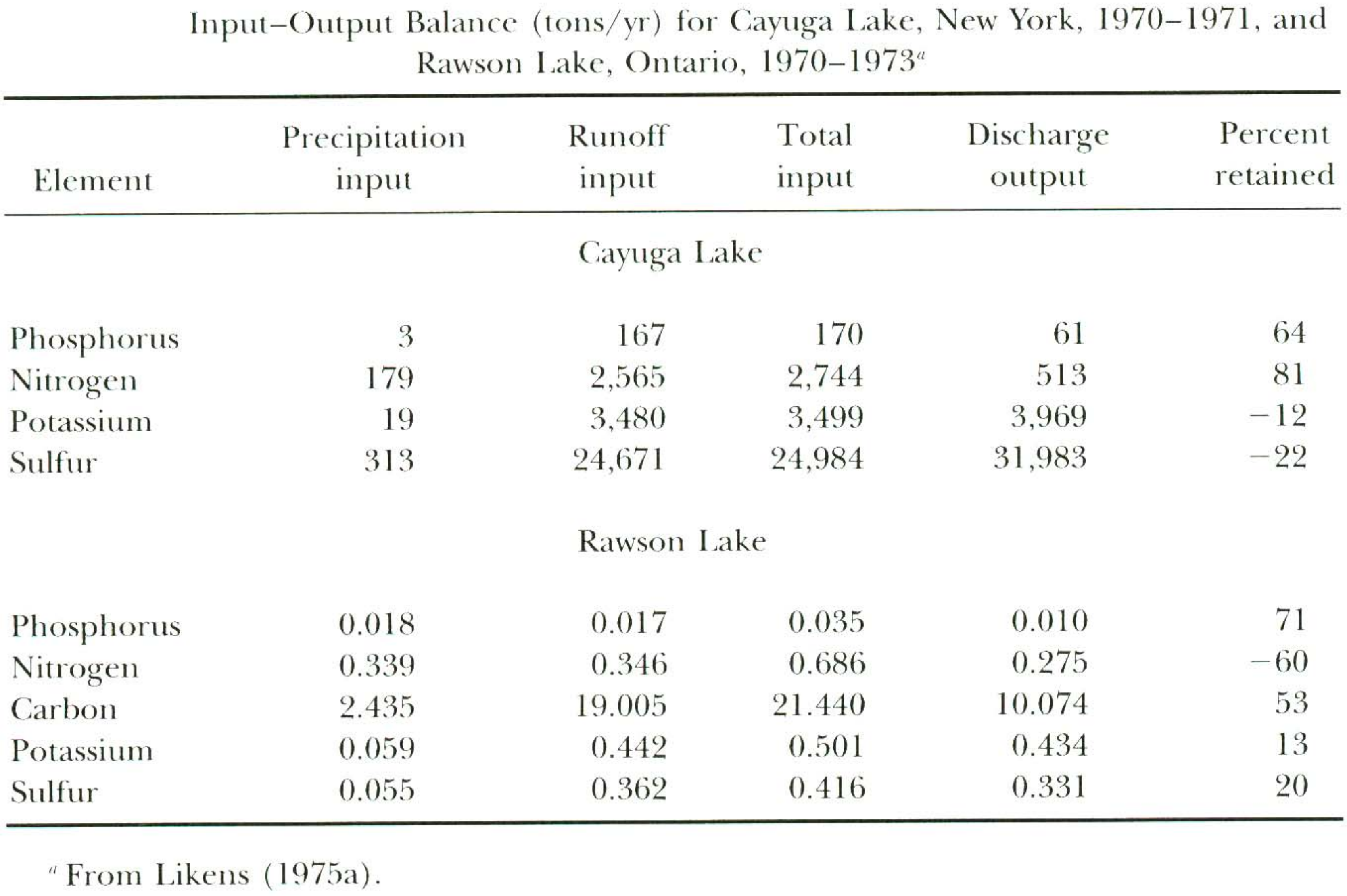


Figure 8.13 Relationship between net primary production and the phosphorus concentration of lakes of the world. From Schindler (1978).

Sources of Nutrients



Input–Output Balance (tons/yr) for Cayuga Lake, New York, 1970–1971, and Rawson Lake, Ontario, 1970–1973[a]

Element	Precipitation input	Runoff input	Total input	Discharge output	Percent retained
			Cayuga Lake		
Phosphorus	3	167	170	61	64
Nitrogen	179	2,565	2,744	513	81
Potassium	19	3,480	3,499	3,969	−12
Sulfur	313	24,671	24,984	31,983	−22
			Rawson Lake		
Phosphorus	0.018	0.017	0.035	0.010	71
Nitrogen	0.339	0.346	0.686	0.275	−60
Carbon	2.435	19.005	21.440	10.074	53
Potassium	0.059	0.442	0.501	0.434	13
Sulfur	0.055	0.362	0.416	0.331	20

[a] From Likens (1975a).

Sources of Nitrogen and Phosphorus as Percentages of the Total Annual Input to Lake Ecosystems[a]

	Precipitation		Runoff	
	N	P	N	P
Oligotrophic lakes	56	50	44	50
Eutrophic lakes	12	7	88	93

[a] From Likens (1975a).

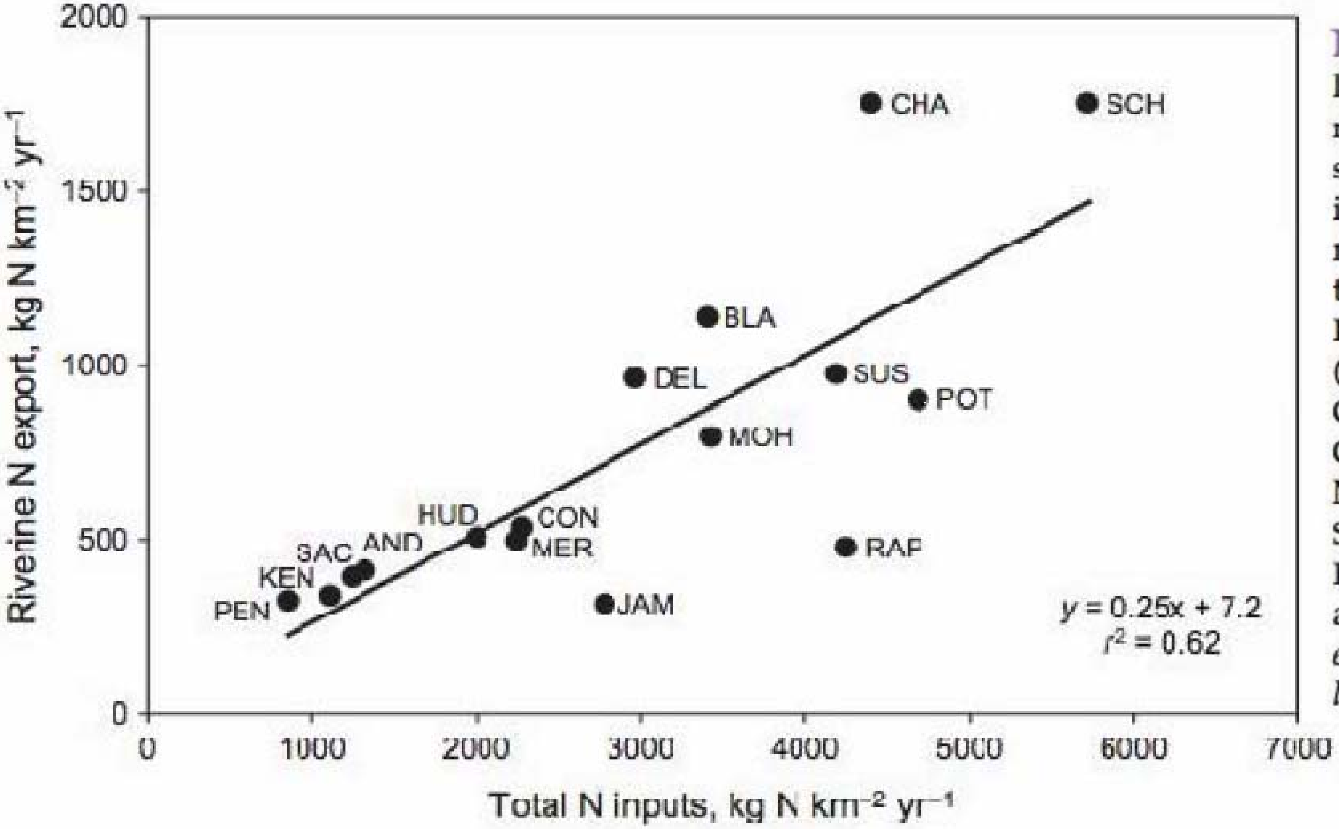


FIGURE 8.5 In an analysis of 16 large rivers in the northeastern U.S. nitrogen exports in streamflow were strongly related to the total new inputs of nitrogen to each catchment measured. From north to south, the catchments are: Penobscot (PEN), Kennebec (KEN), Androscoggin (AND), Saco (SAC), Merrimack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

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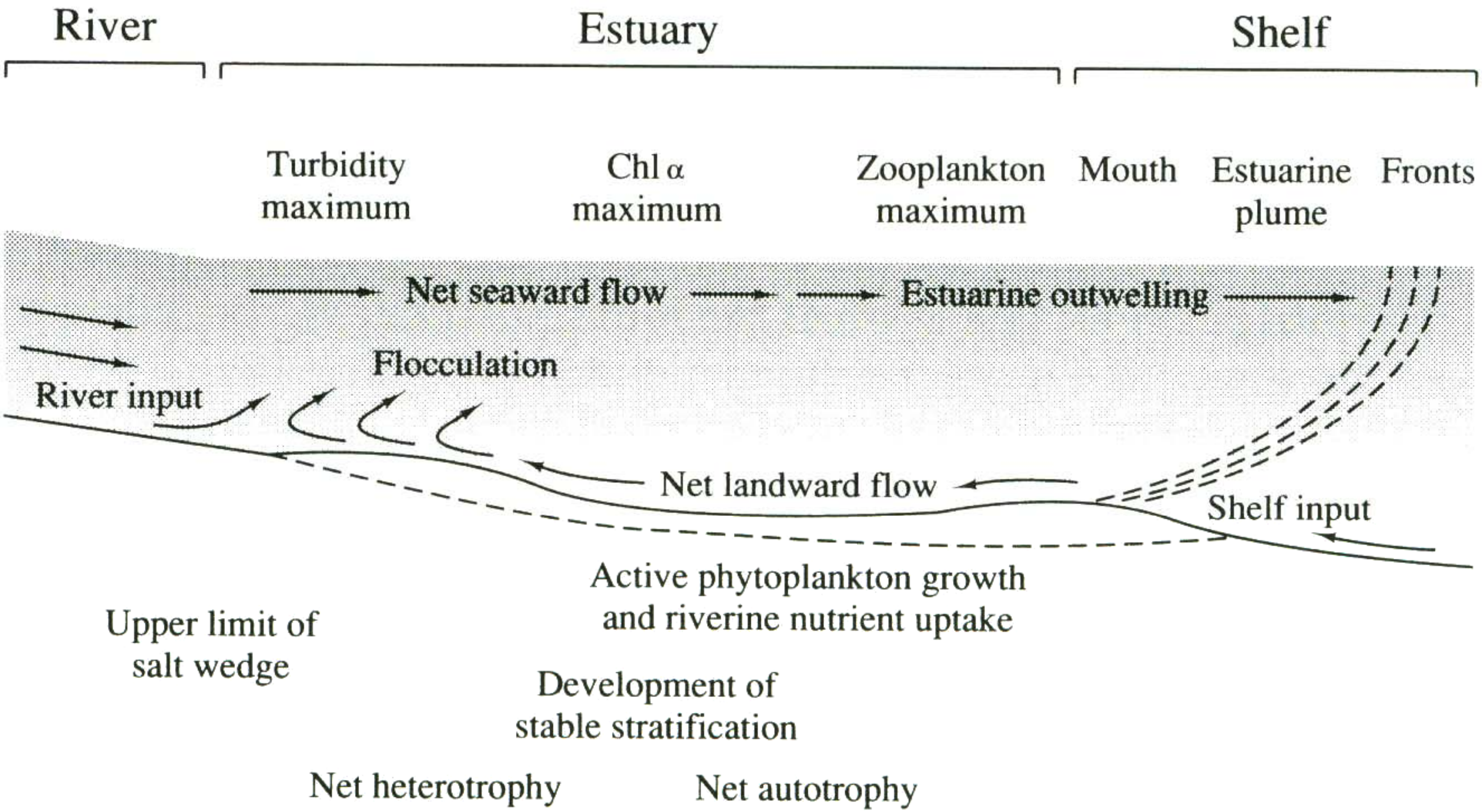

Conceptual model of the chemical and biological structure in estuaries. As the suspended load settles from the entering river waters and nutrients are made available, phytoplankton production increases, fueling an increase in zooplankton production and higher trophic levels. From Fisher et al. (1988).

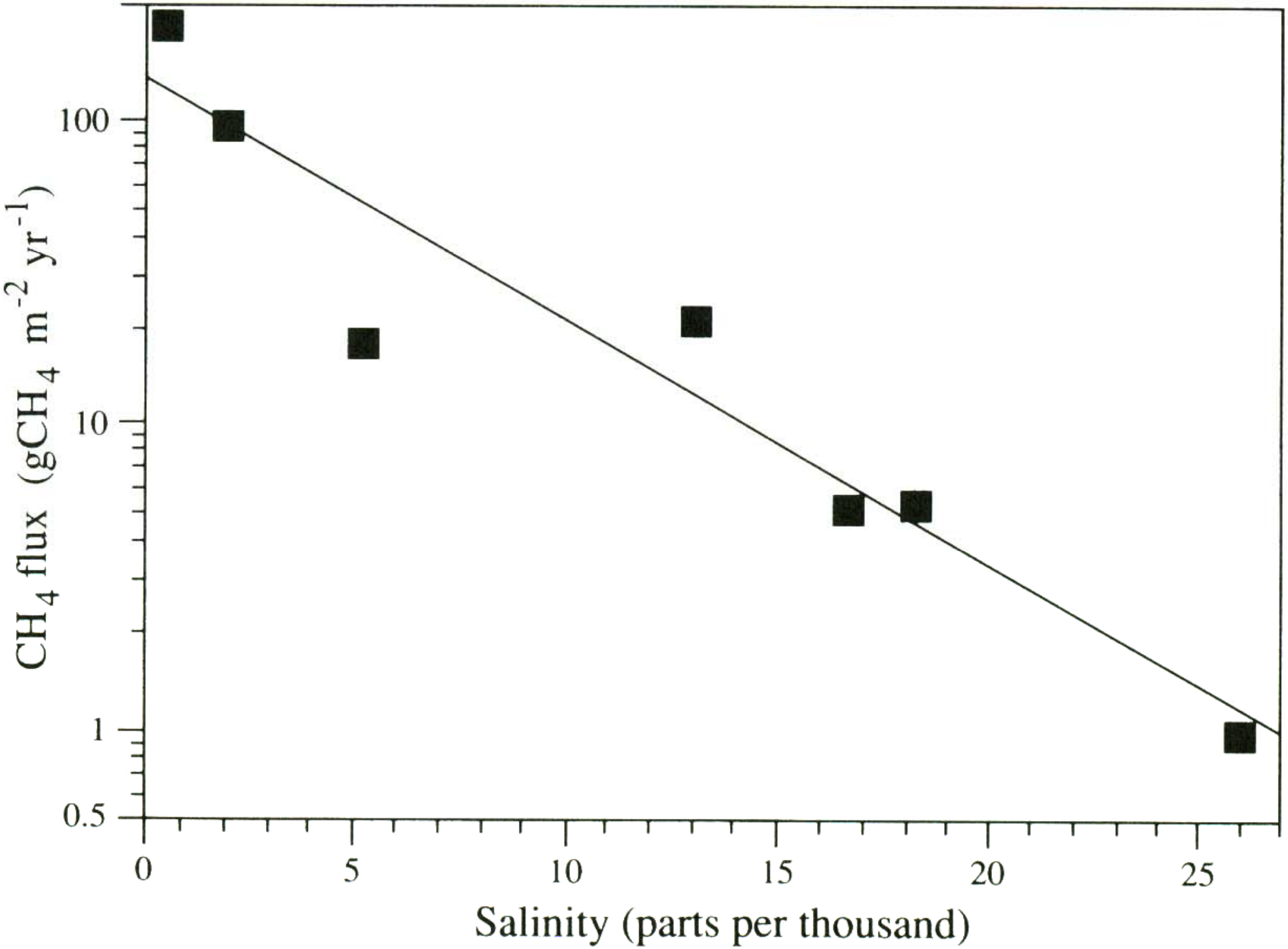

Figure 8.37 Annual methane lost from salt marsh soils as a function of salinity. From Bartlet et al. (1987).

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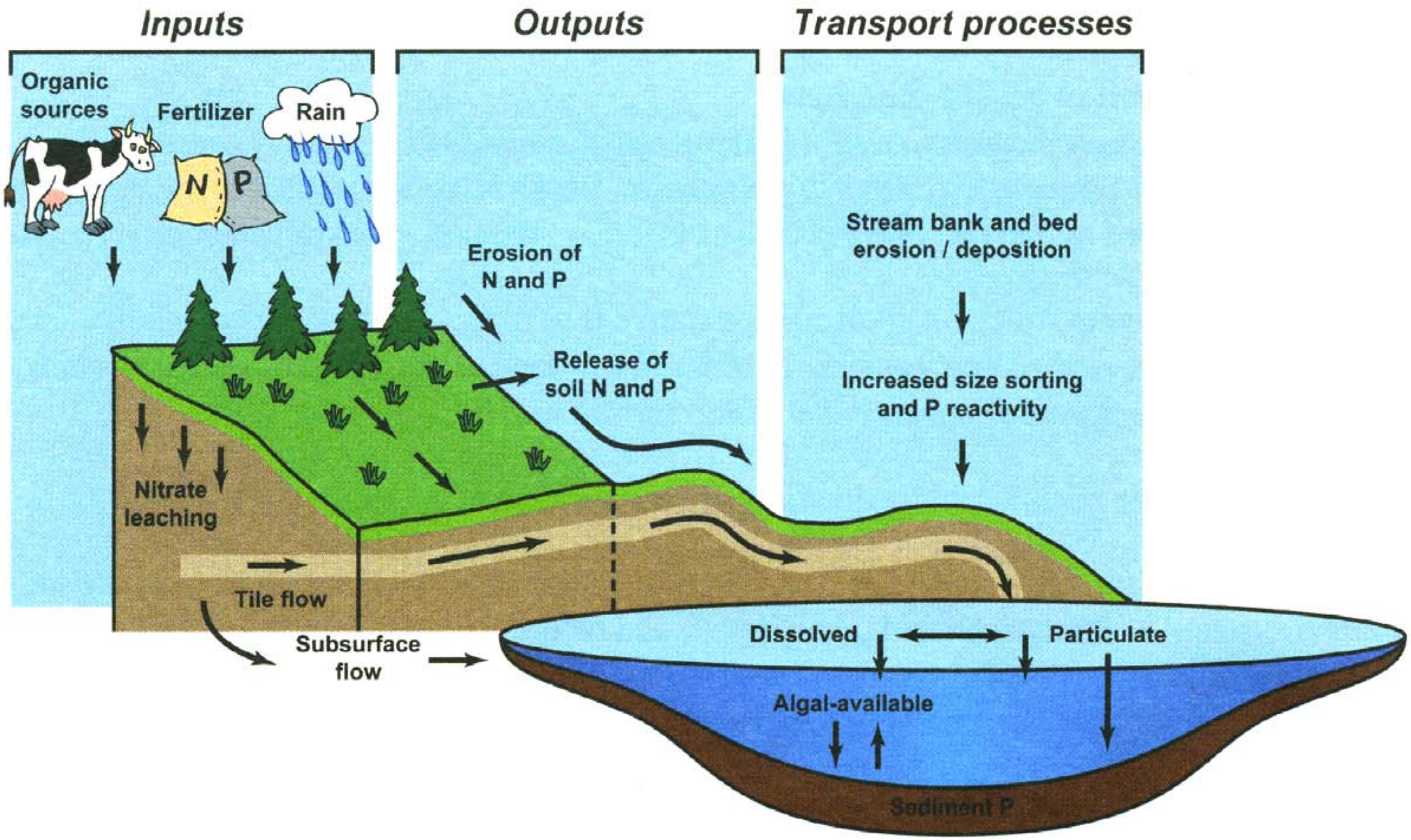
The issue of eutrophication in aquatic ecosystems



Artwork by W. Feeny

Figure 1 - Nutrients in manure and fertilizers are transported to lakes, rivers, and oceans. Excessive nutrient inputs result in degradation of water quality, causing the disruption of aquatic ecosystems.

From Issues in Ecology #3

Based on our review of the scientific literature, we are certain that:

1. Eutrophication caused by over-enrichment with P and N is a **widespread** problem in rivers, lakes, estuaries, and coastal oceans.
2. Nonpoint pollution is a major source of P and N to surface waters of the United States. The major sources of nonpoint pollution are **agriculture and urban activity**, including industry and transportation.
3. In the U.S. and many other nations, inputs of P and N to agriculture in the form of **fertilizers** exceed outputs of those nutrients in the form of crops.
4. High densities of livestock have created situations in which **manure** production exceeds the needs of crops to which the manure is applied. The density of animals on the land is directly related to nutrient flows to aquatic ecosystems.
5. **Excess fertilization and manure production cause a P surplus**, which accumulates in soil. Some of this surplus is transported in soil runoff to aquatic ecosystems.
6. **Excess fertilization and manure production create a N surplus** on agricultural lands. Surplus N is mobile in many soils, and much leaches into surface waters or percolates into groundwater. Surplus N can also volatilize to the atmosphere and be redeposited far downwind as acid rain or dry pollutants that may eventually reach distant aquatic ecosystems.

TABLE 8.2 Lake Classification by Trophic Status

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

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

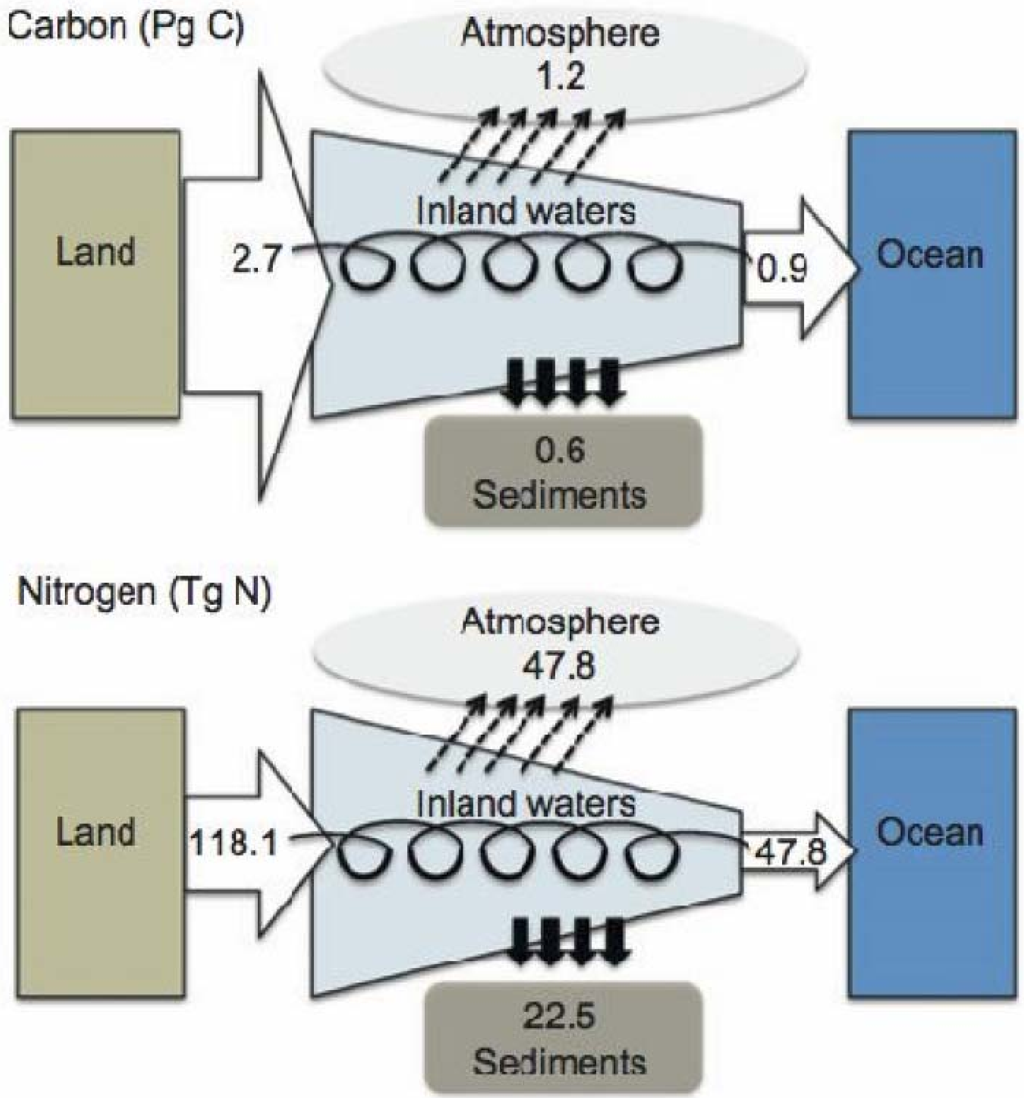
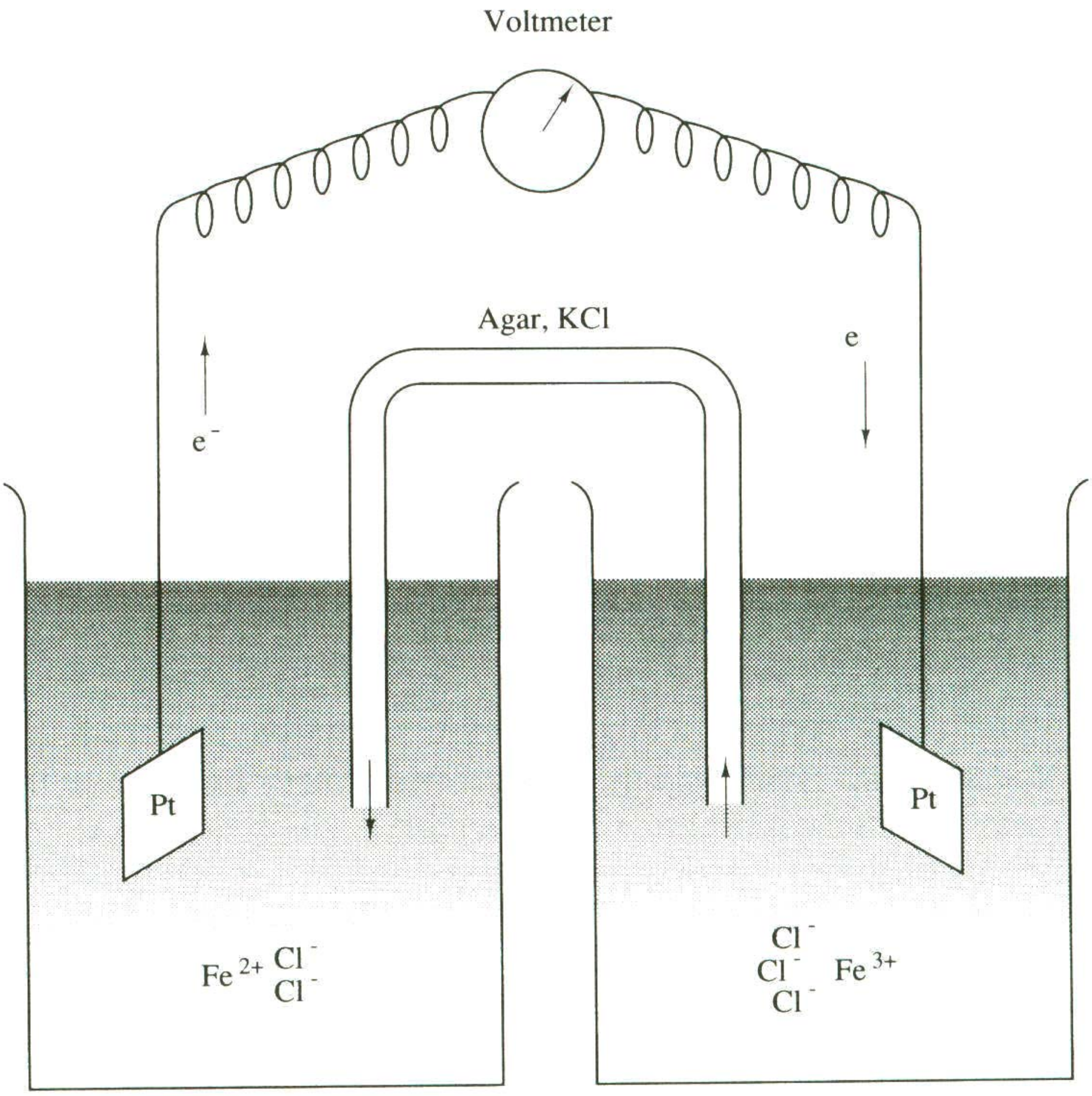


FIGURE 8.42 The cumulative effect of inland waters on global C and N cycling. Note that rivers and lakes deliver as much C and N to the atmosphere as to the ocean, indicating that biological processing of these elements within freshwaters is as important as their physical transport. *Source: Numbers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



$Fe^{2+} - e^- = Fe^{3+}$

$Fe^{3+} - e^- = Fe^{2+}$