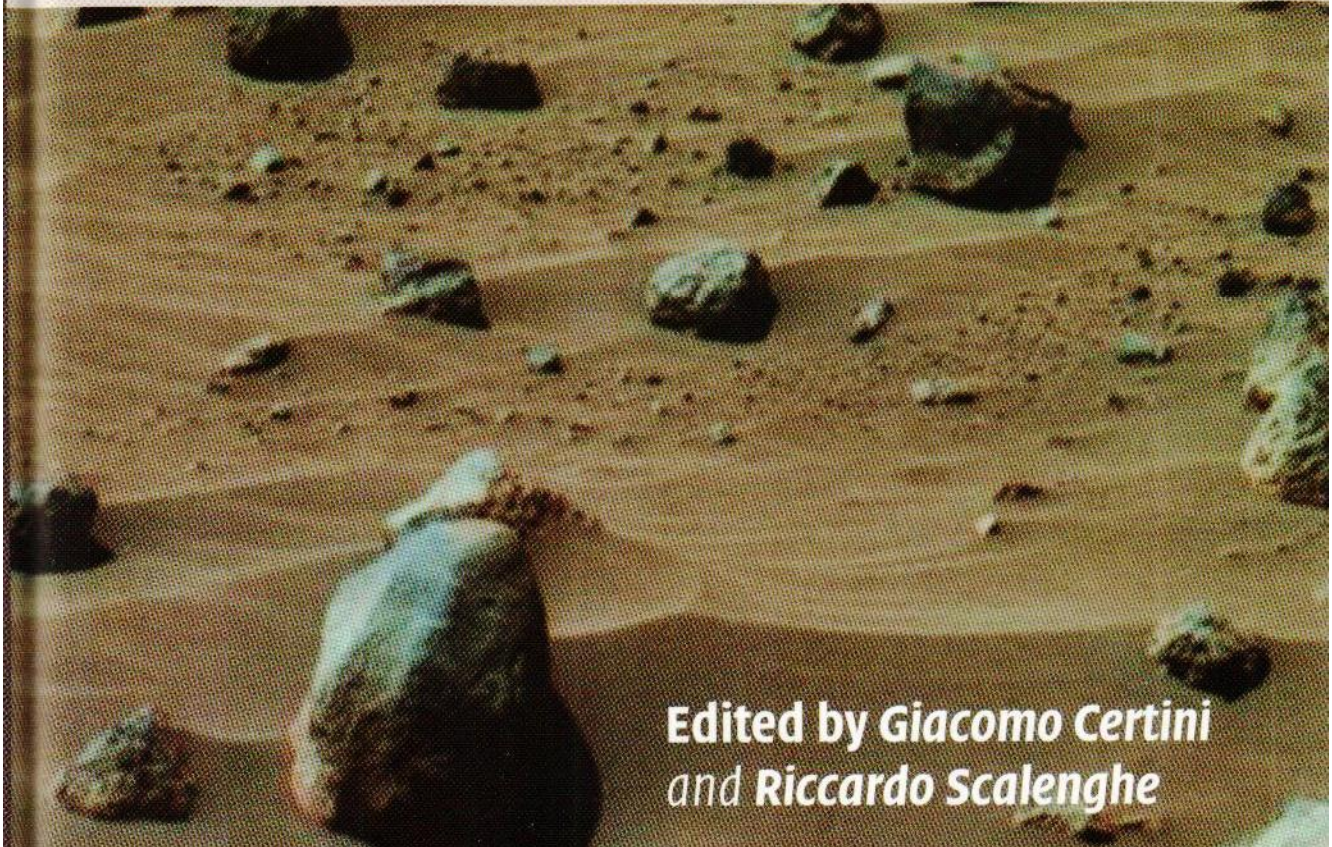
Soils
Basic Concepts *and* Future Challenges



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6

Soil phases: the gaseous phase

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Soil acts as a global source, sink and reservoir of gaseous substances contributing to the control of the composition of the atmosphere and affecting the climate conditions of the planet. Despite the importance of the soil gas phase, the study of the processes of production, consumption, and transport of gases in soils still suffers from many uncertainties, particularly methods of measurement. Most frequently, soil gases are monitored as fluxes, or net gas flows at the surface, from which the soil capacity to adsorb or release some gaseous substances is assessed. Surface flux measurements ignore the processes that operate in the soil, and thus many questions remain regarding the mechanisms controlling the fluxes. Another shortcoming is that often the gaseous phase of soil is studied separately from the liquid and solid phases, resulting in serious errors in quantitative evaluation of the soil's capacity to produce, absorb, release and accumulate gaseous substances. The problem concerning the mechanisms and forms of gas transport in such a complicated porous medium also remains open and this restrains the modelling of the gaseous phase dynamics, its vertical and lateral distribution in different types of soils. The spatial and temporal irregularities in gas dynamics require changes to the standard approach of the field studies being carried out only in warm vegetated seasons. Some of these problems will be discussed in this chapter as related to quantitative analyses of the gaseous phase composition and its state in the soil.

6.1 Gaseous components of soil

Soil atmosphere is a mixture of gases and vapours, filling water-free pore space and interacting with soil liquid and solid phases. The composition of the soil

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gaseous phase is very dynamic and diverse, containing both natural components and pollutants. Inorganic gases (N_2, O_2, CO_2, etc.), vapours (H_2O, NH_4, etc.), and volatile organic components (carbohydrates, organic acids, alcohols, oils, pesticides, etc.) are commonly present. Some of these components are relatively well known and studied, but a large fraction of the gaseous compounds remains poorly investigated and their role and behaviour in the soil is unclear. In particular, trace gases and vapours, which have concentrations in the soil air of 10–100 ppm (parts per million), are particularly poorly studied. However, modern techniques such as gas chromatography and infrared spectroscopy allow solutions to this problem (Smagin, 2003). For example, high-performance gas chromatography on capillary columns enabled the identification of more than 50 natural volatile organic compounds, such as butane, propane, pentane, octane, their chlorine and methyl derivatives, cyclohexane, methanol, ethanol, higher alcohols, isoprene, benzene, etc. (Fukui and Doskey, 1996). These gaseous components are first of all the products of soil metabolism, but some of them supposedly carry out the functions of regulation and signals (information transfer) in the soil as a bio-inert system. In this case a study of the natural volatile organic compounds will be one of the more important tasks in future for soil science, since it enables understanding of complicated mechanisms of the soil and ecosystem organization and management.

Analysis of the soil atmosphere (X) expresses the amount of the gas of interest (V_g) as a ratio to the sampled volume (V_t): $X\% = 100V_g/V_t$, ($0.01\% = 100$ ppm). However, because the gaseous phase volume strongly depends on the atmospheric pressure (P) and temperature (T), it is more accurate to report the mass concentration of the gas:

$$C_g\,(\mathrm{g\ m^{-3}}) = X\%\ PM/(100RT) \tag{6.1}$$

where P is the atmospheric pressure (Pa), M is the molar mass (g m^{-3}), R is the universal gas constant (8.31 J mol^{-1} K^{-1}), T is the absolute temperature (K).

For example 1% CO_2 under normal atmospheric pressure (101.3 kPa) and 20 °C (293 K), according to Eq. (6.1), gives:

$$C_g = 1 \cdot 101.3 \cdot 1000 \cdot 44/(100 \cdot 8.31 \cdot 293) = 18.3\ \mathrm{g\ m^{-3}}.$$

For vapour, which has a critical content or saturated concentration ($C_g{}^0$), it is convenient to use a relative concentration ($C_g/C_g{}^0$). For example, the relative humidity of water ($\mathrm{RH} = C_g/C_g{}^0$) theoretically varies from 0 to 1.

A variety of methods have been developed to sample the gaseous phase of soil. The simplest way is direct probe sampling using thin tubes or needles placed at different depths of the soil and samples collected by vacuum pump or syringe. More complicated techniques require the application of stationary sample devices (chambers). The membrane diffusion technique is based on the capacity of polymeric membranes to pass air and dissolved gaseous components into an isolated chamber. Alternative techniques convenient for wetlands have superseded probe sampling. In these techniques, a small chamber is filled with an inert gas or atmospheric air and is then placed in wet soil until the concentrations of gases within the encapsulated chamber space (air bell) and outer soil air reach equilibrium. Then the gases are collected from the chamber, and the chamber is filled by a new aliquot of inert gas.

Biophysical and biochemical processes of gas production, consumption and mass-transfer in the soil determine the composition of the soil gaseous phase. Due to intensive biological activity, the composition of air in soil differs strongly from that of the atmosphere. Dry atmospheric air consists of 78.1% N_2, 20.9% O_2, 0.95% Ar, and 0.07% other gases, including 0.036% CO_2. The variation in N_2 and Ar contents in soil air is relatively small (77–82% for the sum of these gases), however the concentrations of CO_2 and O_2 can vary from 0.03% to 20% for CO_2 and 0.05% to 20.5% for O_2. Typical gas profiles for different soils and wet porous media are shown in Fig. 6.1. The content of C-gases (CO_2 + CH_4) regularly increases with depth and reaches maximum values (4–6%, up to 12%) at depths of 30–80 cm in hydromorphic soils (Smagin *et al.*, 2000). In contrast, O_2 shows maximum concentrations in topsoil layers since the atmospheric air is the source of this gas. The concentration of O_2 gradually decreases with depth to levels of 15–18% in well-drained soils and 3–6% in wetlands. The relative humidity (RH) or water vapour concentration in the soil is mostly near 1, and only in dry arid soils do RH values reach 0.7–0.5 or less.

6.2 Sources, sinks and transport of gases in the soil

Consumption and generation of gases are controlled by the biological activity of soil as well as by abiotic physicochemical processes. Among abiotic processes dissolution and sorption strongly influence the state of gaseous components in the soil. The simplest equilibrated thermodynamic approach allows estimation of the distribution of gas between liquid, soil and gaseous phases by the following models:

$$C_l = a_s C_g \tag{6.2a}$$

$$C_s = K_h C_g \tag{6.2b}$$

where: $C_{g,l,s}$ ($g\,m^{-3}$) are the concentrations of the gases in the corresponding phases, a_s the specific solubility, K_h the Henry's constant of gases sorption, which usually varies from 1 to 5 in mineral dry soils and reaches 10–60 in organic

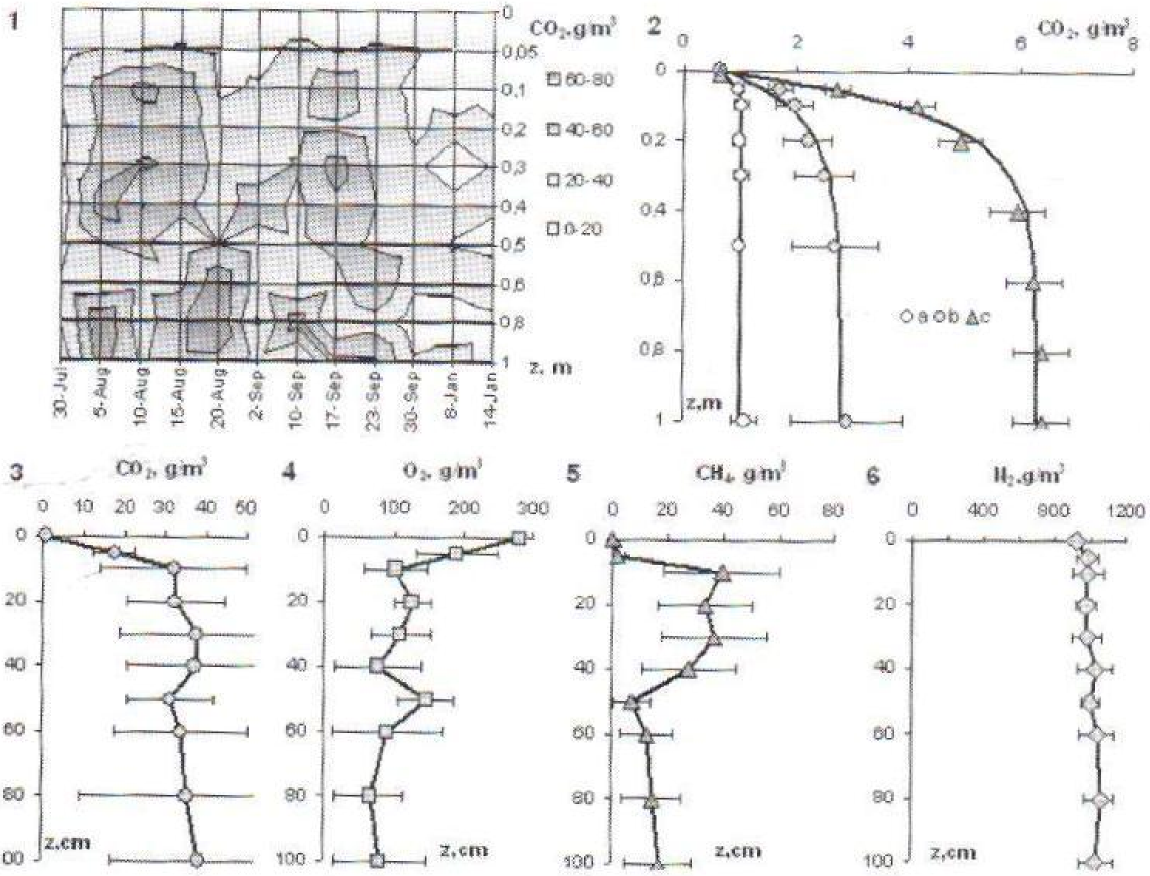

Fig. 6.1. Measurement of gases distribution in different soils: (1) CO_2 dynamics in soddy-alluvial soil (Moscow region, in 2000); (2) average profiles of CO_2 in sandy forest soddy-podzolic soil of the Moscow region (a – winter 1990, b – summer 1989), and in loamy arable soddy-podzolic soil (c – summer 1997); (3–6) average profiles of various gases in Bakcharsky bog (West Siberia, in 2000).

samples such as humus and peat. Some of the gases are dissolved in the water in appreciable amounts (SO_2, NH_3, H_2S, Cl_2, CO_2), but most of them have a small solubility (O_2, N_2, CH_4, CO, NO, H_2). The solubility of many gases in deionised water is well known and easy to obtain from specialized handbooks as a function of temperature. Solubility of gases strongly depends on the composition of the soil liquid phase. For CO_2 the dependence of solubility on pH of the water is:

$$a_s = a_t(1 + K_1/10^{\mathrm{pH}} + K_1K_2/10^{2\,\mathrm{pH}}) \tag{6.3}$$

where a_t is the tabulated solubility (in deionised water), K_1 and K_2 are the tabulated constants of dissociation of carbonic acid at first (HCO_3^-) and second (CO_3^{2-}) stages in deionised water. According to this equation, the specific solubility of CO_2 in acid soils (pH = 5) is the same as the tabulated value, but for alkaline soils (pH = 8–9) a_s exceeds a_t many times. For example, the solubility of CO_2 in deionised water (pH = 6.5 at 20 °C) is 0.88, while it is 38 for pH = 8 $\{a_s = 0.88(1 + 0.42 \cdot 10^{-6}/10^{8} + 0.42 \cdot 10^{-6} \cdot 0.40 \cdot 10^{-10}/10^{16}) = 37.99\}$. Therefore, at pH = 8 and under equilibrated conditions the CO_2 concentration in the liquid phase is approximately 38 times higher than in the gaseous phase.

The application of the equations (6.2) and (6.3) is possible if the time of establishment of the interphases equilibrium is relatively small as compared with the dynamics of gases in soil. Otherwise, more complicated models of gases dissolution and sorption should be applied. An analytical solution of these models takes the form:

$$C(t) = C_e + (C_0 - C_e)\exp(-kt) \tag{6.4}$$

where: $C(t)$ is a variable from time concentration of the gases at liquid or solid phases, C_e its equilibrated value, which is given by Eq. (6.2), k a kinetic constant. Experimental evaluation shows that k in separated liquid phase as well as in wet soils varies from 0.15 to 0.35 h^{-1}. In dry porous medium the value k ranges from 2–5 h^{-1} (mineral soils) to 10 h^{-1} (peat). For example, it may be necessary to estimate how much CO_2 will be dissolved into the fresh rainwater (pH = 6.5, $C_0 = 0.03\% = 0.54$ g m^{-3}), which has penetrated the soil during 2 hours, if the concentration of CO_2 in the soil air is $C_g = 20$ g m^{-3}, temperature is 15 °C, and kinetic constant is $k = 0.2$ h^{-1}. From equations (6.2) and (6.3) it is easy to calculate the specific solubility (a_s) and after that to obtain the equilibrated concentration of CO_2 in the soil solution: $C_e = a_s C_g = 44.2$ g m^{-3}. Then the current concentration of CO_2 in the soil solution can be evaluated by Eq. (6.4) as: $C(t) = 44.2 + (0.54 - 44.2)\exp(-0.2*2) = 14.9$ g m^{-3}. This is only a third of the value at the equilibrium (44.2 g m^{-3}) obtained by Eq. (6.2).

The complete description of gas interactions in wet porous medium is based on a combination of the kinetic model of dissolution of gases with sorption on solid particles following mass-transfer through the water films (McCoy and Rolston, 1992).

6.2.1 Biological consumption and generation of gaseous components

Biological consumption and generation of gaseous components of soil generally predominate over physical (sorption, condensation and dissolution) and physicochemical (chemisorption and reactions in the bulk) mechanisms; in fact, soil sterilization results in an abrupt decrease in gas exchange by the medium. However, neglecting abiotic processes results in serious errors in the interpretation of experimental data about the soil capacity to adsorb, accumulate and emit gaseous substances.

In the case of the laboratory experiment, the specific rate of gas emission (U) is calculated from the net change of concentration (ΔC_g) in the vessel airspace:

$$U = \Delta C_g / (\Delta t \cdot m_s) \tag{6.5}$$

where m_s is the weight of dry soil. The gas produced from the sample during the incubation is partly dissolved in the soil moisture and adsorbed by the solid phase. Therefore, the real emission rate (U^{real}) is higher than the gas increment measured. On the contrary, in field experiments, the CO_2 production may be overestimated, because a part of the gas adsorbed and dissolved in the soil passes into the airspace of the vessel. The discrepancies with the real emission rate can be considerable in both cases (Table 6.1). In the laboratory, the correction is made experimentally upon degassing (desorption) of the sample by rapid heating by microwave or by evacuation.

The biological consumption and production of gases are strongly controlled by such thermodynamic factors as temperature (T) and water content (W) of the soil. It is intuitive that the highest exchanges ($U_{\max}$) occur at the optimal temperature and moisture for biological activity (usually $T_m \approx 25$–30 °C and $W_m \approx 0.6$–0.8 W_s, where W_s is the water content at saturation). For organic matter decomposition and CO_2 emission the following equations are suggested:

$$U_{(\mathrm{T,W})} = f_{(\mathrm{T})} \cdot f_{(\mathrm{W})} \cdot U_{\max},$$

$$f_{(\mathrm{T})} = Q_{10}^{\;0.1(T-Tm)}, \quad f_{(\mathrm{W})} = (W/W_{\mathrm{m}})^{a}\{(1-W)/(1-W_{\mathrm{m}})\}^{b} \tag{6.6}$$

where $W_m = a/(a+b)$ is the moisture at maximum biological activity ($U_{\max}$), a, b are empirical constants, $Q_{10} \approx 2$ is the *temperature coefficient*, definable as the change in the rate of a process as a result of increasing the temperature by 10 °C.

The models of biogenic production and consumption of the gases must thus include biophysical and biochemical kinetic mechanisms, like the simple linear kinetic models or the non-linear Michaelis–Menten's dependency of microbial growth and rate of fermentative reactions with the substrate concentrations (Cho *et al.*, 1997; Kruse *et al.*, 1996; Rudolf *et al.*, 1996). Another approach is through the application of kinetic models of organic matter transformation in the soil in order to forecast emission of gases. For example, the kinetic constant of carbon decomposition in peat compost is $k = 0.5$ y^{-1} and the initial store of organic carbon is $C_0 = 5$ kg m^{-2}. Here, using a well-known linear model for organic matter decay in the soil ($C(t) = C_0 \exp(-kt)$), one could estimate annual emission of CO_2 from the soil as $(C_0 - C(t))44/12 = (5-5\cdot\exp(-0.5\cdot1))44/12 = 7.2$ kg CO_2 m^{-2} y^{-1} (44 and 12 are the molar masses of CO_2 and carbon, respectively). Note that the value obtained exceeds the contribution of automobile exhaust to total CO_2 emission in urban areas (that is 10^5 tonnes per 10^5 ha, or

Table 6.1. *Emission of* CO_2 *measured (U) and real* (U^{real}) *in four soils of the Moscow region, Russia (in mg* kg^{-1} h^{-1}*)*

Layer (cm)	U	U^{real}
Soddy-podzolic forest soil (laboratory experiment)		
0–10	1.30 ± 0.28	2.21 ± 0.43
10–20	0.57 ± 0.17	0.86 ± 0.25
20–30	0.31 ± 0.05	0.49 ± 0.08
30–40	0.27 ± 0.05	0.35 ± 0.05
40–50	0.23 ± 0.09	0.31 ± 0.11
Soddy-podzolic arable soil (field experiment)		
0–10	3.12 ± 0.59	2.35 ± 0.55
10–20	1.33 ± 0.41	0.61 ± 0.21
20–40	1.27 ± 0.22	0.52 ± 0.16
40–60	0.41 ± 0.07	0.20 ± 0.03
60–100	0.20 ± 0.04	0.15 ± 0.04
Alluvial-bog silty-peat-gley forest soil (field experiment)		
0–10	32.33 ± 8.93	8.30 ± 2.39
10–20	30.04 ± 9.12	3.95 ± 1.20
20–40	24.21 ± 6.57	3.79 ± 1.25
40–60	14.13 ± 4.28	3.57 ± 1.02
60–100	9.51 ± 2.87	1.32 ± 0.41
Eutrophic humus-peat arable soil (laboratory experiment)		
Surface	4.8 ± 0.37	10.6 ± 0.49
0–5	1.06 ± 0.15	4.86 ± 1.15
5–10	2.26 ± 0.15	7.00 ± 0.25
10–20	1.31 ± 0.06	3.68 ± 0.35
20–30	1.46 ± 0.37	4.13 ± 0.68
40–50	0.56 ± 0.38	2.46 ± 0.73
60–70	0.17 ± 0.05	0.63 ± 0.35

Source: Smagin (2000).

0.1 kg m^{-2} in Moscow) by approximately 70 times! More complicated non-linear models of organic matter dynamics and gases production in bio-inert systems with vibrations and trigger regimes provide more plausible data (Smagin, 1994, 1999).

6.2.2 *Transport of gases and vapours in the soil*

The problem of mass transfer of gases in soil remains open. Conventional concepts assign the major role of gas transport to molecular mechanisms, in particular isothermal diffusion, a mass transfer proportional to a concentration gradient (dC/dz):

$$q = -D\mathrm{d}C/\mathrm{d}z \tag{6.7}$$

where q is the gas flux and D the diffusion coefficient. This coefficient or its dimensionless analogue – relative gas diffusivity (D/D_0) – depends on air-filled porosity (ε_a). Linear, polynomials, or exponential models are used for approximating this dependence (Campbell, 1985). The simplest Penman equation for macroporous media has the form $D/D_0 = 0.66\varepsilon_a$. The diffusion coefficient of gaseous components in the atmosphere (D_0) is on the order of 10^{-5} m^2 s^{-1} (1.77, 1.39, and $2.13 \cdot 10^{-5}$ m^2 s^{-1} for O_2, CO_2, and H_2O under standard conditions $T = 273$ K, $P = 101.3$ kPa) and may be corrected with temperature and air pressure: $D_0 = D_0^{st}(T/273)^n(101.3/P)$, $n = 2$ for O_2, H_2O, and 1.75 for CO_2 (Campbell, 1985). In water the gas diffusion strongly decreases ($D_l = 2 \cdot 10^{-9}$ m^2 s^{-1} for O_2 and CO_2) and water-saturated soil layers are considered to show gas mass transfer near zero (Campbell, 1985). However, experiments show that in some water-saturated soils ($\varepsilon_a \to 0$), the diffusion coefficient can be 3–10 times higher than in the pure water probably because of the surface diffusion.

Temperature gradients in the soil (dT/dz) lead to a combined thermodiffusion molecular mass transfer:

$$q = -D \cdot \mathrm{d}C/\mathrm{d}z - D \cdot k_T \cdot (\mathrm{d}T/\mathrm{d}z)/T \tag{6.8}$$

where k_T is a thermodiffusion constant proportional to gas concentration. Theoretically, the contribution of the temperature gradient is lower than that of the concentration gradient, and can be neglected for gas mass transfer in soils, except for gases that have low gradients ($dC/dz \to 0$) near the soil surface (N_2, O_2) and for water vapour, where the thermodiffusion can be 3–4 times higher than the simple diffusion flux if the temperature and concentration gradients are co-directional. Other reasons for enhanced thermal diffusion can be the macroscopic movement due to the convective fluxes of soil air in the gravity field (natural convection) and the thermal circulation of air (thermal sliding) in capillary-porous media, which are not well understood in soil science (Smagin, 2000).

Convective macroscopic mass transfer occurs both in the soil air and moisture, with viscous hydrodynamic media capable of moving in the gravity field (natural convection) or under the effect of external pressure differentials (induced convection). Natural convection in the gaseous phase can involve both the downward movement (gravitation flow) of denser air (cold or enriched in heavy gases) and the upward flows of rarefied air (heated or enriched in light components). The reasons for the difference in density of the soil air and the atmosphere – solar radiation (heating) and biogenic activity (composition changes) – are almost constantly present in the soil. Natural convection can be an essential factor of mass transfer, because its rate is comparable to diffusion and its duration is unlimited. Theoretical analysis shows that for evaporation from surfaces with a characteristic length of about 1 m, the convective currents can exceed diffusion more than 100 times. The same theoretical result is obtained for CO_2 gravitation flow in macropores. Another well-known example of natural convection is the upward transport of gases by bubbles to the surface of wetlands and paddy soils. Its contribution to the total mass transfer through the flooding layer is estimated at 10–30%. The biophysical mechanism of bubbles formation under unsaturated conditions is determined by the microbial kinetics of gases production, which lead to local saturation of the solution near the colony of micro-organisms where bubbles are formed. However, in a porous medium such as a wet soil bubbles can only travel short distances because of restriction by the solid phase.

Induced convection in the gaseous phase (transfer under the effect of a pneumatic pressure gradient) is apparently less significant, because its causes (wind gusts, variations in the groundwater table, and movement of rainfall front) are generally episodic. Convective flux of a gas (vapour) with a concentration C_g in the liquid phase can be described by the following equation:

$$q = -(K/\eta)C_g \mathrm{d}P_g/\mathrm{d}z \tag{6.9}$$

where K is the air permeability of the soil, η the dynamic viscosity of the air, and $\mathrm{d}P_g/\mathrm{d}z$ the pneumatic pressure gradient. K depends on the diffusion coefficient and on air-filled porosity or water content in the soil. According to Kozeni–Karman's theory, the second dependence has the form $K = m \cdot \varepsilon_a{}^n$, where ε_a is the air-filled porosity and m and n are empirical constants ($n = 0.5 - 2$ for macroporous media like sands and peat, $n = 2 - 10$ for loamy and clay soils) (Lauren, 1997). In solidly built substrates like soil screens, which cover urban wastes in landfills, air permeability should be low over a large interval of porosity. This guarantees low methane emissions from the landfill until the ε_a value is less than 30–40%. In natural soils, even minor pressure gradients (1 Pa m^{-1}) at the usual levels of air permeability ($K = 10^{-10}$ m^2) and air viscosity ($\eta = 10^{-5}$ Pa·s) can induce fluxes of 10^{-5} m s^{-1}, which are comparable to the diffusion rate of gases in the atmosphere. However, the evaluation of these fluxes in the soil is hampered by the lack of sensors sensitive to minor variations in air pressure.

The physical mechanisms determine a further form of mass transfer of gases: preferential (local) transport. If diffusion was the predominant movement mechanism, gases should be uniformly distributed in the soil. However, when the soil is waterlogged and, hence, the diffusion rate decreases by several orders of magnitude, the movement of gases becomes discontinuous and represents a preferential transfer by the broadest channels in the structure of a porous body, as well as inside and along the surface of plant stems and roots (the so-called 'vascular' transport). In well-drained soils, zones of preferential gas transfer can also form because of irregular moistening, compaction, and the presence of air-bearing channels.

6.3 Agroecological evaluation of the soil air

The composition and state of the soil air strongly influence fertility and productivity of the soil. Air and water in the soil should be balanced and a lack of aeration, as in the case of high water content, suppresses the growth of most terrestrial plants and aerobic microflora. In particular, oxygen in the soil is utilized in respiration to provide the energy for roots to grow and to uptake nutrients. Bacteria, fungi and other soil micro-organisms oxidize organic matter aerobically and therefore consume a large amount of oxygen. In order to evaluate aeration of the soil and its gas regime, it is important to know O_2 and CO_2 concentrations or store in the soil, air-filled porosity (ε_a), water saturation degree (W/W_s), relative gas diffusivity (D/D_0), air entry potential of soil water (P_e) and some other characteristics (Smagin, 2003). For many crops, symptoms of oxygen starvation and root intoxication manifest themselves when the concentration of O_2 is below 15–17% and CO_2 content in the soil air is higher than 3–4% (Campbell, 1985). In wetlands the content of O_2 in the gaseous phase can drop to 3–6% or less; however, a certain amount of O_2 is in the dissolved state. For example, in a 10 cm surface peat layer with porosity 90%, air filled porosity 5% and O_2 volume 6%, the store of gaseous O_2 content would be approximately 400 mg m^{-2}; in these conditions the amount of dissolved oxygen in gas equilibrium with the atmosphere reaches 1200 mg m^{-2}, that is three times more than that in the soil air. The concentration of gases in the soil is not a general criterion for poor aeration because, the soil being an open system, the demands of roots and micro-organisms can be satisfied even under low O_2 content if the velocity of its transport from the atmosphere is equal to the consumption rate. Traditionally, the diffusion of gases in soil is regarded as a general mechanism of aeration. Hence the relative gas diffusivity (ratio between the gas diffusion coefficient in the soil, D, and that in the atmosphere, D_0) is a widespread index of aeration in the soil. For many crops, D/D_0 values lower than 0.06 indicate the first symptoms of O_2 starvation in soils. Crop damage and growth limitation as well as anaerobic conditions in the soil arise if D/D_0 decreases to 0.02 (Letey, 1985; Smagin, 2003). The range of D/D_0 from 0.02 to 0.06 usually corresponds to an air-filled porosity of 6–10%. Taking into account the relationship between air-filled porosity (ε_a), water content (W), soil bulk density (ρ_b), particle density (ρ_s) and water density (ρ_l):

$$\varepsilon_a = 1 - \rho_b/\rho_s - W\rho_b/\rho_l, \tag{6.10}$$

it is easy to calculate, for a wide interval of soil bulk density ($1.0 < \rho_b < 1.6$ Mg m^{-3}), that values of water saturation degree (W/W_s) higher than 0.85–0.90 will be critical for the plantation because the soil is poorly aerated (Smagin, 2003). The water regime analysis of several urban loamy soils in Moscow shows that poor aeration lasts for 10–25% of the field season from May to October, especially for soils with high bulk density (e.g. paths, sports-grounds, lawns). These soils should therefore be managed to provide an adequate amount of O_2 for plant and microbial respiration by tillage, drainage, structure optimization and other measures. If the water regime of the soil is controlled by tensiometers, the lack of aeration can be diagnosed simply based on the air entry water potential (potential at which the largest water-filled pores drain). According to Campbell (1985) this value strongly depends on particle-size distribution and structure of the soil and varies from -0.6 to -9.0 J kg^{-1}. Aeration of the soil and renewal of soil air control the biota respiration and trace-gases emission. These processes as well as the global gas function of soils will be regarded in the next section.

6.4 Gases emissions and global ecological functions of the soil

Emission (Q) is the gas flux from the soil surface to the atmosphere, which can be determined as the mass of gaseous substance (m) that passes through the cross-section area of the soil surface (S) per unit of time (t): $Q = m \cdot S^{-1} \cdot t^{-1}$. Methods used for its measurement can be divided into two main groups: chamber methods and micrometeorological methods.

Chambers can be either closed or open (flow-through). They are installed at the soil surface for a short time ($\Delta t = 10$–20 min) to allow gas accumulation inside the chamber. After determination of the gas concentration increment (ΔC_g) within the closed chamber or in the stream of air (carried gas) that is drawn through the open chamber, the gas emission can be calculated as:

$$Q = \Delta C_g V/(S\Delta t) = \Delta C_g h/\Delta t \text{ (closed chamber)} \qquad (6.11a)$$

$$Q = f\Delta C_g/S \text{ (open chamber)} \qquad (6.11b)$$

where V, S, h are parameters of the chamber (volume, area, height) and f is the air mass flow (mol s^{-1}). For longer time intervals the gas losses by diffusion from the closed chamber should be taken into account, otherwise the results can be underestimated significantly. Another reason why Q can be underestimated using the closed chamber method is the use of simple chemical traps, such as soda lime, rather than instrumental CO_2-analysers. Use of chemical traps has been shown to have a tendency to underestimate soil-surface CO_2 fluxes by 10–100% (Norman *et al.*, 1997).

Micrometeorological methods allow integral evaluation of the fluxes of gases at landscape scales (areas of the order of 10 000 m^2), but they require expensive highly sensitive analytical equipment. The concentrations of gases (C_1, $C_2 \ldots$) emitted from the soil are measured in the atmosphere at different heights (z_1, $z_2 \ldots$) and their fluxes from soil are calculated using a simple model of turbulence gas transfer, $Q = D_T \Delta C_g / \Delta z$, where D_T is a turbulent diffusion coefficient which requires knowledge of meteorological data, such as wind speeds, temperature and water vapour gradients, for evaluation (Campbell, 1985). One of the most popular simple micrometeorological methods, the so-called eddy correlation, allows the calculation of gas emission from the experimental data considering the simultaneous fluctuations of the wind speed (U') and the gas concentration (C_g') at a distance around 1–2 m from the soil surface and using the following formula: $Q = \rho_a U' C_g'$, where ρ_a is the air density (Sitaula *et al.*, 1995). A comparison of the different methods for measuring fluxes of CO_2 from soil shows that a good correspondence between the methods is not always observed (Norman *et al.*, 1997). Among the reasons for such discrepancies are the scale effects and spatial irregularity of the gaseous emission.

Soil respiration (CO_2 emission and O_2 consumption) has been studied in detail, but fluxes of trace gases and organic vapours remain poorly investigated. Carbon dioxide is emitted from the soil due to plant and microflora respiration. Usually, in natural well-aerated soils micro-organisms uptake O_2 and produce CO_2 at double the rate of plant roots. Both autotrophic respiration by roots and heterotrophic respiration by soil organisms are strongly correlated to annual soil surface CO_2 flux across a wide range of forest ecosystems (Bond-Lamberty *et al.*, 2004). However, the proportion changes during the field season and depends on the availability of labile organic matter in the soil, especially that derived from fresh plant residue and manure. Moreover it is practically impossible to separate respiration of roots from the respiration of rhizospheric micro-organisms that are utilizing root metabolites. The evaluation of carbon dioxide emission or soil respiration usually varies from 100 to 1000 (2000) mg CO_2 m^{-2} h^{-1}. There is often a diurnal maximum in the afternoon and a minimum in the morning (4–6 a.m.) due to the dynamics of soil temperature, biological activity and evapotranspiration. However, the presence or absence of roots and a fluctuating soil water content impacts the respiration rate more strongly than any diurnal changes. Seasonal dynamics of soil respiration depend on moisture and temperature regimes of soil. In winter, respiration is often suppressed because of low soil temperatures (Certini *et al.*, 2003), which can even imply low O_2 penetration through a frost-bound surface of the soil. However, in some soils the organic matter decay and CO_2 emission over the cold period from November to March can reach 30% of the annual values (Smagin, 1994). In the summer, low water content may inhibit root and microbial respiration. The highest respiration rates (1–2 g CO_2 m^{-2} h^{-1}) have been observed usually when fresh organic matter (litterfall, root exudates, manure, etc.) is incorporated into moist and warm soil.

Let us turn to the examination of a global role for soils in regulating the atmospheric air composition. Fig. 6.2 shows the results of the statistical processing of information concerning the global aspects of the carbon cycle that have appeared in recent decades. The total amount of organic carbon held in the soil, 1480 Pg C, means that soil is of third importance after the lithosphere and oceans. However, the soil carbon reserve is higher than that in plant phytomass by 2–3 times. The mean residence time of the organic matter in soil is long, ranging from several years for the litter layer and the labile humus to several hundred or thousand years for the most stable humus fractions (Scharpenseel, 1993). A loss of stability in the biocenosis-soil system under anthropogenic pressures can result in a catastrophically rapid mineralization of humus accumulated over centuries, as confirmed by multiple observations of the dynamics of organic matter in arable soils or reclaimed peatlands. On a global scale, the loss of organic carbon from soils during the last 130 years is estimated at 40 Pg C (Houghton *et al.*, 1992).

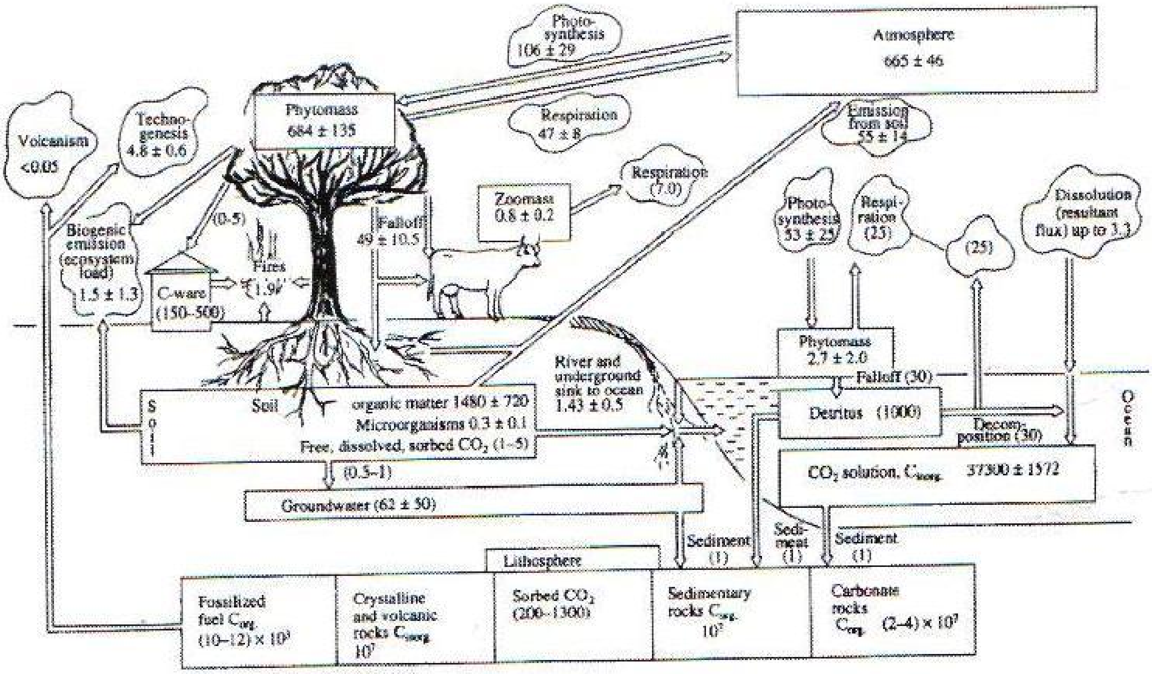

Fig. 6.2. The global carbon cycle. The scheme presents the main carbon reservoirs (the carbon content is expressed in Pg C, 1 Pg = 10^{15} g = 1 billion Mg) as well as the fluxes between them (in Pg C yr^{-1}). The conventional signs in cloud-shaped contours mark the organic carbon fluxes in the gaseous form (CO_2). The data in parentheses refer to poorly studied processes and reservoirs; they were obtained either from a single literature source or by rough calculations.

Table 6.2. *Main sources and sinks of atmospheric methane.*

Sources/sinks	Mean flux (Tg CH_4 y^{-1})
Natural sources	
Wetlands	115 ± 60
Termitaries	20 ± 10
Ocean and fresh water	20 ± 10
Anthropogenic sources	
Industry, transport	110 ± 50
Rice growing	60 ± 40
Ruminant fermentation	80 ± 20
Animal and human waste	50 ± 10
Refuse dumps	30 ± 20
Biomass and agricultural waste combustion	45 ± 15
Sinks	
Atmospheric oxidation	470 ± 50
Absorption by soils	30 ± 15
Increase in the atmosphere	30 ± 5

Source: Smagin, (2000).

It has contributed to more than 25% of the increase in the concentration of C in the atmosphere over the same time period (Smagin, 2000). Currently, the global annual emission of CO_2 from soils is evaluated at 55 ± 14 Pg C, which is near 30% of total global emission, and exceeds 10 times the technogenic contribution.

Among the gaseous microcomponents of the soil, methane exerts the greatest influence on the greenhouse effect, being much more effective than CO_2 in trapping the thermal radiation reflected by the Earth. It forms in poorly drained hydromorphic soils and wetlands. The total amount of CH_4 entering the atmosphere annually is 515–560 Tg (1 Tg = 10^{12} g = 1 million Mg), 70% of which is from biogenic sources (Bridges and Batjes, 1996). The global emissions of methane by hydromorphic soils and paddy fields (Table 6.2) are estimated at 115 and 60 Tg CH_4, respectively, which together amount to more than 30% of the total influx of this gas into the atmosphere and exceed industrial emission (105–115 Tg) by 1.5 times (Houghton *et al.*, 1992).

Methane emission from soils varies significantly in space and time. It ranges from 0.02 to 200 mg m^{-2} d^{-1}, although peak emissions up to 1000 mg m^{-2} d^{-1} can occur when there is an excess of organic substrate under optimal temperature conditions (near 30 °C).

In paddy soils and wetlands CH_4 emission can vary from 1 to 50 mg m^{-2} h^{-1} (3 ± 1 mg m^{-2} h^{-1} is the median value from log normal distribution of 221 data from different publications), while after heavy rains in periodically moistened soils of the temperate zone it ranges from 0.8 to 26.7 mg m^{-2} h^{-1} (Murase and Kimura, 1996; Toop and Pattey, 1997; Smagin, 2003). The biogenic oxidation of CH_4 to CO_2 in the soil is relatively weak (from 3.5 to 10% of the global methane sink). However, stable isotope carbon analyses ($^{13}C/^{12}C$) have shown that in some Siberian wetlands from 30% to 80% CH_4 can be transformed to CO_2 during its movement from methanogenetic horizons to the soil surface because of methanotrophic activity and the large amount of oxygen (60–100 g m^{-3}) in locally unsaturated soil conditions.

The potential absorption of carbon monoxide by soils can vary from 2–20 to 100 mg m^{-2} h^{-1}, and the global estimate of its consumption by the pedosphere is no less than 450 Tg y^{-1} versus a total influx from natural and anthropogenic sources of about 600 Tg y^{-1}. Therefore, soils are considered to be one of the most effective regulators of the content of this dangerous pollutant in the atmosphere (Ingersoll *et al.*, 1974; Seiler, 1974).

Gaseous nitrogen compounds (N_2, NO, NO_2, N_2O, NH_3) are formed and transformed in the soil due to nitrogen fixation, ammonification, nitrification and denitrification. On the whole, the rates of these processes are estimated at 0.1–10 mg m^{-2} h^{-1}, which are hundreds of times lower than the usual rate of soil respiration. Among the gaseous products of the nitrogen cycle, nitrogen monoxide (N_2O) constitutes the highest environmental hazard. The global N_2O emission was estimated 10–20 Tg N y^{-1}, 50–60% of which has a pedogenic origin (70–80% considering also the fertilizers) (Smagin, 2000). Croplands are responsible for more than 80% of anthropogenic N_2O. Field measurements give the values of specific N_2O emissions from soils in the range 0.003–3(10) mg m^{-2} h^{-1} (Smagin, 2000). It is especially important to consider the seasonal dynamics of gas emission from soils because a major share of nitrogen (up to 30% and more) is frequently lost during the short time periods after heavy rainfalls, application of fresh fertilizers, or soil thawing in spring (Bandibas *et al.*, 1994; Nyborg *et al.*, 1997). The problem of determining the role of soil in the turnover of N_2O and other gaseous nitrogen compounds is still far from being solved and estimates are highly variable (Smith, 1981; Bowden, 1986). The simple calculation of gaseous N-losses following annual mineralization of 77 Tg N fertilizer results in the release 50–60 Tg y^{-1} of gaseous nitrogen compounds into the atmosphere.

Two main gaseous compounds traditionally represent the sulphur cycle: biogenic hydrogen sulphide (H_2S) and anthropogenic sulphur dioxide (SO_2). The consumption of SO_2 by soils is characterized by rates of 20–60 mg m^{-2} h^{-1}, or up to 80% of the global anthropogenic emission of this pollutant which is 50 to 55 Tg y^{-1} (Smith, 1981; Smagin, 2000). Similar estimation is given for H_2S emission, which in wet soils can reach significant values (up to 60–100 mg m^{-2} h^{-1}).

There are hypotheses about the important role of organic sulphur gases (dimethyl sulphide, CH_3 SCH_3, carboxyl sulphide, COS, carbon bisulphide, CS_2) and sulphur hexafluoride, SF_6, although their fluxes are estimated by much lower values than for SO_2 and H_2S (Smith, 1981; Smagin, 2000).

The emission of pesticides and other fumigants from the soil is estimated to range from 10 to 100 μg m^{-2} h^{-1}, which generally represents 40–60% (up to 90% for methyl bromide) of the added amount (Smagin, 2000). Several mathematical models have been put forward for the reliable prediction of the behaviour of volatile pollutants in the soil and their release into the environment (Boesten and Van der Linden, 1991; McCoy and Rolston, 1992; Amali *et al.*, 1996; Petersen *et al.*, 1996).