Soil is 3-phase system:

SOLIDS, LIQUIDS, GASES

SOIL AIR

Not identical to atmospheric air because of biological respiration:

$$C_6H_{12}O_6 + 6O_2 \text{ ---> } 6CO_2 + 6H_2O$$

1. **CONSUMES OXYGEN (O_2)**
2. **PRODUCES CARBON DIOXIDE (CO_2)**

Composition of Atmosphere & Aerated Soil

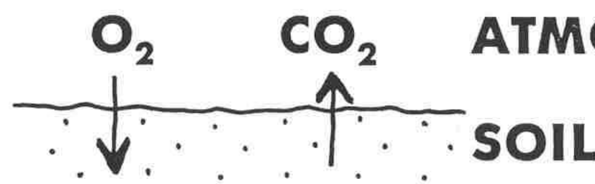
Gas	Soil air (%)	Atmosphere
N_2	79.2	79.0
O_2	20.6	20.9
CO_2	0.25	0.035

Oxygen is necessary for many organisms to live.

Soil air is almost always saturated with water vapor (R.H. = 99-100%)

<u>AIR MOVEMENT</u> - 2 mechanisms:

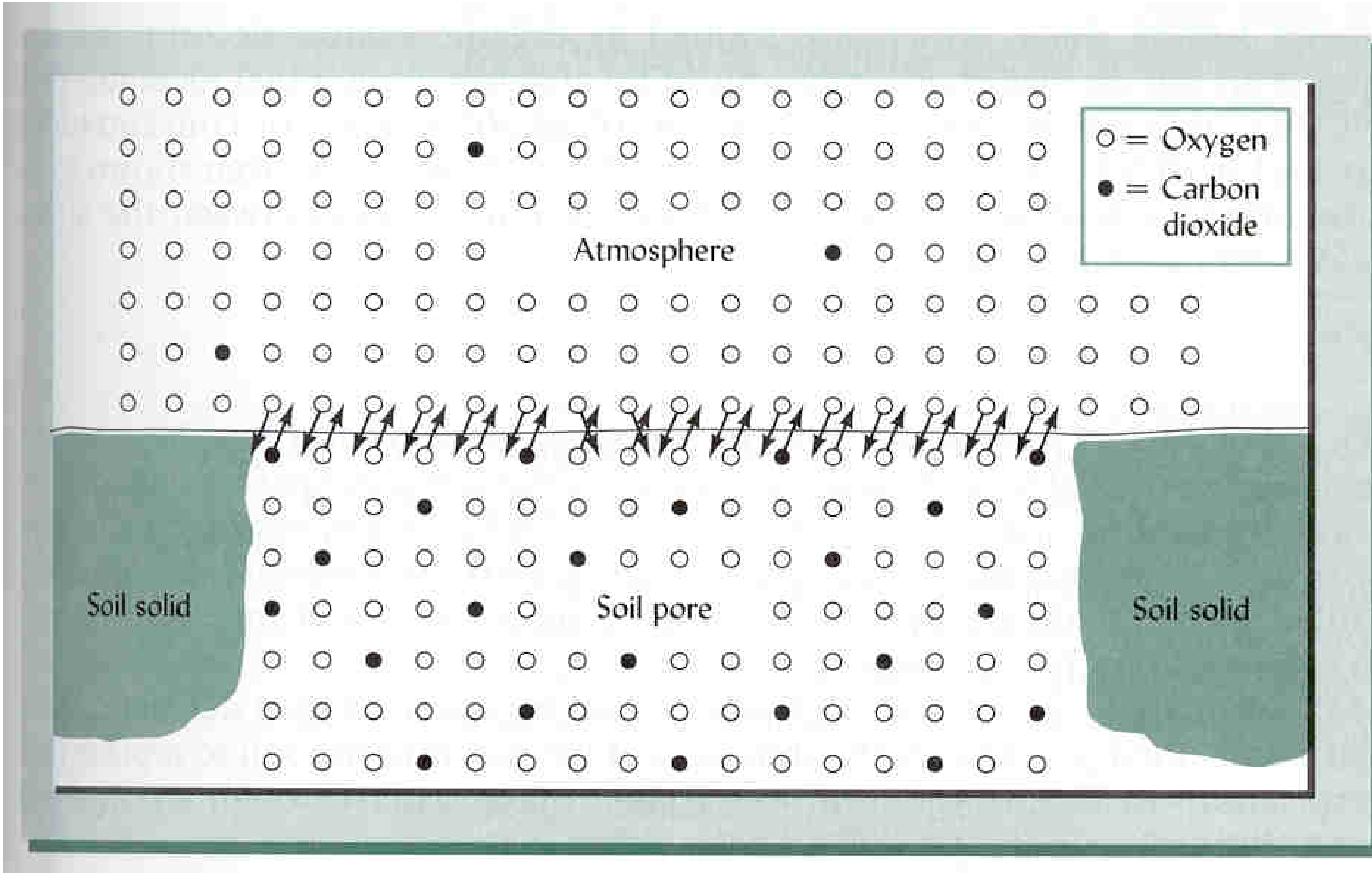
<u>DIFFUSION</u> - molecules move from zone of high concentration to low



Rate of Diffusion depends on:

1. Soil water content
2. Size & number of pores
3. Pore continuity
4. Temperature

<u>MASS FLOW</u> - movement in response to change in pressure in soil <u>or</u> atmosphere
- less important than diffusion


○ = Oxygen
● = Carbon dioxide
Atmosphere
Soil solid
Soil pore
Soil solid

Saturated soils quickly become O_2-deficient (Why?)

Plant roots & aerobic microbes die

AIR-WATER RELATIONSHIPS

Total air volume in soil is THE difference between total pore space and volumetric water content.

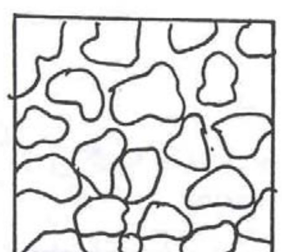
$$P_A = P_T - O$$

P_A = fraction of total soil volume occupied by air

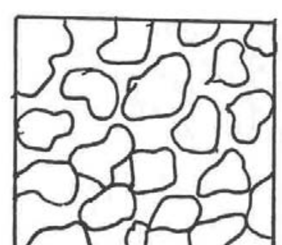
P_T = total soil volume composed of pores (porosity)

θ = fraction of total soil volume occupied by water

$\theta \approx 0$
$P_A = .5$
$P_T = .5$

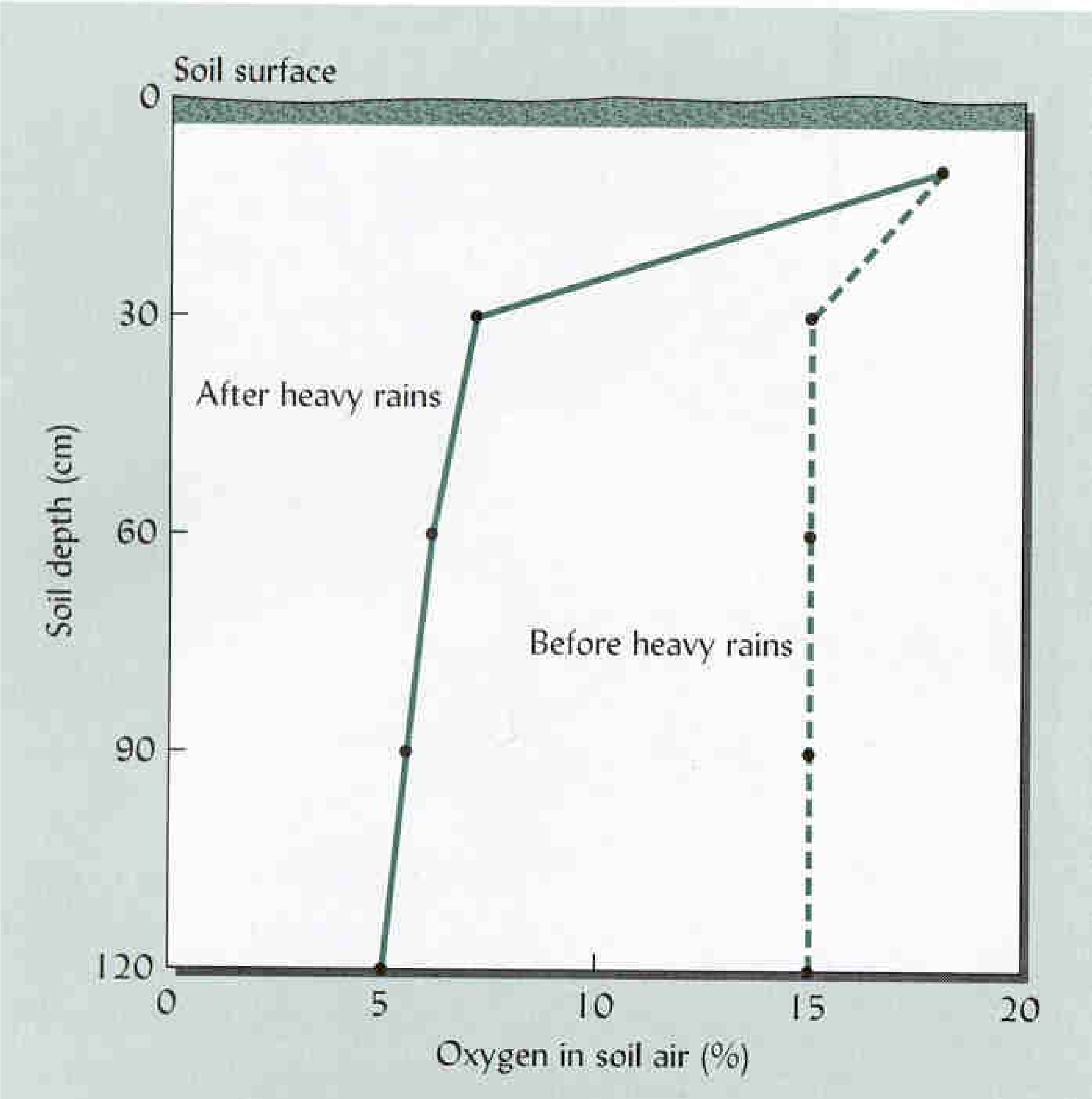


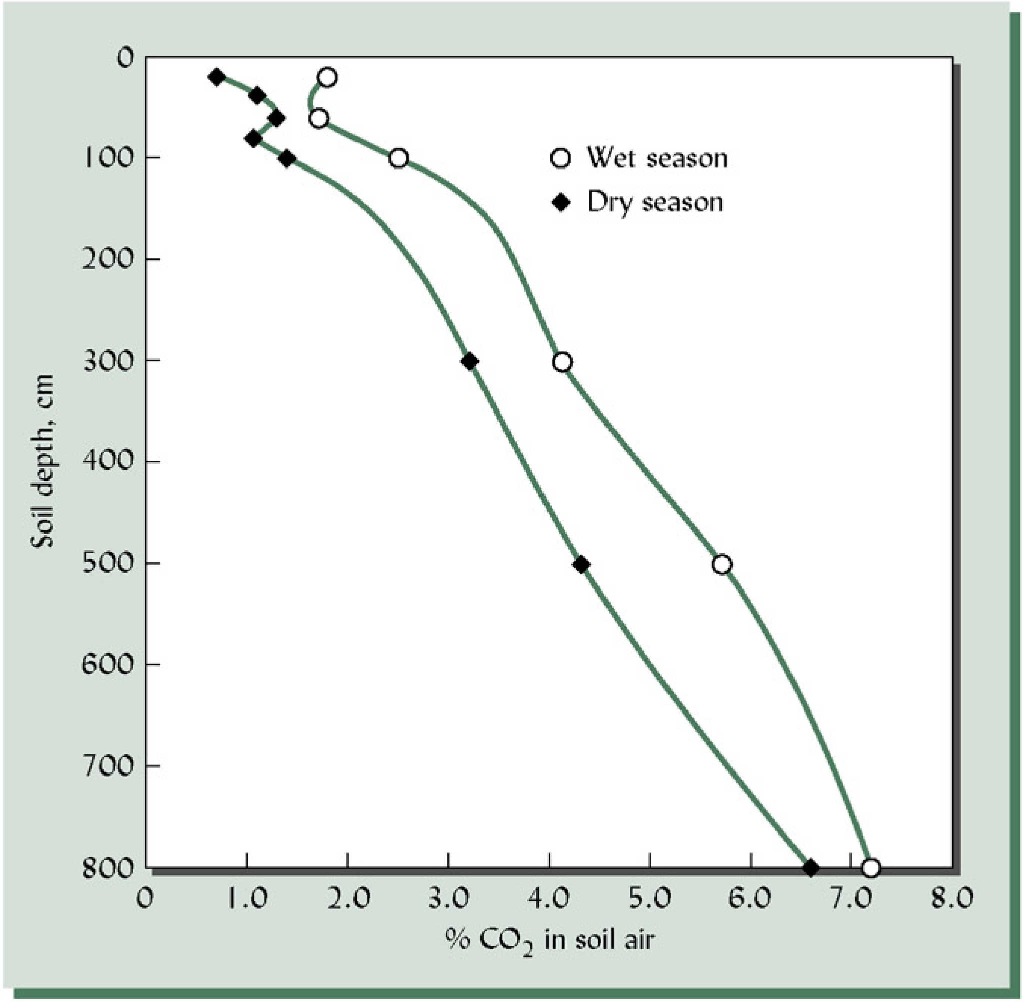
dry



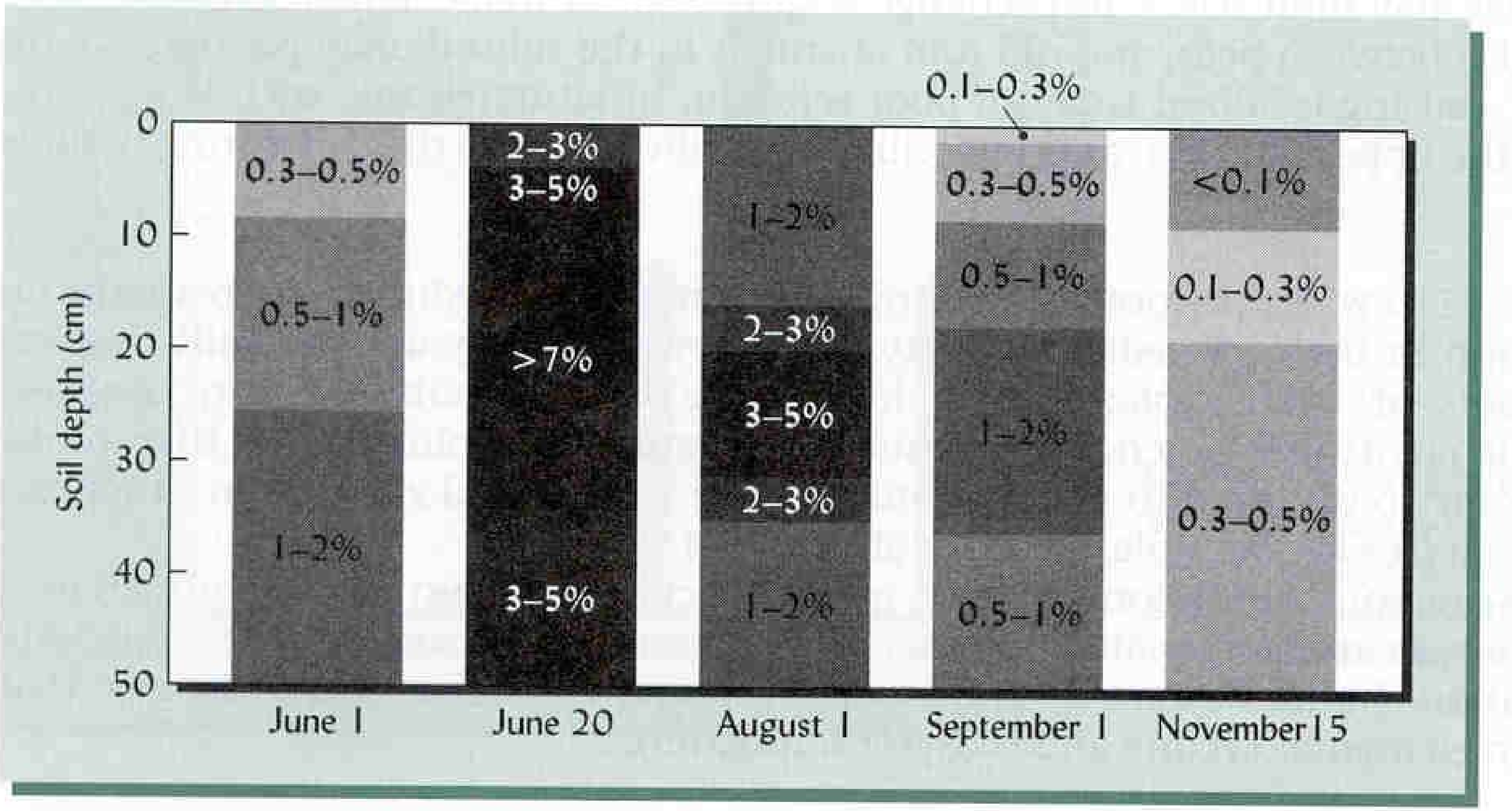
wet

$\theta = .25$
$P_A = .25$
$P_T = .5$


Soil surface
0
30
60
90
120
Soil depth (cm)
After heavy rains
Before heavy rains
0
5
10
15
20
Oxygen in soil air (%)



Soil depth, cm
0
100
200
300
400
500
600
700
800
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
% CO_2 in soil air
Wet season
Dry season

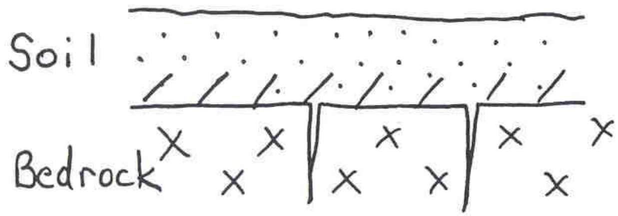


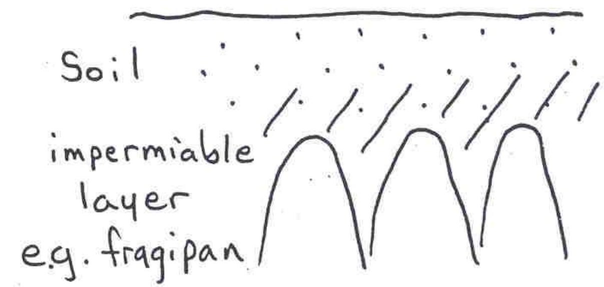
Soil depth (cm)
0
10
20
30
40
50
0.3–0.5%
0.5–1%
1–2%
2–3%
3–5%
>7%
3–5%
1–2%
2–3%
3–5%
2–3%
1–2%
0.1–0.3%
0.3–0.5%
0.5–1%
1–2%
0.5–1%
<0.1%
0.1–0.3%
0.3–0.5%
June 1
June 20
August 1
September 1
November 15

Saturated soils have little or no air in their pores.

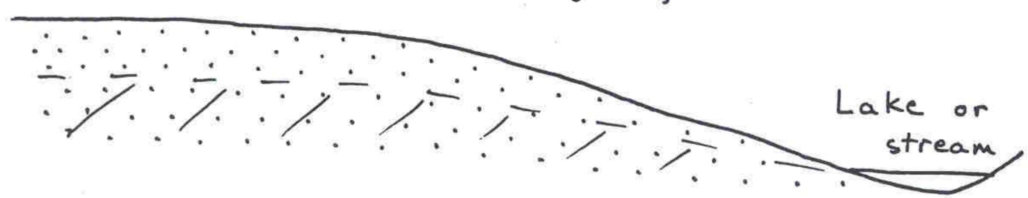
Saturation can be:

Temporary - e.g. rainstorm, irrigation, snow melt (days ---> weeks)





Permanent - e.g.

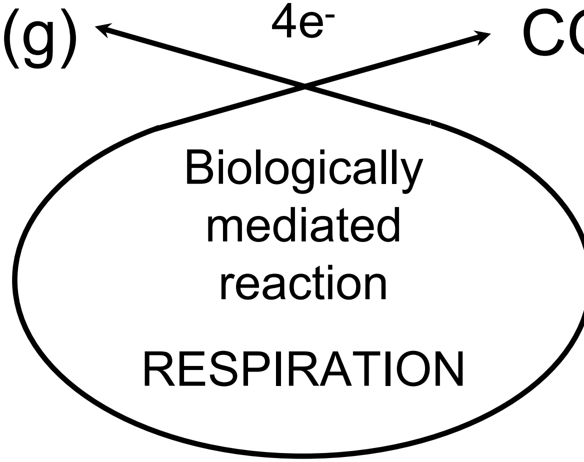


Lack of oxygen produced ANAEROBIC (ANOXIC) conditions, in which only anaerobic microorganisms are active.

AEROBIC MICROBES	ANAEROBIC MICROBES
- require O_2	- do not require O_2
- produce CO_2	- produce methane, nitrous oxide, hydrogen sulfide (CH_4, N_2O, H_2S)

IT'S ALL ABOUT ENERGY!
And it's a REDOX reaction

$$CH_2O\ (s) + O_2\ (g) \quad 4e^- \quad CO_2\ (g) + H_2O\ (g)$$



Respiration is a redox process in which O_2 serves as an electron acceptor.

Aerobic respiration

$$\overset{0}{C_6H_{12}O_6} + 6\,\overset{0}{O_2^{*}} + 6\,H_2O \rightarrow 6\,\overset{+IV}{CO_2} + 12\,\overset{-II}{H_2O^{*}}$$

Anaerobic respiration

$$CH_2O + 2Fe_2(III)O_3 + 7CO_2 + 3H_2O \rightarrow 4Fe(II) + 8HCO_3^-$$

Oxidation / Reduction Potential (Redox)

- The redox potential (E_h) is the potential of a substance to accept or donate an electron (e^-)

$$\overset{(2+)}{2FeO} + 2H_2O \leftrightarrow \overset{(3+)}{2FeOOH} + 2H^+ + 2e^-$$

$$\tfrac{1}{2}\overset{(0)}{O_2} + 2H^+ + 2e^- \leftrightarrow \overset{(2-)}{H_2O}$$

$$2FeO + \tfrac{1}{2} O_2 + H_2O \leftrightarrow 2FeOOH$$

- Free electrons do not exist in aqueous solns
- Reduction/oxidation occur simultaneously

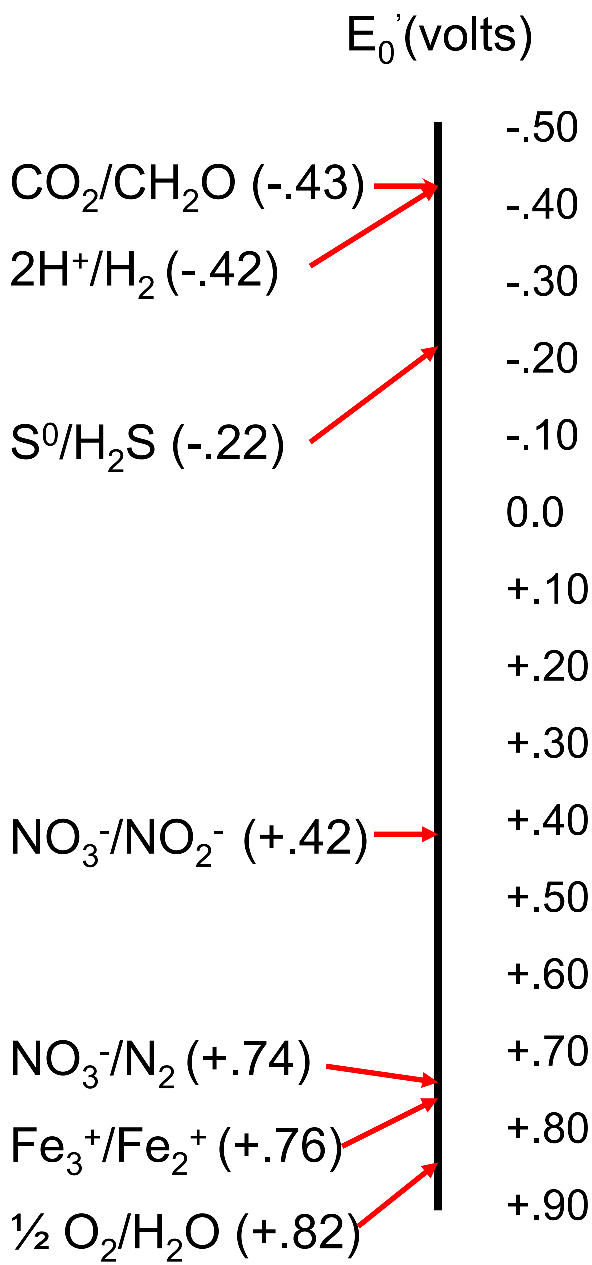
Redox

- E_h is the redox potential (volts)
- Measures the tendency of a substance to donate or accept an electron
- Related to a reference state (half reaction)

$$H^+ = e^- + 1/2\ H_2$$ (arbitrarily taken at zero)

- More positive the E_h the easier the substance can be used as an terminal electron acceptor

Electron Tower



Oxidation / Reduction Pairs

- where first in pair is oxidizer (accepts e^-)
- and second in pair is reduced (donates e-)

Due to energy required to build molecules, strong e^- donors are found at the top of tower, while strong e^- acceptors are found at the bottom of tower.

Therefore the amount of potential energy released by coupled redox reactions, is greatest the farther the e^- "falls"

E_0' (volts)

CO_2/CH_2O (-.43)	-.50
$2H^+/H_2$ (-.42)	-.40
	-.30
	-.20
S^0/H_2S (-.22)	-.10
	0.0
	+.10
	+.20
	+.30
NO_3^-/NO_2^- (+.42)	+.40
	+.50
	+.60
NO_3^-/N_2 (+.74)	+.70
Fe_3^+/Fe_2^+ (+.76)	+.80
½ O_2/H_2O (+.82)	+.90

Reaction	E^0_h (volts)
¼ O_2 (g) + H^+ + e^- = ½ H_2O	@1.229

Table 7.1. Standard-State Reduction Potentials of Half-Reactions Involving Important Elements in Soils

Reaction	E_h^0 (volts)[a]
$Mn^{3+} + e^- = Mn^{2+}$	1.51
$MnOOH(s) + 3H^+ + e^- = Mn^{2+} + 2H_2O$	1.45
$\frac{1}{5}NO_3^- + \frac{6}{5}H^+ + e^- = \frac{1}{10}N_2(g) + \frac{3}{5}H_2O$	1.245
$\frac{1}{2}MnO_2(s) + 2H^+ + e^- = \frac{1}{2}Mn^{2+} + H_2O$	1.23
$\frac{1}{4}O_2(g) + H^+ + e^- = \frac{1}{2}H_2O$	1.229
$Fe(OH)_3(s) + 3H^+ + e^- = Fe^{2+} + 3H_2O$	1.057
$\frac{1}{2}NO_3^- + H^+ + e^- = \frac{1}{2}NO_2^- + \frac{1}{2}H_2O$	0.834
$Fe^{3+} + e^- = Fe^{2+}$	0.711
$\frac{1}{2}O_2(g) + H^+ + e^- = \frac{1}{2}H_2O_2$	0.682
$\frac{1}{8}SO_4^{2-} + \frac{9}{8}H^+ + e^- = \frac{1}{8}H_2S + \frac{1}{2}H_2O$	0.303
$\frac{1}{6}N_2(g) + \frac{4}{3}H^+ + e^- = \frac{1}{3}NH_4^+$	0.274
$\frac{1}{8}CO_2(g) + H^+ + e^- = \frac{1}{8}CH_4(g) + \frac{1}{4}H_2O$	0.169
$H^+ + e^- = \frac{1}{2}H_2(g)$	0.000

[a] The E_h^0 can be converted to the equilibrium constant for the half-reaction, K, using the equation $E_h^0 = (0.059/n) \log K$.

M. McBride, 1994

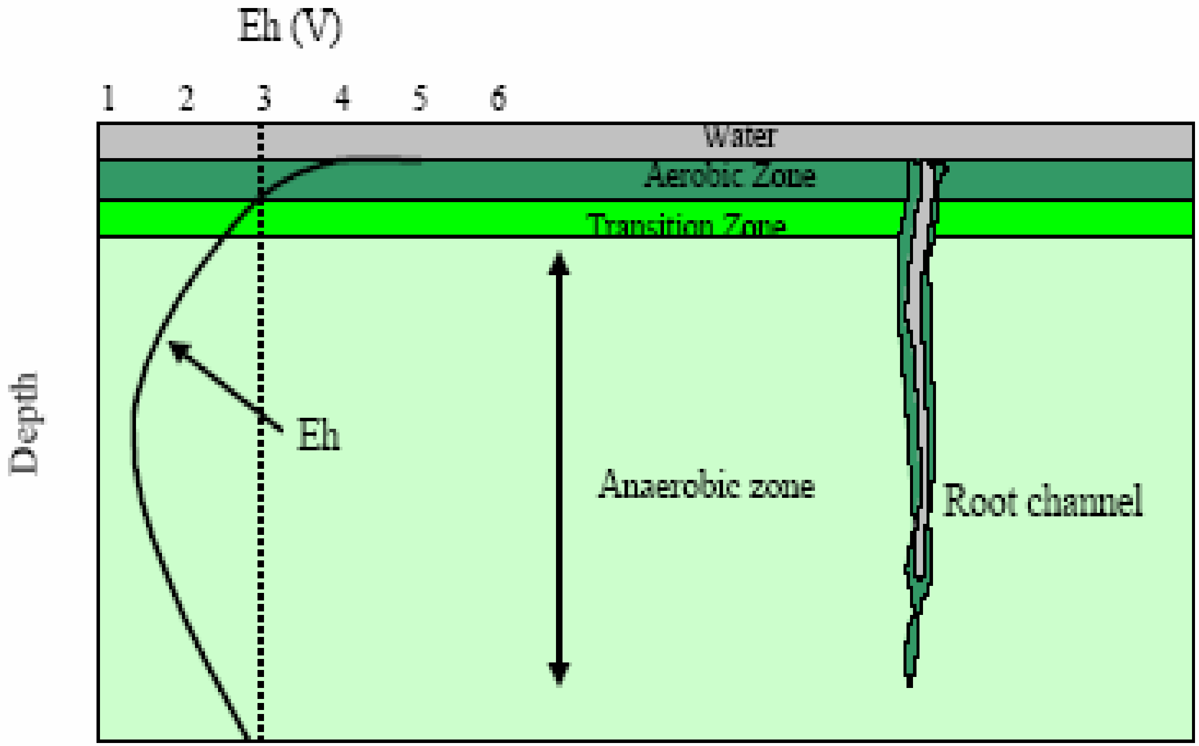
TABLE 7.3 Oxidized and Reduced Forms of Several Important Elements

Element	*Normal form in well-oxidized soils*	*Reduced form found in waterlogged soils*
Carbon	CO_2, $C_6H_{12}O_6$	CH_4, C_2H_4, CH_3CH_2OH
Nitrogen	NO_3^-	N_2, NH_4^+
Sulfur	SO_4^{2-}	H_2S, S^{2-}
Iron	Fe^{3+} [Fe(III) oxides]	Fe^{2+} [Fe(II) oxides]
Manganese	Mn^{4+} [Mn(IV) oxides]	Mn2+ [Mn(II) oxides]

Oxidized form	*Reduced form*	*Eh at which change of form occurs, V*
O_2	H_2O	0.38 to 0.32
NO_3^-	N_2	0.28 to 0.22
Mn^{4+}	Mn^{2+}	0.22 to 0.18
Fe^{3+}	Fe^{2+}	0.11 to 0.08
SO_4^{2-}	S^{2-}	-0.14 to -0.17
CO_2	CH_4	-0.20 to -0.28

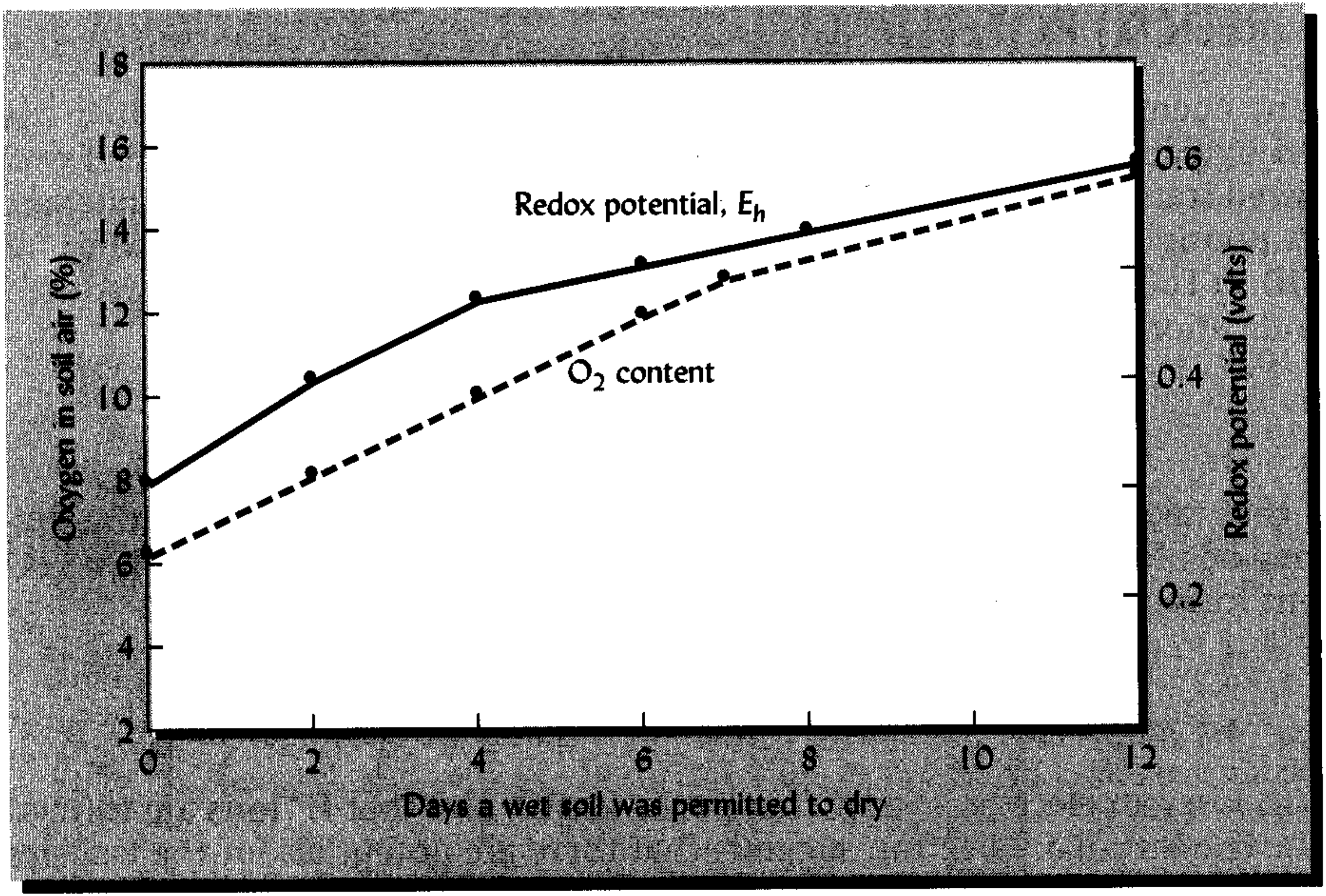
From Patrick and Jugsujinda (1992).

- Soil values:
- E_h = 0.4 to 0.60 volts (well drained soil)
- E_h = 0.3 to 0.35 volts (flooded, O_2 reduced)
- E_h = 0.25 to -0.3 volts (prolonged flooding)

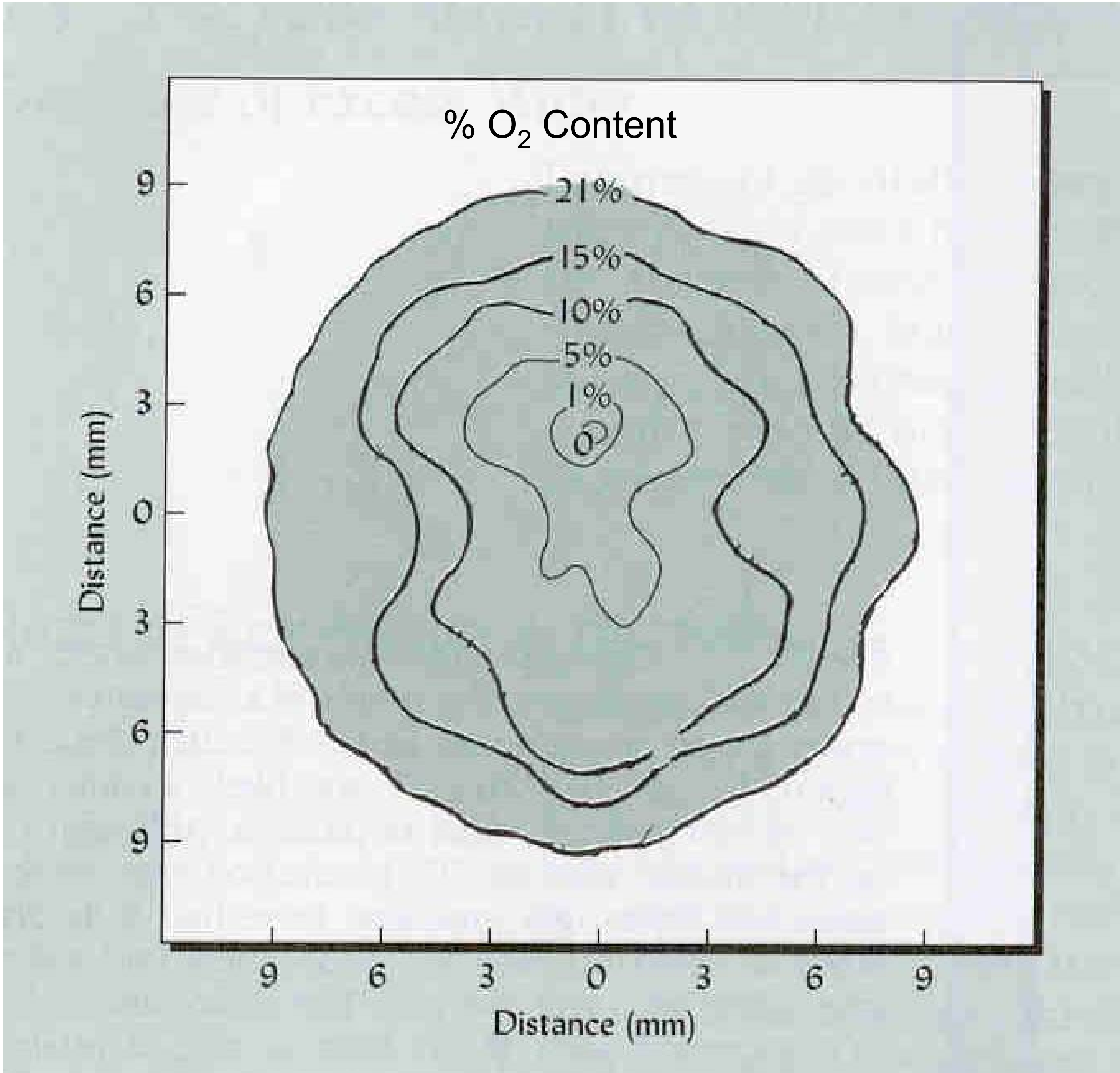

Eh (V)
1 2 3 4 5 6
Water
Aerobic Zone
Transition Zone
Depth
Eh
Anaerobic zone
Root channel

Redox

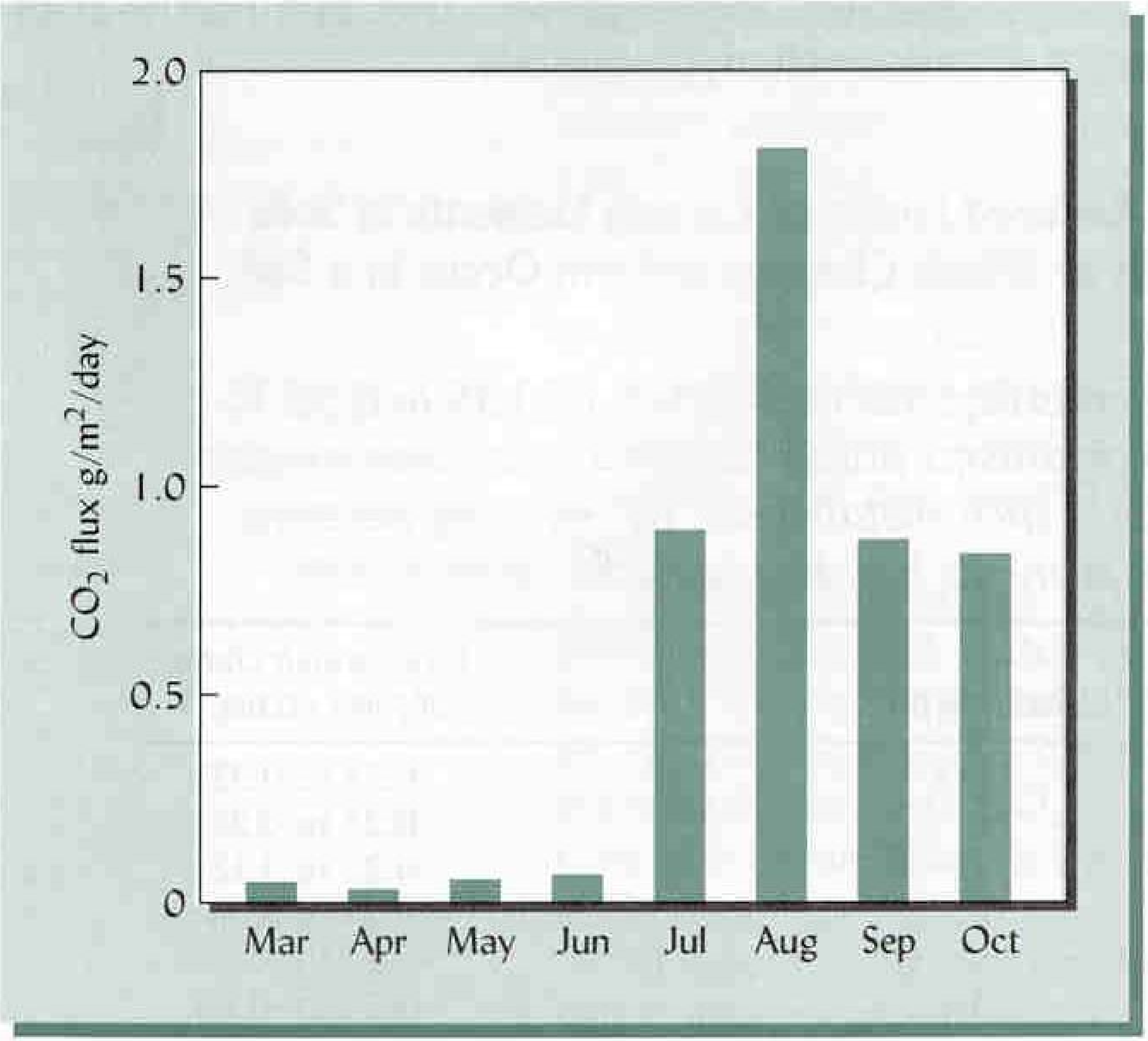
- Redox sequence in waterlogged soils
  - O_2 depleted due to displacement by H_2O, low H_2O solubility and consumption by biological activity
  - Soil becomes anaerobic and microbes must use other substances as TEA
  - pH rises because most redox reactions consume protons
  - NO_3^- ---> N_2 (denitrification)



Redox potential, E_h
O_2 content
Oxygen in soil air (%)
Redox potential (volts)
Days a wet soil was permitted to dry
18
16
14
12
10
8
6
4
2
0.6
0.4
0.2
0
2
4
6
8
10
12



% O2 Content
21%
15%
10%
5%
1%
0
9
6
3
0
3
6
9
Distance (mm)
9
6
3
0
3
6
9
Distance (mm)



2.0
1.5
1.0
0.5
0
CO_2 flux g/m^2/day
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct

Ecological Importance of Soil Aeration

- OM degradation
  - Fastest under oxidized conditions
  - Toxic by-products may accumulate (reduced)
    - Ethylene gas, alcohols, and organic acids
- Redox of elements
  - Nutrients (Fe^{3+} vs. Fe^{2+}, SO_4^{2-} vs. S^{2-})
  - Toxic elements
  - Soil colors
  - CH_4 production
  - Plant growth