#### **17.14 HEAT FLOW IN SOILS**

Fourier (1822) analyzed the heat conduction in solids and developed a mathematical relationship, which is analogous to the diffusion equation by Pick (see Chapters 16 and 18), conduction of fluid flow in porous media by Darcy (refer to Chapters 12 and 13), and conduction of electricity by Ohm (Table 17.10). The first law of heat conduction is known as Fourier's law and under steady state condition in one-dimension, the heat flux density (qh,  $Jm^{-2}s^{-1}$ ) equation and the heat energy balance equation for

Process	Law	Equation
Water movement	Darcy's	$q = -K \frac{\partial H}{\partial x}$
Air movement	Fick's	$q_x = -D\frac{\partial C}{\partial x}$
Heat movement	Fourier's	$h = -k \frac{\partial T}{\partial z}$
Electric flow	Ohm's	$a = -k \frac{\partial \phi}{\partial x}$

### **TABLE 17.10** The Analogous Laws of Water, Air, Heat, and Electricity Flow

homogeneous soils is expressed as follows:

$$q_{h} = -K_{T} \frac{\partial T}{\partial z}$$
(17.32)  
$$\frac{\partial H}{\partial t} = -\frac{\partial q_{h}}{\partial z}$$
(17.33)

where *H* is the volumetric heat content  $(Jm^{-3})$ , and volumetric heat capacity of soil  $(C_v)$  is equal to dH/dT. The early developments of heat conduction dealt with dry media, i.e., solids only (Carslaw and Jaeger, 1959). The theory was later expanded to soils containing water. At first the heat flow was studied for homogeneous soils with constant  $C_v$  and  $K_T$ .

Combining these two equations [(17.32) and (17.33)], which ignores the existence of a sink or source term, results in general heat conduction equation. These equations can be solved numerically for nonhomogeneous soil profiles by assuming that heat transfer takes place by conduction only. The addition of water complicates the process as water may evaporate and condense. As the heat energy inside a soil matrix is transported by convection (by flowing water, air, and latent heat), conduction, and radiation. The first two are the most important heat transport process through soil. The convection can be represented as given by Eq. (17.21). The expression for net flux of heat through soil can be written as

$$q_h = -k_T \frac{\mathrm{d}T}{\mathrm{d}z} + L * E_v \tag{17.34}$$

where  $E_v$  is the water vapor mass flux (gcm<sup>-2</sup> s<sup>-1</sup>). The temperature gradient across a moist soil results in movement of water both as liquid and gas along with heat, therefore, the effective value of  $K_T$  exhibits a temporal variation and therefore cannot be measured in the soil directly (de Vries, 1958). If  $D_v$  is the thermal vapor diffusivity then water vapor flux in soil in one-dimension flow where relative humidity is above unity can be written as

$$E_{\nu} = -D_{\nu} \frac{\mathrm{d}T}{\mathrm{d}z} \tag{17.35}$$

Transferring Eq. (17.35) into Eq. (17.34) results in

$$q_h = -(K_T + D_v L) \frac{\mathrm{d}T}{\mathrm{d}z} \cong -K_{Te} \frac{\mathrm{d}T}{\mathrm{d}z}$$
(17.36)

where  $K_{Te}$  is the effective thermal conductivity of the porous medium, which includes the effects of conduction and convection of latent heat.

#### **17.15 HEAT CONSERVATION EQUATION**

The heat conservation equation for a small cubic soil matrix (Fig. 17.7) can be derived by accounting for the amount of heat energy entering a system, leaving a system, and change in the heat energy of a system. Mathematically a heat balanced equation can be written as follows (Jury et al., 1991)

The amount of heat energy entering soil matrix

= amount of heat leaving the soil matrix

(17.37)

+ increase in heat energy of the soil matrix

+ loss of heat energy from the soil matrix.



**FIGURE 17.7** Schematic of a soil matrix for heat conservation equation.

Assuming the heat flow is in *z*-direction, the one-dimensional heat flow in vertical direction during time interval  $\Delta t$  through the soil matrix (Jury et al., 1991; Scott, 2000)

$$=h(x, y, z, t + \frac{1}{2}\Delta t)\Delta x\Delta y\Delta t$$
(17.38)

where *h* is the heat flux at the average time  $t+(\Delta t/2)$  and  $\Delta x$  and  $\Delta y$  are the cross-sectional area of the soil matrix. The amount of heat flowing out of the matrix for the same time interval

$$= h(x, y, z + \Delta z, t + \frac{1}{2}\Delta t)\Delta x \Delta y \Delta t$$
(17.39)

The net change in *H* within the soil matrix

$$[H(x, y, z + \frac{1}{2}\Delta z, t + \frac{1}{2}\Delta t) - H(x, y, z + \frac{1}{2}\Delta z, t)]\Delta x \Delta y \Delta z$$

$$= \Delta H \Delta x \Delta y \Delta z$$
(17.40)

where *H* is at the middle or  $z+(\Delta z/2)$ . If the amount of heat lost from the soil matrix per unit system is  $r_s$ , the total heat loss

$$= r_r \Delta x \Delta y \Delta z \Delta t \tag{17.41}$$

Transferring Eqs. (17.38), (17.39), (17.40), and (17.41) into Eq. (17.37), and after rearranging and assuming that  $\Delta Z$  and  $\Delta t \rightarrow 0$ , the resultant equation is known as the differential form of heat conservation equation (Jury et al., 1991; Scott, 2000)

$$\frac{\partial H}{\partial t} + \frac{\partial h}{\partial z} + r_r = 0 \tag{17.42}$$

The *H* can also be expressed as a function of volumetric heat capacity of soil  $C_{\nu}$  and temperatures

$$H = C_{\nu}(T - T_{ref}) \tag{17.43}$$

where  $T_{ref}$  is the reference temperature at which H=0. Transferring Eq. (17.43) into (17.42), and assuming  $C_v$  a constant, we obtain

$$C_{v}\frac{\partial T}{\partial t} = \frac{\partial}{\partial z}\left(K_{T}\frac{\partial T}{\partial z}\right)$$
(17.44)

if  $k_t$  is assumed to be independent of z then following heat flow equation is obtained.

$$\frac{\partial T}{\partial t} = D_T \frac{\partial^2 T}{\partial z^2} \tag{17.45}$$

where  $D_T = K_T / C_V$ , and is known as soil thermal diffusivity ( $L^2 T^{-1}$  or  $m^2 s^{-1}$ ).  $D_T$  can be expressed in three different ways for soil water diffusivity, diffusion in air, and soil thermal diffusivity as follows:

Definition	Equation	Unit
Soil water diffusivity	$D_{\theta} = K_{\theta}(d\Phi_m/d\theta)$	$cm^2 s^{-1} or L^2 T^{-1}$
Diffusion coefficient in air	$D_s = D_0 * 0.66 * f_a$	$\text{cm}^2 \text{ s}^{-1}$ or $\text{L}^2 \text{ T}^{-1}$ (see Chapter 18)
Soil thermal diffusivity	$D_T = K_T / C_V$	$cm^2 s^{-1} or L^2 T^{-1}$

#### 17.16 MEASUREMENT OF THERMAL CONDUCTIVITY OF SOIL

Similar to hydraulic conductivity ( $K_s$ ), thermal conductivity ( $K_T$ ) can be measured using the steady state method or transient methods. Let us assume a soil column of thickness Lplaced between two glass plates of thickness d. The outer surface of each of these two plates is at constant temperature. The temperature is measured at several different positions as shown in Fig. 17.8. Let us assume the datum at point A, i.e., z=0 at  $A_1$  and that heat flux through soil and glass plates is equal, glass and soil are in good contact, and lateral movement of heat is negligible. If the temperature measured at the plate at A is  $T_0$ , then according to Fourier's law, the heat flux across the plate and soil column can be written as

$$q_h = -K_T \frac{(T_2 - T_0)}{d} \tag{17.46}$$

$$q_h = -K_{Te} \frac{(T_3 - T_2)}{L} \tag{17.47}$$



**FIGURE 17.8** Apparatus for measurement of thermal conductivity under steady state.

where  $K_{Te}$  is the effective thermal conductivity of porous media. Equating these two equations [(17.46) and (17.47)] and rearranging them gives the expression for effective thermal conductivity as follows

$$K_{Te} = -\frac{K_T L (T_2 - T_0)}{d(T_3 - T_2)}$$
(17.48)

The steady state methods are useful for measurement of  $K_T$  in the laboratory. The basic drawback of this method is that a nonuniform profile within the column is created due to the redistribution of water under the influence of a steady state temperature gradient (Jury and Miller, 1974). The transient method for the measurement of  $K_T$  can be used in situ and does have the drawback of the steady state method (De Vries and Peck, 1968). The method consists of a thin metal wire, which serves a heat source. The wire and the sensors for temperature measurement (for example thermocouples) are kept inside a cylindrical tube, which is inserted into the soil. The flow of heat takes place radially from the wire and the temperature of the thermocouple probe in contact with the soil is given by the following equation (Carslaw and Jaeger, 1959)

$$T = T_0 = \frac{q_h}{4\pi k_T} [d + \ln(t + t_0)]$$
(17.49)

where  $T_0$  is the temperature at t=0,  $T-T_0$  is rise in temperature, q is heat flowing per unit time and length of wire, d is a constant, which depends on the location of thermocouple, and  $t_0$  is a correction constant, which depends upon the dimensions of the probe. The equation (17.49) can be rearranged for  $t > t > t_0$  and the  $K_T$  can be calculated by the following relationship

$$K_T = \frac{q_h}{4\pi m} \tag{17.50}$$

where *m* is the slope measured by plotting *T* versus ln(t). The  $q_h$  is calculated from the current (*I*) applied to the wire and the measured resistance per unit length of wire.

#### **17.17 MANAGEMENT OF SOIL TEMPERATURE**

Soil temperature can be managed in a number of ways, which includes mulching, tillage, irrigation, drainage, cover crop or shading, and application of dark or light powder. The management options depend whether the temperature of soil needs to be increased or reduced. The duff layer, which is the thatch of plant material on the surface, reduces the frequency of freeze-thaw cycles in the seed zone, maintains aggregates, and prevents crusting. Different types of mulches are used to either lower or raise the soil temperature, depending upon the need. Light-colored mulches (e.g., chopped straw, plastic mulches) reflect a portion of incoming solar radiation and reduce the amount of radiant flux reaching the soil surface, thus lowering the soil temperature (Fig. 17.9). On the other hand, application of thick and dark mulches (e.g., charcoal or bitumen) enhance the soil temperature. Dark plastic mulch absorbs most of the radiant solar energy but transmits

very little to the soil, keeping the soil cool (Fig. 17.10). On the other hand, transparent plastic mulch transmits short-wave (visible



**FIGURE 17.9** A light-colored mulch (aluminium foil) decreases soil temperature. (Lal, 1975, field experiments.)



# **FIGURE 17.10** A dark-colored plastic mulch decreases soil temperature. (Field experiments, IITA, Ibadan, Nigeria, 1975.)

light) radiation to the soil surface while preventing infrared (long-wave) radiation, creating a greenhouse effect and warming the soil (Fig. 17.11) (Lal, 1979). Soil temperature (in °C) at 5 cm depth under a maize crop one week after planting and under black plastic, clear plastic, straw mulch, ridges, bare flat, and aluminum foil shows that the soil temperature fluctuation is the minimum for straw mulch and the maximum for ridges (Fig. 17.12). The soil temperature for bare flat treatment under different crops was in the order cassava > soybean > maize=cowpea (Fig. 17.13) (Lal, 1979).

Ridge tillage increases surface soil temperature by increasing the area exposed to radiation and decreasing soil moisture (Fig. 17.14). The surface 5 cm, or the seed zone, of no-till soils, may warm more slowly in spring and cool more slowly in autumn than in cultivated soils. Below 5 cm, in the root zone, no-till soils may be warmer and wetter from fall through spring. The amplitude of temperature variation at the soil surface is greater in plowed than no-till soils. However, because of the lower thermal conductivity of plow-till soil, the amplitude decreases more rapidly in plow-till than in no-till soils (van Duin, 1956). The maximum and minimum temperatures at the surface of a plow-till soil are also much higher than a no-till soil. Soil temperature in early spring is significantly affected by tillage methods (Table 17.11) (Fausey and Lal, 1989). Similar to no-till, mulching with crop residue decreases the maximum soil temperature and increases the minimum soil temperature (Fig. 17.15).



**FIGURE 17.11** A clear plastic creates a greenhouse effect and increases soil temperature. (Field experiments, IITA, Ibadan, Nigeria, 1975.)



**FIGURE 17.12** Soil temperature at a 5 cm depth under different mulches one week after planting crops during the first growing season in 1977 in Ibadan, Nigeria. (Redrawn from Lal, 1979.)



**FIGURE 17.13** Soil temperature at a 5 cm depth under different crops for bare flat seedbed preparation during the first growing season in 1977 in Ibadan, Nigeria. (Redrawn from Lal, 1979.)



## **FIGURE 17.14** Ridge tillage may decrease the minimum and increase the maximum soil temperature.

Irrigation with cold water during the summer results in bringing down the temperature of surface soil (Fig. 17.16). Similarly, drainage has a strong influence on soil temperature. During spring, wet soils are cold at the soil surface, because of the increase in  $K_T$  of soil, which results in the conduction of heat in a downward direction reducing the temperature of the surface of

		Distance from drain (m)		
Tillage	0	9	27	
No-till	6.2	6.1	6	
Ridge-till	5.4	5.3	5.1	
Plow-till	6.2	5.8	5.5	
Beds	6	5.7	5.7	

### **TABLE 17.11** The Tillage and Drainage Effects on Mean Daily Maximum Soil Temperature in °C

Source: Modified from Fausey and Lal, 1989.



**FIGURE 17.15** Mulching with crop residue decreases the maximum and increases the minimum soil temperature.

soil. The high water content also increases heat capacity of soil, thus reducing the temperature of the surface of soil. The evaporation of water from wet soil also consumes the energy, which results in a reduction of temperature of the soil surface. Therefore, removal of excess water by surface or subsurface drainage increases soil aeration, which in turn warms the soil surface and improves seed germination and root growth. Building large mounds in a poorly drained (hydromorphic soil) increases soil temperature (Fig. 17.17). The effects of tillage and drainage on soil temperature are presented in Table 17.11, which show that as distance from drain increases, the mean daily temperature of soil reduces for all the treatments namely, no-till, ridge-till, plow-till, and beds.



**FIGURE 17.16** Irrigation lowers the soil temperature in summer and raises it in winter.



**FIGURE 17.17** Farmers in West Africa construct large mounds in hydromorphic soils to create wellaerated root zones and raise soil temperature. (Field experiments, IITA, Ibadan, Nigeria.)

#### Example 17.1

If the Stefan–Boltzmann constant (a) is 5.67  $10^{-8}$ Wm<sup>-2</sup>K<sup>-4</sup> and emissivity ( $\varepsilon$ ) is 0.94, calculate the long-wave thermal radiation energy flux Dearth for a temperature 300 K.

#### Solution

The energy flux density can be calculated as

$$R_{\text{earth}} = \varepsilon \sigma T^4 = 0.94 * 5.67 \times 10^{-8} * (300)^4$$
  
= 431.713 Wm<sup>-2</sup> = 0.61 calcm<sup>-2</sup>min<sup>-1</sup>

#### Example 17.2

A soil column contains 40 cm of dry sand over 20 cm of dry loam soil. Both ends are attached to a constant temperature bath with the top maintained at 25°C and the bottom at 4°C. If the thermal conductivity of sand  $(K_{Ts})$  is 0.5 meal<sup>-1</sup> s<sup>-1</sup> °C<sup>-1</sup> and that of loam  $(K_{Tl})$  is 0.25 mcal<sup>-1</sup>s<sup>-1</sup> °C<sup>-1</sup>, calculate the steady state heat flux through the two layers and the temperature at the sand-loam interface.

#### Solution

The equivalent thermal conductivity of the sand-loam system  $(k_{eq})$  for the total thickness of the sand-loam system (i.e., 60 cm) can be calculated as below

$$\frac{60}{K_{eq}} = \frac{40}{K_{Ts}} + \frac{20}{K_{Tl}} \Rightarrow K_{Teq} = \frac{60}{(40/0.5) + (20/0.25)} = \frac{60}{(80 + 80)}$$
$$= 0.375 \,\mathrm{mcal}^{-1} \mathrm{s}^{-1} \mathrm{c}^{-1}$$

The heat flux equation across the entire soil column of sand and loam will provide the steady state heat flux across column as follows

$$q_h = -\frac{K_{Teq}}{(40+20)}(25-4) = -\frac{0.375*21}{60} = -0.131 \,\mathrm{calcm}^{-2}\mathrm{s}^{-1}$$

The temperature across the sand-loam interface (T) can be calculated as

$$q_h = -\frac{K_{Tl}}{20}(T-4) \Leftrightarrow -0.131 = -\frac{0.25*(T-4)}{20} \Leftrightarrow T = 14.48^{\circ}\text{C}$$

#### Example 17.3

If the bulk density of a soil 1.45 gcm<sup>-3</sup> and is at two different volumetric water contents: (i) 0.50 and (ii) 0.25, what will be the ratio of volumetric heat capacity,  $C_{\nu}$ , for these two situations?

#### Solution

The  $C_v$  can be calculated from Eq. (17.26). For  $\theta$ =0.50,  $C_{v1}$ =(1.45+ 0.5)  $C_g$ And for  $\theta$ =0.25,  $C_{v2}$ =(1.45+0.25)  $C_g$  $\frac{C_{r1}}{C_{v2}} = \frac{1.95}{1.70} = 1.15$ 

#### Example 17.4

If the particle density of a soil is  $2.65 \times 103$  kgm<sup>-3</sup>, and bulk density is  $1.45 \times 10^3$  kgm<sup>-3</sup>, assuming the soil is water-saturated, calculate the volumetric heat capacity ( $C_{\nu}$ ) of the soil if volumetric organic matter content is 15% of solid mass. Assume volumetric heat capacity of mineral, organic matter, and water as  $2 \times 10^6$ ,  $2.5 \times 10^6$ , and  $4.2 \times 10^6$  Jm<sup>-3</sup> deg, respectively.

#### Solution

The total porosity of the soil can be calculated as

$$f_t = \frac{(\rho_s - \rho_b)}{\rho_s} = \frac{2.65 * 10^3 - 1.45 * 10^3}{2.65 * 10^3} = 0.453,$$

since soil is saturated volumetric fraction of water is equal to porosity Therefore volumetric fraction of solids is=1 - 0.453=0.547 Organic matter fraction=0.547\*0.1 =0.0547 Mineral matter fraction=0.547\*0.9=0.492 Therefore volumetric heat capacity ( $C_v$ ) can be calculated as  $C_v = f_m C_m + f_0 C_0 + f_w C_w$  $C_v = 0.492*2*10^6 + 0.0547*2.5*10^6 + 0.453*4.2*10^6$ = 4.25\*106 Jm<sup>-3</sup> degree

#### Example 17.5

For a temperature difference of 20°C across a 30-cm thick soil sample, calculate the onedimensional thermal flux and total heat transfer under steady state condition. Assume thermal conductivity of soil as  $1.6 \text{ Jm}^{-1} \text{ s}^{-1} \text{ °C}^{-1}$ .

#### Solution

The heat flux across a soil column is expressed as

$$q_h = -K_T \frac{(T_2 - T_0)}{L} = \frac{1.6 * 20}{0.3} = 106.67 \,\mathrm{Jm}^{-2} \mathrm{s}^{-1}$$

Total heat transfer= $q_h * t = 106.67 * 3600 = 3.84 \times 10^5 \text{Jm}^{-2}$ 

#### Example 17.6

Assuming that the diurnal temperature wave is symmetrical and mean temperature is equal throughout the soil profile with surface temperature equal to mean temperature at 6 A.M. and 6 P.M., calculate the temperatures at noon and midnight for depths 10 cm and 25 cm. Assume daily maximum and minimum soil surface temperature 36°C and 8°C, respectively, and damping depth as 10 cm.

#### Solution

The temperature T at any depth z and time t can be calculated as follows

$$T(z,t) = T_{\text{ave}} + \frac{A_0[\sin(\omega t - (z/d))]}{e^{z/d}}$$

where  $A_0$  is minimum value above mean,  $\omega$  is the radial frequency (2 $\pi$ /24), z is depth, and d is the damping depth. The average temperature  $T_{ave}=(38+8)/2=23^{\circ}$ 

Temperature above mean  $A_0=38-23=15^{\circ}$ 

At soil surface z=0

Temperature 6 h after mean temperature, i.e., noon temperature

$$T(0, 6) = 23 + \frac{15 * [\sin((\pi/2) - 0)]}{e^0} = 23 + 15 = 38^{\circ}\text{C}$$

At midnight

$$T(0, 18) = 23 + \frac{15 * [\sin((3\pi/2) - 0)]}{e^0} = 23 - 15 = 8^{\circ}C$$

At depth 10 cm  $T(10, 6) = 23 + \frac{15 * [\sin((\pi/2) - 0.1/0.1)]}{e^{0.1/0.1}} = 26^{\circ}C$ 

and at midnight  $T(10, 18)=22^{\circ}C$ 

#### PROBLEMS

1. If the particle density of a soil is  $2.65 \times 10^3$ kgm<sup>-3</sup>, and bulk density is  $1.45 \times 10^3$  kgm<sup>-3</sup>, assuming the soil is (a) dry and (b) volumetric water content is 30%, calculate the volumetric heat capacity ( $C_{\nu}$ ) of the soil if volumetric organic matter content is 8% of solid mass. Assume volumetric heat capacity of mineral, organic matter, and water as  $2 \times 10^6$ ,  $2.5 \times 10^6$ , and  $4.2 \times 10^6$ Jm<sup>-3</sup> deg, respectively.

2. Calculate one-dimensional thermal flux and total heat transfer under steady state condition for a temperature difference of 10°C across a 25-cm thick soil sample. Assume thermal conductivity of soil as 1.6 J m<sup>-1</sup> s<sup>-1</sup> °C<sup>-1</sup>

3. How much heat is required to change 20 kg of ice at  $-8^{\circ}$ C to steam at 100°C?

4. A soil column contains 35 cm of dry sand over 15 cm of dry loam soil. Both ends are attached to a constant temperature bath with top maintained at 28°C and bottom at 8°C. If the thermal conductivity of sand (k<sub>s</sub>) is 0.48 meal<sup>-1</sup> s<sup>-1</sup> °C<sup>-1</sup> and that of loam (k<sub>L</sub>) is 0.23 meal<sup>-1</sup> s<sup>-1</sup> °C<sup>-1</sup>, calculate the steady state heat flux through the two layers and the temperature at the sand-loam interface.

5. Compute the amount of heat required to raise the temperature of a unit area of soil  $(\rho_b=1.25 \text{gcm}^{-3}, \text{w}=0.2 \text{gg}^{-1})$  from an initial temperature of 10°C to 20°C to a depth of 50 cm.

6. Calculate the direction and quantity of heat per unit that will flow in one day, when soil temperature at the surface is 30°C and at 5 cm depth is 25°C. Assume thermal conductivity  $=3 \times 10^{-3}$  cal cm<sup>-1</sup> s<sup>-1</sup>c<sup>-1</sup>.

7. Why is soil temperature more important than air temperature?

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#### 18 Soil Air and Aeration

#### 18.1 AIR

Earth is surrounded by a gaseous envelope of air about 80 km thick called the atmosphere. The origin of Earth's atmosphere is still a subject of speculation. One theory seems fairly certain that some five billion years ago when Earth was formed, it was extremely hot and did not have an atmosphere. It is generally accepted that the first atmosphere, created when Earth cooled down, consisted of helium (He), hydrogen (H<sub>2</sub>), ammonia (NH<sub>3</sub>), and methane (CH<sub>4</sub>). Assuming that five billion years ago volcances emitted similar gasses as in the modern era, Earth's second atmosphere probably consisted of water vapor (H<sub>2</sub>O), carbon dioxide (CO<sub>2</sub>), and nitrogen (N<sub>2</sub>), because these gasses are emitted from Earth's interior by a process known as "outgassing." With colonization by plants, which absorb CO<sub>2</sub> and emit O<sub>2</sub> during photosynthesis, the atmosphere eventually contained a large concentration of O<sub>2</sub>, which now constitutes one-fifth of its volume.

In fact, the envelope of air is a mixture of many discrete gases. Each gas has a distinct physical and chemical property. The atmosphere com prises two types of gases: those whose concentration remains essentially constant or permanent (by percent), and those that are variable and have changing concentrations over a finite period of time. Among the permanent gases, nitrogen (78.1%) and oxygen (20.9%) constitute about 99% of the atmosphere. Other permanent gases are argon (Ar, 0.9%), neon (Ne, 0.002%), helium (He, 0.0005%), krypton (Kr, 0.0001%), and hydrogen (H<sub>2</sub>, 0.00005%). The variable gases are water vapor ( $H_2O$ , 0 to 4%), carbon dioxide ( $CO_2$ , 0.037%), methane ( $CH_4$ , 0.0002%), ozone  $(O_3, 0.000004\%),$ and nitrous oxide  $(N_2O,$ 0.00009%) (www.met.fsu.edu/explores/atmcomp.html). A brief description on some of these gases is given in the following sections.

#### 18.1.1 Nitrogen

Nitrogen gas  $(N_2)$  is composed of molecules of two nitrogen atoms, and occupies 78.1% of Earth's atmosphere. It is colorless, odorless, and tasteless. The atomic weight of  $N_2$  is 14. Nitrogen is a principal nutrient. The low content of nitrogen in most soils exists in stark contrast to its abundance in the air. This is because gaseous  $N_2$  molecules have very strong bonds, which make the gas chemically stable, but unusable by most biological

organisms. Some species of bacteria absorb  $N_2$  from the air and convert it to ammonium, which can be used by plants. This process is called "biological nitrogen fixation" and is the principal natural means by which atmospheric nitrogen is added to the soil by nitrogen-fixing bacteria living in nodules on the plant roots. An example of a leguminous nitrogen-fixing crop is soybean (*Glycine max*).

#### 18.1.2 Oxygen

Oxygen gas  $(O_2)$  is composed of molecules of two oxygen atoms, and occupies 20.9% of Earth's atmosphere by volume. It is colorless, odorless, and tasteless, and constitutes 86% of the oceans and 60% of the human body. It is the third most abundant element found in the Sun. The atomic weight of oxygen is 16. Almost all plants and animals require oxygen for respiration to maintain life. Oxygen is flammable, reactive, and oxidizes most elements. A chemical reaction in which an oxide is formed is known as "oxidation." The rate at which oxidation occurs varies with the element with which oxygen is reacting, (e.g., burning involves a rapid oxidation, whereas rust, or iron oxide, forms slowly). Carbon in fossil fuels, for example, can be quickly oxidized to carbon monoxide (CO) and carbon dioxide (CO<sub>2</sub>), with a considerable amount of heat being given off. Within the stratosphere (the second major layer of the atmosphere, which occupies the region of the atmosphere from about 12 to 50 km above Earth), O<sub>2</sub> molecules combine with free oxygen atoms to form ozone (O<sub>3</sub>). It absorbs ultraviolet (UV) radiation from the Sun.

#### 18.1.3 Trace Gases

Oxygen and nitrogen together constitute about 99% of the atmosphere, and the remaining 1 % is made up of trace gases whose concentrations are very small. The most abundant of the trace gases is the noble gas argon (atomic weight=39.9). Noble gases, which also include neon (20.2), helium (4), krypton (83.8), and xenon (131.3), are very inert and do not generally involve any chemical transformation within the atmosphere. Hydrogen (1.008) is also present in trace quantities in the atmosphere. Although low in concentrations, the important trace gases in Earth's atmosphere are the so-called "greenhouse gases." These greenhouse gases include carbon dioxide (44), methane (16), nitrous oxide (44), water vapor (18), ozone (48), and sulfur hexafluoride (SF<sub>6</sub>, 146.1). These gases allow sunlight, which is radiated in the visible and ultraviolet spectra, to enter the atmosphere unimpeded, but prevent most of the outgoing infrared radiation from the surface and lower atmosphere from escaping into outer space. The greenhouse gases absorb reflected infrared radiations (heat), thus trapping the heat in the atmosphere. Thus, these gases keep Earth warm through the so-called natural "greenhouse effect," which has raised Earth's temperature from  $-18^{\circ}$ C to  $15^{\circ}$ C, an increase of  $33^{\circ}$ C. (Refer to the footnote on p. 532.)

Variable greenhouse gases, can be divided into two categories: (i) those that occur naturally in the atmosphere (e.g., water vapor,  $CO_2$ ,  $CH_4$ , and  $N_2O$ ) and (ii) those that result from human activities (e.g., chlorofluorocarbons (CFCs), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulfur hexafluoride). Human activities can also enhance the concentration of naturally occurring greenhouse gases. Each greenhouse gas differs in its ability to absorb heat in the atmosphere, and HFCs and PFCs are the most

heat-absorbent. The atmospheric lifetime of  $CH_4$ , a greenhouse gas 21 times more effective than  $CO_2$  in trapping its long-wave radiation, is approximately ten years. Methane ( $CH_4$ ) can trap 21 times more long wave radiation per molecule than  $CO_2$ , and  $N_2O$  can absorb 310 times more long wave radiation per molecule than  $CO_2$  (IPCC, 2001). Methane, in contrast to  $CO_2$  and other greenhouse gases, has the unique property of being partly converted to  $H_2O$  by cosmic radiation in the mesosphere.

The global mean surface air temperature has increased between approximately 0.3 and 0.6°C during twentieth century (IPCC, 2001). Globally, sea level has risen 10–20 cm over the past century. Worldwide precipitation over land has increased by about one percent. The frequency of extreme rainfall events has increased throughout much of the

Gas	Formula	Volume (gmol-1)	Concentration (% vol.)	Molar mass (gmol <sup>-1</sup> )	Concentration (g cm <sup>-3</sup> )	
Nitrogen	$N_2$	22.4	78	28	$9.75 \times 10^{-4a}$	
Oxygen	O <sub>2</sub>	22.4	21	32	3.0×10 <sup>-4</sup>	
Carbon dioxide	$CO_2$	22.4	0.033	44	$6.0 \times 10^{-6}$	
Methane	$CH_4$	22.4	0.0002	18	1.6×10 <sup>-9</sup>	

### TABLE 18.1 Concentration of Some of theAtmospheric Gases in 1 cm<sup>3</sup> Volume

 $a_{\frac{289}{mol}} \cdot \frac{78}{100} \cdot \frac{1L}{10^3 \text{ cm}^3} \cdot \frac{\text{mol}}{24.4L} = 9.75 \times 10^{-4} \text{ g cm}^{-3}.$ 

United States (IPCC, 2001). Some of the sinks, which absorb  $CO_2$ , are oceans, soils, and trees. Each year those sinks absorb hundreds of billions of tons of carbon in the form of  $CO_2$ . Concentration of trace/greenhouse gases in the atmosphere is also highly variable over time and space. Gaseous concentration is expressed on the basis of density or  $gL^{-1}$ , and can be calculated using Avogadro's law (see the footnote to Table 18.1).

Avogadro's law (1811) states, "Identical volumes of any gas at a standard identical temperature and pressure contain the equal number of molecules regardless of their chemical nature and physical properties." This number, known as "Avogadro's number" (N'), is  $6.023 \times 10^{23}$ . It is the number of molecules of any gas present in a volume of 22.41 L and is the same for a very light gas (e.g., H<sub>2</sub>) as for a heavy gas (e.g., CO<sub>2</sub> or Bromine, Br). Avogadro's number is now considered to be the number of atoms present in 12 grams of the carbon-12 isotope (one mole of carbon is 12 g).

The concentration of atmospheric gases in a 1 cm<sup>3</sup> volume, can be calculated from the fact that a gram molecular weight of a gas occupies 22.4L of volume at standard temperature and pressure (STP). Thus, the concentration of  $O_2$  in the atmosphere is  $3 \times 10^{-4}$  gcm<sup>-3</sup>. Similarly, the atmospheric concentration of other gases can be computed (Tables 18.1).

#### **18.2 SOIL AIR**

Soil air refers to air in the soil. It is located in the air porosity, whose volume is inversely proportional to that of the soil water  $(f_a \propto \theta^{-1})$ . Thus, as the volume of soil water  $(\theta)$ increases, that of soil air  $(f_a)$  decreases, and vice versa. A compacted soil or an undrained soil has smaller amounts of soil air than a well-structured and drained soil. In a wellstructured soil the soil air content is higher with soil air occupying most of the large or macropores. In general, soil air content ( $f_a$ ) and water content ( $\theta$ ) are nearly equal at field moisture capacity for well-structured soils. The increase in bulk density ( $\rho_b$ ) decreases the total porosity  $(f_i)$  and for given water content  $(\theta)$  decreases the soil air content  $(f_a)$ . Soil air content is also affected by drainage conditions in the field as poor or improper drainage increases the water content of soil thus lowering the air content. Composition of soil air is highly variable and depends on numerous factors (e.g., soil structure, bulk density, drainage conditions). In a well-aerated soil, the oxygen content of soil air is similar to that of the atmosphere because the consumed O2 is readily replaced and CO2 generated is readily removed from the soil-air system. In soils with restricted exchange, soil air differs from atmospheric air in several respects. The  $CO_2$  concentration in soil air is much higher and  $O_2$  concentration much lower than atmospheric air. Soil air is also relatively moister than atmospheric air, and it contains numerous trace gases (e.g.,  $H_2S$ ). The composition of soil air varies greatly from place to place in the soil, as plants consume some gases and microbial processes release others (Tables 18.2 and 18.3). The amount and composition of soil air is determined by the water content of soil unless the soil is very dry. The  $O_2$  content in a well-aerated soil is higher than that of a poorly aerated soil. The latter has higher concentrations of CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O than atmospheric air. As the depth of soil profile increases, the concentration of  $CO_2$  increases with a corres-ponding decrease in O2 concentration; however, the sum of these two

	02 (	(%)	CO <sub>2</sub> (%)	
Soil management	15 cm	46 cm	15 cm	46 cm
Arable land manured	20.52	20.33	0.34	0.50
Arable land unmanured	20.32	20.35	0.34	0.45
Grassland	18.44	17.87	1.46	1.64

**TABLE 18.2** Measured O<sub>2</sub> and CO<sub>2</sub> Content in Soil Air (% by Volume) at Two Depths

Source: Modified from Russel and Appleyard, 1915.

## **TABLE 18.3** Measured O<sub>2</sub> and CO<sub>2</sub> Content (% by Volume) in Soil Air Collected During Summer and Winter

Cropping systems		$O_{2}(\%)$	N <sub>2</sub> (%)	CO <sub>2</sub> (%)
Arable land manured and cropped	Summer	20.74	79.03	0.23
	Winter	20.31	79.32	0.37
Arable land unmanured and cropped	Summer	20.82	78.99	0.19
	Winter	20.42	79.37	0.21

Source: Modified from Russel and Appleyard, 1915.



**FIGURE 18.1** Schematic of variation of concentrations of  $O_2$  and  $CO_2$  in soil air with depth.

Water table position	Date	CO <sub>2</sub> (%)	02 (%)	N <sub>2</sub> (%)
No water table	2 July	1.2	17	78
	30 July	2.0	18.5	76
	17 August	0.3	17.8	76.5
1 5 cm depth	2 July	6.8	15	75.8
	30 July	8.5	11	81
	16 August	8	7	80.2
30 cm depth	2 July	2.2	16.5	77
	30 July	6.2	11.5	73.5
	16 August	3	17	77

**TABLE 18.4** CO<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub> Contents in Soil Air for Well-Drained Treatments with Constant Water Table Depths

Source: Modified from Lal and Taylor, 1969.

concentrations never exceeds 21% (Fig. 18.1). A soil is considered healthy if the air filled pore spaces are about 50% of the total porosity, and composition of soil air is similar to that of atmospheric air. The reduced soil aeration results from excess water in the soil profile, which may be due to the poor drainage, a shallow groundwater table, soil compaction, swelling clays, or decomposition of organic matter by microorganisms with low  $O_2$  replenishment. As the water table falls below the root zone, the  $CO_2$  concentration in soil air decreases with a corresponding increase in  $O_2$  (Table 18.4). Air permeability of soil, tillage practices (Table 18.5), soil

#### **TABLE 18.5** Soil CO<sub>2</sub> Concentration Data for No-Till (NT) and Moldboard Plow (MB) Plots for Early (21 July), Mid (24 August), and Late (1 October) Season, 1998

	Average CO2 concentration (ppm)					
		no-till		moldboard plow		v
Depth (cm)	early	mid	late	early	mid	late
5	2000	3000	1000			
10	8000	6000	2000			
20	28000	23000	4000			
30	34000	24000	5000	20000	9000	3000
50	36000	28000	9000	25000	18000	8000
70	35000	27000	13000	27000	16000	10000

Source: Modified from Reicosky et al., 2002.

**TABLE 18.**6 O<sub>2</sub> Consumption and CO<sub>2</sub> Release for a Cropped and Bare Soil in January (Soil Temperature 3°C) and July (Soil Temperature 17°C)

	Cro	$pped (gm^{-2}d^{-1})$	Bare $(gm^{-2}d^{-1})$		
	Januar	y July	January	July	
02	2	24	0.7	12	
CO <sub>2</sub>	3	35	1.2	16	

Source: Modified from Curry, 1970.

temperature, and microbial activities (Table 18.6) also affect concentration of  $CO_2$  in soil air. Soil management practices, which improve soil structure, also improve soil aeration. These include no-till, residue mulch, application of manures, conversion of cropland to pasture, etc.

#### **18.3 SOIL AERATION**

Soil aeration, the process of the exchange of air ( $O_2$  and  $CO_2$ ) between soil (or plant roots and soil microorganisms) and the atmosphere is important to plant growth because it maintains  $O_2$  concentration in the root zone at the level needed for root and microbial respiration. Soil aeration is a vital process for controlling the twin processes of respiration and photosynthesis. Plant roots absorb  $O_2$  and release  $CO_2$  during respiration. The  $O_2$  in soil air also governs the chemical reactions, which provide the necessary conditions for oxidation of reduced elements (Fe<sup>+2</sup>, Mn<sup>+2</sup>), which may otherwise be toxic to plant growth. Respiration involves the oxidation of organic compounds (such as glucose), and can be represented as follows:

$$C_6H_{12}O_6 + 6O_2 \xrightarrow[Photosynthesis]{Respiration} 6CO_2 + 6H_2O + energy$$
 (18.1)

In photosynthesis, the above reaction is reversed (right to left). The total energy is 2883 kJ and biologically useful energy is 1270 kJ. The respiration process increases the concentration of  $CO_2$  in the soil pores and at the same time reduces the  $O_2$  concentration, which creates a concentration gradient, and  $O_2$  flows in the soil profile through the process of diffusion and pushes the  $CO_2$  out of the soil. The rate of  $O_2$  diffusion into the soil profile is proportional to the aeration porosity. The aeration porosity has been defined as the pore space filled with air when the soil sample is placed on a porous plate and equilibrated at 50 cm of suction ( $\Phi m$ ). The air circulation in and out of soil matrix also moderates the temperature of the soil. In addition to plant growth, soil air composition alters production and emission of trace gases (e.g.,  $CH_4$  and  $N_2O$ ).

#### **18.4 OXYGEN DEFICIENCY AND PLANT GROWTH**

The influence of soil air on plant growth is a complex process and can be grouped into direct and indirect effects. The direct influences are related to the physiological effects of  $O_2$  and  $CO_2$  while the indirect influences affect the biological and chemical transformations in the soil. A decrease in soil  $O_2$  concentration results in a decrease in aerobic microbial population and at the same time an increase in anaerobic microbial population, which is responsible for the changes in soil respiration, enzyme activity, and oxidation-reduction or redox potential. Among physiological influences, most of the effects are solely caused by the lack of  $O_2$  for metabolic activities. The  $O_2$  deficiency restricts the root respiration, growth of plant, water, and nutrient uptake, and changes root metabolism toward fermentation. The reliable index of  $O_2$  availability to plant roots is termed the oxygen diffusion rate (ODR; Glinski and Stepniewski, 1985). The diffusion coefficient of  $O_2$  increases with temperature as a result of decrease in  $O_2$  solubility (Letey et al., 1961). After a certain value of ODR, the seedling emergence remains almost a constant, below this value the seedling emergence declines very rapidly with decrease in ODR. The limiting and critical values of ODR for some crops are presented in Table 18.7. At a critical value of ODR  $(20 \times 10^{-8} \text{g O2 cm}^{-2} \text{min}^{-1})$  (Stolzy and Latey, 1964), the emergence falls to zero, i.e., no germination of seedling takes place. The

	ODR ( $\mu g \ m^{-2} \ s^{-1}$ )		
Crop	Limiting	Critical	
Barley	25	8	
Oats	30	12	
Beans	33	12	
Wheat	40	8	
Flax	40	13	
Maize	40	16	
Tomato	40	25	
Sugar beet	50	13	
Rye	50	12	

### **TABLE 18.7** Limiting and Critical Values of ODRfor Some Crops

Source: Modified from Glinski and Stepniewski, 1985.

deficiency of  $O_2$  results in restricted root respiration, which has adverse influences on plant growth, and nutrient and water uptake. The deficiency of  $O_2$  for root metabolism also leads to increase in ethanol ( $C_2H_5OH$ ) concentration, which decreases the emergence of seedlings. The adjustment of stomata aperture regulates the transpiration, heat balance, photosynthe-sis, and respiration in plants (Glinski and Stepniewski, 1985). The factors affecting stomata aperture are the partial pressures of  $CO_2$ , light, water stress, and temperature. The  $O_2$  deficiency to roots results in stomata closure (Sojka and Stolzy, 1980). The wilting thus caused, despite inundation, is called "scalding."

#### **18.5 OXYGEN DEFICIENCY AND SOIL PROPERTIES**

Increase in the degree of saturation reduces  $O_2$  content in the soil air. This scenario is very common in undrained or poorly drained soils, where waterlogging or inundation results in  $O_2$  deficiency in soil. The high water content alters soil structural and water transmission properties such as airfilled porosity at a given suction, air permeability, saturated hydraulic conductivity, infiltration characteristic, and compressive strength (Hundal et al., 1976). Soil bulk density may be higher in undrained than drained soil (Table 18.8). The saturated hydraulic conductivity, air-filled porosity at 1 bar (100 kPa), and soil strength may increase with drainage or lowering of the water table (Table 18.8). Soil organic carbon concentration also decreases with drainage or lowering of the water table (Table 18.9). Increase in soil water content also decreases soil temperature (see Table 17.11 in Chapter 17)

	Und	Undrained		ined
Property	0–15 cm	15–30 cm	0–15 cm	15–30 cm
$\rho_{\rm b}({\rm g~cm}^{-3)}$	1.29	1.36	1.22	1.32
w (%)	30.4	29.2	30.1	29.6
$K_s (cm h^{-1})$	0.1	0.08	2	0.8
P <sub>a</sub>	9	7	15	10
UCS (kg cm <sup><math>-2</math></sup> )	2.5	3.0	1.8	2.2

### **TABLE 18.8** Effect of Drainage on Soil PhysicalProperty

<sup>a</sup>Where  $\rho_b$  is bulk density; w is gravimetric moisture content at 1 bar (%); K<sub>s</sub> is saturated hydraulic conductivity; P<sub>a</sub> is air filled porosity at 0.5 bar; UCS is unconfined compressive strength. *Source:* Modified from Hundal et al., 1976.

			Depth (cm)		
Treatment		Sample number	8 to 16	16 to 24	
Drained	7		2.37	2.3	
	4		2.53	2.37	
Undrained	7		2.58	2.34	
	4		2.62	2.59	

### TABLE 18.9 Effect of Water Table Depth on SOC (Mgm<sup>-3</sup>)

Source: Modified from Sullivan et al., 1997.

, which depending upon the prevalent climate of area, can increase the intensity of hot/cold, and freeze/thaw cycles, thereby causing a change in soil aggregation and overall structural properties.

#### **18.6 SOIL RESPIRATION**

Soil respiration is the amount of oxygen consumption or CO2 evolution in the soil. The rate of soil respiration varies with space and time and depends upon soil water content, soil type, plant cover, and agriculture measures and amendments. Soil respiration can be measured both under field and laboratory conditions using various types of respirators or respirometers. The respiratory coefficient, which provides useful information on soil aeration, is the ratio of the volume of  $CO_2$  produced to the volume of  $O_2$  consumed. For a well-aerated soil, the respiratory quotient is equal to one. The aerobic or anaerobic conditions of soil can be checked as follows (Monteith et al., 1964):

 $R = R_0 Q^{T/10}$ 

(18.2)

where *R* is the flux at  $T^{\circ}C$  and  $R_0$  at 0°C and *Q* is equal to 3 (Monteith et al., 1964). The concentration of O<sub>2</sub> consumed and CO<sub>2</sub> released in a cropped and bare soil is also presented in Table 18.6 as an example.

#### **18.7 OXIDATION REDUCTION PROCESS IN SOIL**

The chemical and biochemical reactions, which occur in soil under anaerobic condition, are dentrification and reduction of manganese (Mn), iron (Fe), and sulfate (SO<sub>4</sub>). Nitrate (NO<sub>3</sub>) is reduced to nitrite (NO<sub>2</sub>), then to nitrous oxide (N<sub>2</sub>O), and eventually to elemental nitrogen (N<sub>2</sub>). The process of decrease in nitrate content with time in a flooded or saturated soil is known as denitrification. The rate of denitrification depends on soil saturation, pH, and temperature. Denitrification is an anaerobic process and an indicator of the absence of O<sub>2</sub> in at least a part of soil volume. The end products in a denitrification process are gaseous (N<sub>2</sub>O, NO, and N<sub>2</sub>) (Ponnamperuma, 1972).

$$3NO_{3}^{-} + 6H^{+} + 6e^{-} \rightarrow 3NO_{2}^{-} + 3H_{2}O \rightarrow N_{2}O + NO_{x} + 3H_{2}O$$

$$2NO_{2}^{-} + 8H^{+} + 6e^{-} \rightarrow N_{2} + 4H_{2}O$$
(18.3)
(18.4)

Manganese reduces from a manganic  $(Mn^{+4})$  to magnous  $(Mn^{+2})$  state, iron from a ferric  $(Fe^{+3})$  to ferrous  $(Fe^{+2})$  state, and sulfate  $(SO_4)$  to hydrogen sulfide  $(H_2S)$ .

 $Mn^{4+}+2e \rightarrow Mn^{2+}$ 

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+}$$
(18.5)

$$SO_4^{2-} + 10H^+ + 8e^- \rightarrow H_2S + 4H_2O$$
 (18.7)

Some of the toxic substances produced during anaerobic conditions are (H<sub>2</sub>S), ethylene (C<sub>2</sub>H<sub>4</sub>), and acetic (C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>), butyric (C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>) and phenolic (C<sub>6</sub>H<sub>5</sub>OH) acids.

The process of production of  $CH_4$  is known as methanogenesis. Methanogenic bacteria generate  $CH_4$  biologically, largely from acetate ( $CH_3COOH$ ) dissimilation and  $CO_2$  reduction. The methanogens are capable of obtaining energy for growth by converting  $CO_2$  and molecular hydrogen into  $CH_4$  and  $H_2O$ .

$$CO_2+4H_2 \rightarrow CH_4+2H_2O$$

Some methanogenic bacteria are also capable of transforming acetate into  $CH_4$  and  $CO_2$ .  $CH_3COOH \rightarrow CO_2 + CH_4 + 35.6 \text{ kJmol}^{-1}$ 

(18.9)

(18.8)

The H<sub>2</sub> is a product of anaerobic degradation of organic matter. The H<sub>2</sub> with acetate is one of the most important intermediates in the methanogenic degradation of organic matter and serves as a substrate for methanoge-nic process (Conrad, 1999). Methanogenesis is a major pathway for organic matter decay in sediments. The factors controlling methanogenesis are temperature, concentration of other electron acceptors, water table position, substrate (e.g., H<sub>2</sub>) availability, and oxygen supply (Boon and Mitchell, 1995; Grunfeld and Brix, 1999). As temperature increases, water table in the root zone rises and other electron acceptors (e.g., NO<sub>3</sub>, Fe<sub>3</sub>, SO<sub>4</sub>) reduce, methanogenesis increases (Kluber and Conrad, 1998). Methanogenesis occurs in flooded soils, as well as in soils at low water content incubated under anaerobic condition (Boon and Mitchell, 1995). Rice fields are estimated to contribute  $100\pm50$ Tg yr<sup>-1</sup> of the greenhouse gas CH<sub>4</sub> (Kluber and Conrad, 1998). Production of CH<sub>4</sub> occurs during fermentation process by anaerobic bacteria. In flooded soils, CH<sub>4</sub> appears from several days to weeks after flooding. The organic matter amendment stimulates CH<sub>4</sub> formation in alkaline soils, whereas it is suppressed in acid soils (Glinski and Stepniewski, 1985).

$$C_6H_{12}O_6 \rightarrow 2CH_3COOH + CO_2 + CH_4 + 346.8 \text{ kJmol}^{-1}$$

(18.10)

The electron transfer is the primary source of energy needed by microorganisms for various processes. Glucose releases electron upon oxidation as follows

$$C_6H_{12}O_6=2CH_3COCOOH+4H^++4e$$
 (18.11)

In anaerobic conditions O<sub>2</sub>, NO<sub>3</sub>, H<sup>+</sup>, and high valency iron and manganese accept electrons and are reduced to H<sub>2</sub>O, N<sub>2</sub>, H<sub>2</sub>, lower valency Fe<sup>+2</sup>, and Mn<sup>+2</sup>, respectively.  $0_2+4H^++4e^-\rightarrow 2H_2O$ 

$$2H^{+}+2e^{-}\rightarrow H_{2}$$
(18.12)
(18.13)

This tendency of a substance to accept or donate electrons is measured in terms of the oxidation-reduction potential, commonly known as the oxidation-reduction potential or "redox potential." It is defined as "the potential in volts required in an electric cell to produce oxidation at the anode and reduction at the cathode." The redox potential is a relative term and is measured relative to a standard hydrogen electrode also known as reference electrode whose potential is assumed to be zero. The potential has an inverse relationship with the rate of reduction of substances. The redox potential of soil is closely linked to the availability of  $O_2$ , especially at low  $O_2$  levels, and can identify the changes in availability of  $O_2$ . The redox potential can be represented as follows:

$$E_h = E_0 - \frac{RT}{nF} \ln\left(\frac{\mathrm{Ox}}{\mathrm{Red}}\right) \tag{18.14}$$

where  $E_h$  is the potential difference between the reference electrode and inert platinum (Pt) electrode,  $E_0$  is the potential of reference electrode, R is the gas constant, T is

absolute temperature, *n* is the number of electrons transferred in the reaction, *F* is Faraday's constant, "Ox" is activity of oxidized specie, and "Red" is the activity of reduced specie. From Eq. (18.14), it is clear that the  $E_h$  is proportional to the natural log of reduced and oxidized products. In well-drained soils, a sufficient amount of O<sub>2</sub> is available, therefore, they can be called oxidized systems. The typical  $E_h$  values for oxidized systems are > 400 mV. The O<sub>2</sub> disappears at about 300 mV, NO<sub>3</sub><sup>-</sup> is removed between 200 and 300 mV, and Fe<sub>3</sub><sup>+</sup>, Mn<sub>4</sub><sup>+</sup> and SO<sub>4</sub><sup>-</sup> are reduced sequentially with decrease in Eh value (Poonamperuma, 1972; Scott, 2000).

#### **18.8 FLOW OF AIR IN SOIL**

The gaseous exchange between soil and atmosphere occurs by two processes: convection and diffusion. The convective flow of air in soil occurs as a result of the total pressure difference between the soil air and

<b>TABLE 18.1</b> 0 Increase in CO <sub>2</sub> Content for
Calcareous Silty Clay Loam (SCL) and Sandy
Loam (SL) Near Field Capacity Under Tensions for
Short Period of Time

Soil	Duration minute	Tension (kPa)	CO <sub>2</sub> (%)
SCL	35	35	6.6
SCL	40	29	8.7
SCL	67	41	4.8
SL	18	39	17.4
SL	20	28	4.6

Source: Modified from Boynton and Reuther, 1938.

outer atmosphere. The pressure difference is caused as a result of  $O_2$  consumption by plant roots,  $CO_2$  production in the soil (Table 18.10), change in the barometric pressure in the atmosphere, soil temperature, moisture content, or water table depth of soil due to evaporation, drainage, or water supply by rainfall or irrigation, etc. Various studies have pointed out that convection of air in soil is predominant for shallow depths and in soils with large pores (Rolston, 1986). The convective flow of air in the soil is similar to water flow and is proportional to the pressure gradient across the flow domain. However, since air is compressible, the density and viscosity are also the functions of pressure and temperature. Unlike water flow, gravity is not important for airflow. Air is not attracted to mineral particles and occupies the larger pores. Using Darcy's law for water flow [refer to Eq. (12.3)] the convective flux ( $q_a$ ) for laminar airflow is given as follows

$$q_a \propto - \nabla P$$

(18.15)

where is the three-dimensional gradient of soil air pressure. If the permeability of airfilled pore space is  $k_{a}$  and viscosity of soil air is  $\eta a$ , then one-dimensional convective flow can be given as follows (Hillel, 1998)

$$q_a = -\frac{k_a}{\eta_a} \left(\frac{\mathrm{d}P}{\mathrm{d}x}\right) \tag{18.16}$$

If the density of soil air is  $\rho_{a}$ , then air flux  $(q_a)$  expressed as mass flow per unit area per unit time is

$$q_a = -\frac{k_a \rho_a}{\eta_a} \left(\frac{\mathrm{d}P}{\mathrm{d}x}\right)$$

If soil air is assumed to be an ideal gas at pressure, P, occupying a volume, V, then the ideal gas equation for soil air can be written as

 $PV = nRT \tag{18.18}$ 

where *n* is number of moles of gas, *R* is the universal gas constant per mole, and *T* is absolute temperature. Substituting the density,  $\rho_a = M/V$ , and M = nm, in Eq. (18.18) where *m* is the molecular weight, and after rearranging, the following relationship for density is obtained.

$$\rho_a = \frac{m}{RT}P\tag{18.19}$$

For a one-dimensional compressible fluid, the rate of change of pressure with respect to time is equal to the rate of change of mass flux with respect to length of fluid mass and can be expressed as

$$\frac{\partial \rho}{\partial t} = -\frac{\partial q_a}{\partial x}$$

Substituting Eqs. (18.17) and (18.19) into Eq. (18.20) results in

$$\frac{m}{RT}\frac{\partial P}{\partial t} = \frac{\partial}{\partial x} \left( \frac{\rho_a k_a}{\eta_a} \frac{\partial P}{\partial x} \right)$$
(18.21)

For small pressure differences,  $\rho_a k_a / \eta_a$  can be assumed a constant (Hillel, 1998).

$$\frac{\partial P}{\partial t} = \alpha \frac{\partial^2 P}{\partial x^2} \tag{18.22}$$

where  $a = (RT\rho_a k_a)/m\eta_a$ . The above equation is an approximate equation for the transientstate convective flow of air in soil. Convective flow rarely meets more than 10% of the  $O_2$  demand of plant roots (see Example). Thus, diffusion is the more important mechanism of soil aeration (Russell, 1952).

#### **18.9 FICK'S LAW AND GASEOUS DIFFUSION IN SOIL**

The gaseous transport of  $O_2$  and  $CO_2$  in the soil occurs both in the gaseous and liquid phases. The process of diffusion (random thermal molecular movement from high to low concentration; also refer to Chapter 16) maintains the air exchange between soil and surrounding atmosphere, whereas the supply of  $O_2$  and removal of  $CO_2$  from the plant roots or live tissues takes place by diffusion through water films. According to Fick's law, the mass rate of transfer of a diffusing gas through a unit area of bulk soil is proportional to the concentration gradient measured normal to the surface through which diffusion is taking place. If D is the diffusion rate (cm<sup>2</sup> s<sup>-1</sup>), C is the concentration of diffusing substances (g cm<sup>-3</sup>),  $q_x$  is the rate of transfer of mass per unit area (gcm<sup>-2</sup>s<sup>-1</sup>), and x is the distance of diffusion (cm), the diffusion of gases in both phases can be represented by the following one-dimensional equation

$$q_x = -D\frac{\partial C}{\partial x} \tag{18.23}$$

The three-dimensional diffusion of gases according to Fick's law is represented as follows:

$$q_x + q_y + q_z = -\left(D_x \frac{\partial C}{\partial x} + D_y \frac{\partial C}{\partial y} + D_z \frac{\partial C}{\partial z}\right)$$
(18.24)

where  $q_x$ ,  $q_y$  and  $q_z$  are the rate of transfer of mass per unit area, and  $D_x$ ,  $D_y$ , and  $D_z$  are gaseous diffusivity, in x, y, and z directions. The partial differential equation of diffusion can be derived, similar to Laplace's equation, by equating the difference between the inflow and outflow of a diffusing substance in a volume element to the change in concentration with time.

$$\frac{\partial C}{\partial t}\Delta x \Delta y \Delta z = -\left(\frac{\partial q_x}{\partial x} + \frac{\partial q_y}{\partial y} + \frac{\partial q_z}{\partial z}\right)\Delta x \Delta y \Delta z \tag{18.25}$$

or

$$\frac{\partial C}{\partial t} = -\left(\frac{\partial q_x}{\partial x} + \frac{\partial q_y}{\partial y} + \frac{\partial q_z}{\partial z}\right)$$
(18.26)

From Eqs. (18.24) and (18.26), assuming the diffusion coefficient is independent of direction, the differential equation for three-dimensional gas flow is obtained as follows:

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial C^2}{\partial x^2} + \frac{\partial C^2}{\partial y^2} + \frac{\partial C^2}{\partial z^2}\right) = \nabla D \tag{18.27}$$

		Diffusion coefficient $(m^2 s^{-1})$	
Gas	Density (kgm <sup>-3)</sup>	In air	In water
O <sub>2</sub>	1.429	$1.78 \times 10^{-5}$	2.6×10 <sup>-9</sup>
CO <sub>2</sub>	1.977	$1.39 \times 10^{-5}$	$1.91 \times 10^{-9}$
N <sub>2</sub>	1.251	$1.8 \times 10^{-5}$	$1.9 \times 10^{-9}$
H <sub>2</sub>	0.08	$6.34 \times 10^{-5}$	5.85×10 <sup>-9</sup>
Water vapor	0.768	2.39×10 <sup>-5</sup>	
NH <sub>3</sub>	0.771	$1.98 \times 10^{-5}$	2.0×10 <sup>-9</sup>
$N_2O$	1.978	1.43×10 <sup>-5</sup>	
$C_2H_4$	1.261	$1.37 \times 10^{-5}$	

### **TABLE 18.1**1 Diffusion Coefficient of SomeGases Under Standard Pressure and Temperature

Source: Data from Weast et al., 1989.

The one-dimensional form of gaseous diffusion in a porous medium is given by

$$\frac{\partial C}{\partial t} = D \frac{\partial C^2}{\partial x^2} \tag{18.28}$$

which is similar to Eq. (16.17) when mass flow (second term on the right hand side) is zero. *D* varies inversely with the molecular weight of gas and is a direct function of temperature and pressure of the gaseous medium. Under standard pressure and temperature, the *D* in soil air is 10,000 times greater than in soil water (Table 18.11). Under normal atmospheric pressure and 25°C, the *D* ranges from 0.05 and 0.28 cm<sup>2</sup> s<sup>-1</sup>; the value depends on the volume of phase available for diffusion. The *D* is not affected by the shape of solid surfaces or by the particle size or pore size distribution of soil solids because mean free path of diffusing molecule is generally much smaller than the width of the pores.

Considering the diffusive path in the air phase of soil, the diffusion coefficient in soil  $D_s$  is much smaller than in air  $D_a$ . The ratio  $D_s/Da$  is known as relative diffusion coefficient. The  $D_s$  and  $D_a$  are related by some function of air-filled porosity ( $f_a$ ), which are presented in Table 18.12. The tortuosity coefficient of 0.66 (Table 18.12) (Penman, 1940) suggests that straight-line paths are only 66% of total average path of diffusion in soil. Van Bavel (1952) suggested the value of coefficient to be 0.61 rather than 0.66. The advantage of using the dimensionless coefficient or ratio is that the effects of state variables such as pressure, temperature, and type of gas are cancelled.

Relationship	Reference
$\frac{D_s}{D_a} = \kappa f_a^2$	( $\kappa$ is a constant), Buckingham (1904)
$\frac{D_s}{D_a} = \frac{f_a}{[k - f_a(k-1)]}$	Burger (1919)
$\frac{D_s}{D_a} = 0.66 f_a$	Penman (1940)
$\frac{D_s}{D_a} = 0.61 f_a$	Van Bavel (1952)
$\frac{D_s}{D_a} = f_a^{1.5}$	Marshall (1959)
$\frac{D_s}{D_a} = \alpha f_a^\beta$	Currie (1960)
$\frac{D_s}{D_a} = \frac{f_a^{10/3}}{\phi^2}$	Millington (1959), Millington and Quirk (1961)
$\frac{D_s}{D_a} = -0.12 + 0.9f_a$	Wesseling and Van Wijk (1957)
$\frac{D_s}{D_a} = -0.1 + 0.9f_a$	Wesseling (1962)

### **TABLE 18.12** Models of $D_s/D_a$ as a Function of Volumetric Air Content

The  $O_2$  and  $CO_2$  can diffuse both in gaseous and aqueous systems, a diffusion constant  $K_a$  can be defined, which separates the contribution from these two phases. The diffusion constant in air ( $K_a$ ) is given as follows:

 $K_a = f_a D_a$ 

(18.29)

And diffusion constant in water  $K_w$  is  $K_w = \theta D_w$ 

(18.30)

The ratio of Eqs. (18.29) and (18.30) after rearrangement yields

$$K_W = \frac{\theta}{f_a} \frac{D_W}{D_a} K_a = a_b \frac{D_W}{D_a} K_a \tag{18.31}$$

where  $a_b$  is Bunsen's solubility coefficient.

#### **18.10 SOURCES AND SINKS OF GASES IN SOIL**

The continuity equation states that the rate of change of concentration of a diffusing gas equals the rate of change of flux with distance. Mathematically, it is expressed as follows:

$$\frac{\partial C}{\partial t} = -\frac{\partial q_x}{\partial x} \tag{102}$$

Equation (18.32) implies that a diffusing substance follows the law of conservation of matter. However, during the transport of  $CO_2$  and  $O_2$  through the soil system, the plant roots or anaerobic activities along diffusional path absorb  $O_2$  and release  $CO_2$ . Considering  $S_g$  to be a source and sink term in time and space, Eq. (18.32) is modified as follows (Hillel, 1998; Scott, 2000):

$$\frac{\partial C}{\partial t} = -\frac{\partial q_x}{\partial x} \pm S_g(x, t) \tag{18.33}$$

Substituting Eq. (18.23) into Eq. (18.33) and assuming D constant in diffusional path yields

$$\frac{\partial C}{\partial t} = -\frac{\partial}{\partial x} \left( -D \frac{\partial C}{\partial x} \right) \pm S_g(x, t)$$
(18.34)

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \pm S_g(x, t)$$
(18.35)

After a rainstorm or irrigation, the larger pores drain quickly and smaller pores or intraaggregate micropores drain slowly. The gaseous diffusion also takes place rather rapidly from interaggregate macropores. The plant roots are also confined to larger pores between aggregates but do not penetrate them. Therefore, larger pores remain well aerated whereas micropores remain anaerobic.

#### **18.11 MEASUREMENT OF SOIL AERATION**

Measurement of soil aeration involves assessing: (i) fractional pore space, (ii) composition of soil air, and (iii) rate of diffusion of  $O_2$  from atmosphere into the soil. The aeration is measured by measuring the air-filled porosity at a standard value of soil suction or soil water content. This is done by collecting a core sample from a soil at field capacity (normally 24 to 48 h after a deep wetting or at soil water suction of about 50 cm of water) and measuring air-filled space with an air pycnometer. Alternately, first obtaining total porosity from bulk density ( $\rho b$ ) and particle density ( $\rho s$ ), and subtracting the water content of Core can calculate the air-filled porosity (fa). Measurement of the relative concentration of  $O_2$ , CO<sub>2</sub>, and other gases in the soil air provides important information on the aeration and soil structure. Depletion of  $O_2$  level content in soil air is a good indicator of the restricted gas exchange in the soil matrix. This method, although static, is better than the measurement of air volume alone. However, it requires extraction

of a sample that is large enough to provide a measurement but at the same time small enough to be representative. Another drawback of this method is soil disturbance and contamination or mixing of air from the atmosphere. The repeated measurements of  $O_2$  or  $CO_2$  concentrations in soil air without extracting a sample can also be obtained by the electrode methods (McIntyre and Philip, 1964; Phene, 1986). The measurement of depletion of  $O_2$  or increase in  $CO_2$  can be made both in situ or in a laboratory by gas chromatography technique, which provides reliable measurements. The method allows rapid and precise measurement of  $N_2$ ,  $O_2$ , Ar,  $CO_2$ ,  $CH_4$ , Ne,  $H_2$ , CO, NO,  $C_2H_4$ , and  $C_2H_6$  by employing a wide range of methods, detectors, and column packing (Blackmer and Bremner, 1977). The in situ method for measuring  $O_2$  and  $CO_2$  are based on detecting the thermal conductivity by paramagnetic oxygen analyzer and potable carbon analyzer (van Bavel, 1965), respectively.

An early approach to measure aeration involved the determination of the fractional air space or air filled porosity  $(f_a)$  at a standardized value of soil wetness. This was measured by either taking a core sample from the field two days after a deep wetting, or saturating the core sample with water and then subjecting it to a suction of 50 cm. All the pores with an effective diameter greater than 0.06 mm (r =0.147/50 cm) are drained of water. The air space as a fraction of porosity now can be determined with an air pycnometer (Page, 1948; Vomocil, 1965). Alternatively, the air space can be determined by the difference of porosity and volumetric wetness  $(f_a=f_t-\theta)$ . However, these two methods are not adequate as considerable uncertainties exist in the measurement and aeration dynamics remains almost untouched.



**FIGURE 18.**2 Soil air diffusion tube installed in a greenhouse water table management experiment. Similar

#### diffusion tube is used under field conditions. Soil air sample is taken from the tube using a syringe.

The other traditional method involves the determination of the composition of soil air (Fig. 18.2). This method, although again static, is better than the measurement of air volume alone. The depletion of  $O_2$  content in soil air can be a good indicator of the restricted gas exchange in the soil matrix and between soil and the atmosphere (Fig. 18.3). Still, the main concern here is how to extract a sample that is large enough to provide a measurement but at the same time small enough to represent the sample point and to avoid disturbances and mixing of soil air or contamination from the atmosphere. The gas chromatography technique can provide reliable measurements. An alternative method, which permits repeated measurements of oxygen concentrations in soil air without extracting a sample, is based on the use of membrane-covered electrodes (McIntyre and Philip, 1964).

Soil aeration can be characterized by the oxygen diffusion rate in the soil or ODR, (Erickson and van Doren, 1960). The method is based on the hypothesis that the moisture films around plants roots and organism limit the rate of  $O_2$  diffusion. The ODR can be measured by a platinum electrometer under a constant electric potential (Lemon and Erickson, 1955). Once the  $O_2$  present near electrode surface is depleted further depletion is a function of  $O_2$  diffusion to electrode surface or current. The electric current (I, A) is proportional to the rate of  $O_2$  flux at the electrode



**FIGURE 18.3** A static chamber is used under field conditions to assess the gaseous emission over a short period of 10 to 15 minutes. (Waterman Farm, Columbus, OH, 1998.) surface and can be expressed as follows:

$$ODR = \frac{60MI}{nFA} \tag{18.36}$$

where ODR is oxygen diffusion rate (g m<sup>-2</sup>s<sup>-1</sup>), *M* is the molar mass of oxygen (32g mol<sup>-1</sup>), F is the Faraday's constant (96,500 coulombs equiv.<sup>-1</sup> mol<sup>-1</sup>), *A* is the electrode surface area (m<sup>2</sup>), and *n* is equal to four (equiv. mol<sup>-1</sup>) and is the number of electrons required to reduce one molecule of O<sub>2</sub>. The ODR values in soils vary from 0 to 200 µg m<sup>-2</sup> s<sup>-1</sup> and increase with suction and air-filled porosity of soil (Glinski and Stepniewski, 1985). The ODR method is satisfactory in soils having higher aeration and is less effective for poorly drained or flooded soils. The methods of soil aeration measurement are listed in Table 18.13. Another approach of characterizing soil aeration is to measure the air permeability.

#### **18.12 AIR PERMEABILITY**

The gaseous exchange between soil and the atmosphere and the transport of gases within the soil are complex phenomena. Characterizing soil aeration by measuring content and composition of soil air are inadequate because they do not take into account the process dynamics, directions, and rate of change. Air permeability of soils has been recognized as an important

Method	Reference
Air pycnometer	Page (1948), Vomocil (1965)
Membrane covered electrodes	McIntyre and Philip (1964)
Gas chromatography	Bremner and Blackmer (1982)
Closed chamber	Matthias et al. (1980)
Flow through chamber	Denmead (1979)

### **TABLE 18.13** Methods of Measurement of Soil Aeration

parameter for soil aeration and contaminant remediation techniques and is fundamental to our understanding of environmental problems in the vadose zone. The vadose zone comprises the region between the land surface and underlying groundwater aquifers varying in depth and composition. It is the geologic zone through which water, solutes, nutrients, and/or contaminants travel prior to reaching groundwater. In agricultural research, knowledge of air-filled pores, pore size distribution, tortuosity, air permeability, and their variation along the cross section or depth is important to describe aeration, structure, and compaction of the soil. Precise impact of these parameters on crop yield is not known. In general, poor structure, low air-filled porosity, and water permeability adversely affect crop yield (Moore and Attenborough, 1992). Air permeability of porous media, including soils, is governed by the convective transport of air through the media under a pressure gradient. The gaseous flow as a consequence of the pressure head difference is often reported as the mass flow of gas. The other mechanism of gas transport is the diffusion, which occurs due to the change in concentration gradients or the partial pressures of the components of the gaseous mix. If the concentration and pressure gradients exist concurrently, both these processes can occur simultaneously. The mass flow of gas is important when differences in pressure are due to the change in barometric pressure, temperature, or soil water content. However, diffusion is considered the primary mechanism.

In general, a soil matrix consists of a mixture of fluid and gaseous phases. Since viscosity of air is small compared to that of water, soil air remains at most phases in the soil matrix at or near atmospheric pressure. A small pressure gradient is sufficient for soil air to move into or out of the soil system. As a result it has a negligible effect on flow of water and therefore most water transport analysis ignores the simultaneous movement of soil air. The negligible influence due to the low-pressure gradients in soil air is generally, but not necessarily always, true. In case of border irrigation, effects of air compression ahead of the wetting front during infiltration of water into the soil can occur (Dixon and Linden, 1972; Morel-Seytoux and Khanji, 1974). During drainage, air entry through the restrictions within the soil pore space causes surge of water in the draining soil columns (Corey and Brooks, 1975). Airflow through soils is essentially nondestructive and air permeability is sensitive to the changes in soil structure (Corey, 1986). Air permeability can be used as a soil quality indicator to characterize the changes in soil structure resulting from different soil management practices (Ball et al., 1988).

Air permeability is a function of pore characteristic and several soil hydrological properties, which are often more difficult to measure. Air permeability at -100 cm soil suction is a potential indicator for providing information about changes and differences of soil structure (Kirkham et al., 1958). Air permeability is related to air-filled macroporosity at different water contents to identify the changes in soil structure and soil water dynamics by soil management practices and biological activities (Blackwell et al., 1990), which are useful for studying the remediation of contaminated soils by modeling the soil-vapor extraction system (Moldrup et al., 1998). Tortuosity expresses a structural condition of soil and can be used as an index of soil structure (Moldrup et al., 2001). Soil structure has a strong influence on air permeability, and convective transport of air takes place through the larger pore networks in well-structured soils. The flow pattern in wellstructured soils can be different for the air and water flow because of the differences in geometries and tortuosities of the two mediums. The saturated hydraulic conductivity is strongly correlated to air permeability at -100 cm of suction (Loll et al., 1999). The relationship between air permeability and saturated hydraulic conductivity in undisturbed soil media can be developed using pore scale network models (Fisher and Celia, 1999).

#### **18.12.1 Governing Principles**

According to Darcy's law for laminar flow, velocity of a given fluid is proportional to the pressure difference and inversely proportional to the length of flow path (Kirkham, 1946). Therefore, Darcy's law is applicable for the airflow through soils. The pore sizes and macropores or cracks greatly contribute to airflow in a soil. According to Poiseuille's