

Weathering in Terrestrial Ecosystems: Carbon Sink

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Abstract: In the framework of "active planetary cover" concept the influence of weathering on the atmosphere carbon and, as a consequence, on the climate is considered. The relatively slow process of chemical weathering, which is accompanied by an uptake of carbon from the atmosphere and its transportation to the intercontinental and epicontinental seas, is significantly amplified by terrestrial ecosystems. The mechanism of amplification is explained by an increase in CO₂ concentration in the "soil" atmosphere caused by root respiration and the metabolism of micro-organisms, the so-called "respiration of soil". In accordance with Zavarzin's estimation, the concentration of CO₂ in the soil air is 60-80 times larger than in the atmosphere. All this leads to a significant acceleration of weathering in soil. It seems that such a concentration gradient cannot be maintained and it will be eroded by diffusion. It is true if we consider bare soil. But in real ecosystems the litter covers soils, so that molecular diffusion becomes prevalent. In other words, the litter can be considered as a semi-permeable membrane for CO₂. The second stage is to describe the chemical transformations of carbon within the system. However here we deal with an open system, and therefore we were compelled to develop some partial case of the theory of chemical equilibrium in open systems.

Keywords: Weathering; Carbon sink.

1. INTRODUCTION

V. Vernadsky was the person who first created the modern concept of the biosphere as an active planetary cover, which does not only passively reflected its geochemical environment but also transformed it. So that J. Lovelock [1979] has done only a next step when he has postulated that this transformation is an act of self-regulation creating optimal conditions for the biosphere existence.

Any model developed on the base of these axioms will be already the model of Vernadsky's biosphere, but any change of any axiom will give us some new model (of virtual biosphere). Svirezhev [1994, 1999] suggested the concept, in which an evolutionary tree of virtual biospheres is considered instead of the almost linear graph of Vernadsky's biosphere. In general, in our investigation we follow these works.

2. ACTIVE PLANETARY COVER AND POSSIBLE CANDIDATES TO PLAY THIS ROLE

If keeping in mind that life is a phenomenon, which can exist in some relatively narrow interval of temperatures, then immediately the following question arises: how is the planetary temperature kept within the interval? Is this a result of self-regulated interactions between the biosphere and climate (Lovelock [1979]; Schwartzman [1999]) or a purely random combination of different terrestrial and extra-terrestrial processes (Budyko et al. [1985])? Before to answer the question we introduce the following definition.

We define an active planetary cover ("planetary skin") as some system which directly affects on the climate, forms it and, in turn, its dynamics depends on the climate. The system has to possess multiple equilibria (Svirezhev et al. [2001]).

Let $T(t)$ be the mean annual temperature of the Earth, $S(t)$ be the mean solar radiation, C be the total amount of atmospheric carbon, $\sigma(C) = \sigma_0 \varphi(C)$ where σ_0 is the Stefan-Boltzmann constant and $\varphi(C)$ is a monotonous decrease function describing the greenhouse effect. The "skin" will be described by the variable p , which is

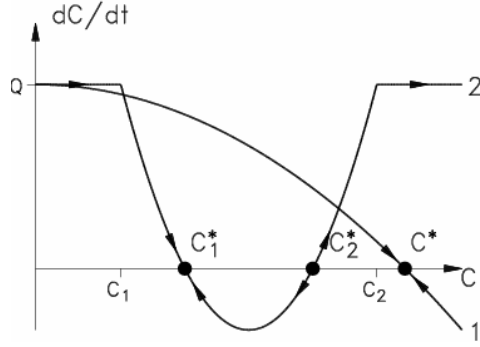


Figure 1. System phase portraits: (1) - the planet surface is weathered, only the weathering "sucks" carbon from the atmosphere; (2) the planet is covered by "green cover" with an unimodal temperature function.

a part of the Earth surface "covered" by skin with albedo α_p ; a remaining part of the surface has albedo α_q . For instance, this can be the percent of the Earth area taken over the continents. We assume that $S(t)$ and $p(t)$ are the given functions of "slow" time. Then the simplest zero-dimensional model of such sort of planetary skin can be presented in the form:

$$T \approx \left(\frac{S[1 - \alpha_q - (\alpha_p - \alpha_q)p](1 + \rho)}{\sigma(C)} \right)^{1/4}, \quad (1)$$

$$\frac{dC}{dt} = Q - \beta(T)pf_c(C), \quad (2)$$

where ρ is the coefficient of spatial correlation between $\lambda = 1 - \alpha(x)$ and $S(x)$, x is spatial coordinates that reflect a spatial interposition of skin and "free" surface on the Globe. The value $\beta(T)$ describes dependence of rate, with which the skin "sucks" carbon from the atmosphere, on the temperature. $Q(t)$ is the inflow of carbon from the mantle (volcanism).

Let us consider different candidates for the role of active cover, which can actively regulate the Earth temperature.

a) "planet with weathering". For this process $\beta = \beta_w \sim \exp(\delta T)$, $f_c \sim \sqrt{C}$. Phase portrait of the system described by (1)-(2) is shown in Figure 1. There is only one stable equilibrium C^* , which "floats" in slow time. It is the

solution of equation $\beta[T(C^*, p)]pf_c(C^*) = Q$. It is obvious that corresponding to C^* the temperature T^* can get into the tolerable interval $[T_1, T_2]$ only accidentally;

b) "planet with vegetation" (green cover). In this case $\beta = \beta_v$ is a finite unimodal function within the interval $[T_1, T_2]$ and $\beta_v \equiv 0$ outside of it. The function f_c is a monotonous increase function with saturation. The corresponding phase portrait is also shown in Figure 1. Here there are two "slow floating" equilibria: stable with lower temperature, C_1^* , and unstable with higher one, C_2^* . Because of there is one-valued connection between T and C then later on we shall use the value C as the value of T . Since $T_1 < T(C_1^*) < T(C_2^*) < T_2$ then this means that the "green cover" can maintain the equilibrium temperature $T(C_1^*)$ belonging to the tolerable interval and lying in its low part, but the stability domain of the equilibrium is very small. Its upper boundary is $C_2^* < C_2$ that corresponds to $T(C_2^*) < T_2$, i.e. it lies lower than the upper tolerable temperature;

c) "planet with vegetation + weathering". The best results in the sense of stability and maintenance of the tolerable interval for life gives the combination of "chemical" (like weathering crust) and "biological" (like vegetation) covers. Let us assume that chemical and biological pumps work simultaneously. Then the equation for atmosphere carbon is written as

$$\frac{dC}{pdt} = Q/p - [\beta_v(T)f_c^v(C) + \beta_w(T)f_c^w(C)] \quad (3)$$

From its phase portrait (Figure 2) one can see that the system behaviour became more complicated, where this complexity depends on the value of bifurcation parameter Q/p . Let us consider its slow evolution from large to small values. When Q/p was large (high volcanism, small continental area that corresponds to the early Earth history), only single already stable equilibrium exists. A leading role plays the weathering. The total area of continents increases, the volcanism decreases, the value of bifurcation parameter Q/p also decreases. In the system arises an interesting transition regime with three equilibria: two are stable and one (intermediate) is unstable. If the first stable equilibrium corresponds to lower temperature lying within the tolerable interval then the second stable equilibrium corresponds to higher temperature lying outside of it. In order

to shift it even if to the high border of the tolerable interval we additionally have to manipulate the cover albedo and its relative area. At last, let us consider the case with low value of Q/p when the volcanism is small and the continental area is large (present time). The single equilibrium with tolerable temperature only is already stable. The main role in the regulation of the Earth temperature plays the vegetation. Further decrease in Q/p takes the stable temperature outside of tolerable limits. The biosphere would be finished, the Earth would be transformed into an "ice desert";

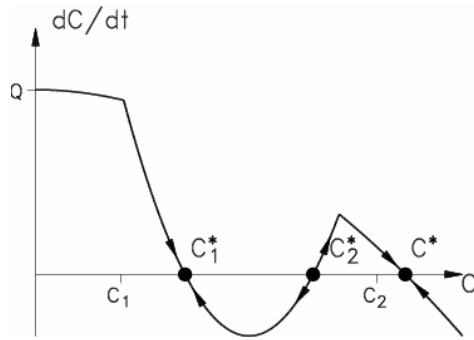


Figure 2. A system phase portrait: the planet cover is a combination of "chemical" (weathering) and "biological" (vegetation) covers. It is assumed that chemical and biological pumps work simultaneously.

- d) "planet - chameleon". At the beginning the skin of planet had been "lunar" color with $\alpha_l = 0.07$ that did not differ from the oceanic albedo (0.07- 0.10). The radiation temperature of this planet was equal to 275°K. The mantle degassing can rise the planetary temperature up to 60°-70°. If the new atmosphere contains H₂O, CO₂, NH₃, H₂S, S₂, HCl then an optical (not chemical) result of interaction between these gases and the matter of "lunar" surface was the increase in albedo. The analogous result will be if assuming that the atmosphere contains a sufficient amount of oxygen to oxygenate a surface rocks. The finale stages of weathering are carbonates and sands with $\alpha = 0.3-0.4$. A rise of living skin of green color (cyanobacterial mats, vascular plants, etc.) was also increased the albedo up to $\alpha = 0.12-0.22$. All these processes led to one result: drop of initial temperature of the planet shifting it to tolerable values for life. On the other hand, if the planet was initially covered by snow then the vegetation arose and its further propagation increased the temperature also shifting it to tolerable values.

In order to get into the tolerable life interval we need in a suitable combination of abiotic factors. But after the life has been arisen, it can maintain the global thermostat for its self-existence.

3. WEATHERING IN OPEN SYSTEMS

Above we considered the carbon dynamics only qualitatively, without any numerical estimation. For this we have to use a weathering model. The weathering is a process of chemical interaction between the gaseous or soluble CO₂ and the solutions of calcite, silicate, magnetite, etc. We shall consider only the calcite case.

A standard description of the weathering assumes that the total amounts of different ions in the solution are constant, i.e., the system is closed, and the chemical equilibrium takes place in the system. In our case all the considered systems are open, and the chemical equilibrium changes depending on the exchange of different forms of carbon between the atmosphere and reservoirs (soil, intercontinental and epicontinental seas, and the ocean).

Let m_i and x_i , $i=0, \dots, 7$ be the molar concentrations and chemical activities of CaCO₃, Ca²⁺, CO₃²⁻, H⁺, HCO₃⁻, H₂CO₃, OH⁻ and CO₂, respectively. The value $x_7 = m_7 = p$ is a partial pressure of CO₂ in the water. $x_i = \gamma_i m_i$, $i=1, \dots, 6$; $\gamma_i \leq 1$ where γ_i are so-called "activity coefficients". They are the given functions of the ionic strength of solution $I = 3m_1 + m_2 + m_3$; $\gamma_1 = \gamma_2$, $\gamma_3 = \gamma_4 = \gamma_6$, $\gamma_5 = 1$. The equations of chemical equilibrium are

$$\frac{x_1 x_2}{x_0} = K_0; \quad \frac{x_2 x_3}{x_4} = K_4; \quad \frac{x_3 x_4}{x_5} = K_5; \\ x_3 x_6 = K_{H_2O}; \quad x_5 = K_{CO_2} x_7, \quad (4)$$

where K_0 , K_4 , K_5 , K_{H_2O} , K_{CO_2} are the chemical constants. They depend on the temperature and the pressure, these dependencies are known. Since the dependence on the pressure is very weak then we shall neglect it.

If the conservation law of charge

$$2m_1 + m_3 = 2m_2 + m_4 + m_6 \quad (5)$$

has to be already fulfilled then the conservation law of matter for calcium and carbon

$$C^0 = m_0 + m_1; \quad C = m_0 + m_2 + m_4 + m_5 + m_7, \quad (6)$$

is true only for the closed systems, and the values C^0 and C are constant. On the contrary, in the open systems these values change. We assume that they change slowly (in comparison with establishment time of chemical equilibrium). It is very important that C^0 and C change

continuously, while the variables x_i and m_i have a jump as a result of chemical reactions. Then

$$\frac{dm_{1,2,3}}{dt} = \frac{\partial m_{1,2,3}}{\partial C^0} \cdot \frac{dC^0}{dt} + \frac{\partial m_{1,2,3}}{\partial C^\beta} \cdot \frac{dC^\beta}{dt}, \quad (7)$$

where $C^\beta = C - C^0$.

The expressions for $m_{1,2,3}$ are given in the form of implicit functions

$$\begin{aligned} F_1(m_1, m_2, m_3) &= m_1(\gamma_1^2 m_2 + K_0) - K_0 C^0 = 0, \\ F_2(m_1, m_2, m_3) &= 2m_1 - 2m_2 + m_3 - \frac{\gamma_1 m_2 m_3}{K_4} - \\ &\quad - \frac{K_{H_2O}}{\gamma_3^2 m_3} = 0, \\ F_3(m_1, m_2, m_3) &= C^\beta + m_1 - m_2 - \frac{\gamma_1 m_2 m_3}{K_4} - \\ &\quad - \frac{\gamma_1 \gamma_3^2 m_2 m_3^2}{K_4 K_5} \left(1 + \frac{\alpha}{K_{CO_2}}\right) = 0, \end{aligned} \quad (8)$$

where

$\gamma_1 = \gamma_1(m_1, m_2, m_3)$, $\gamma_3 = \gamma_3(m_1, m_2, m_3)$; $\alpha = 0$, if we deal with the rain-falls weathering and $\alpha = 1$, if CO_2 is presented in the gaseous phase. The other variables are calculated with use of the following formulas:

$$\begin{aligned} m_4 &= \frac{\gamma_1 m_2 m_3}{K_4}; \quad m_5 = \frac{\gamma_1 \gamma_3^2 m_2 m_3^2}{K_4 K_5}; \\ m_6 &= \frac{K_{H_2O}}{\gamma_3^2 m_3}; \quad m_7 = \frac{\gamma_1 \gamma_3^2 m_2 m_3^2}{K_4 K_5 K_{CO_2}}. \end{aligned} \quad (9)$$

Finally, if the dynamics of C^0 and C are given either from other models or from scenarios then the dynamics of all chemical variables can be calculated. We shall consider two types of models: a) the weathering in a shallow water-body system ("Zavarzin's pot") and b) the weathering in soil covered by vascular plants.

4. WEATHERING DYNAMICS IN "ZAVARZIN'S POT"

For the description of slow dynamics of the integrals C^0 and C we have to start with the equations for biological components. Let B be the biomass (in molC) of phytoplankton without calcium skeleton, and B_s be the biomass of phytoplankton, which forms calcium skeleton. D and D_s are their dead organic matter. The dynamics of the first type are described by the following equations:

$$\frac{dB}{dt} = G(m_7, T) - rB - \frac{B}{\tau_B} - q_w B; \quad (10)$$

$$\frac{dD}{dt} = \frac{B}{\tau_B} - \frac{D}{\tau_D} - V_{sed}^B D - q_w D, \quad (11)$$

where r is the respiration coefficient, τ_B is the residence time of carbon in living biomass, τ_D is the mean time of decay of dead organic matter, $1/V_{sed}^B$ is the mean time of sedimentation for dead organisms of the first type. G is the annual gross production, which is presented as

$$G = G_{\max} f_T(T) \cdot \frac{m_7}{K_{m7} + m_7}. \quad (12)$$

The analogous equations for the second type of phytoplankton will be:

$$\frac{dB_s}{dt} = G^s(m_1, m_2, m_7, T) - r_s B_s - \frac{B_s}{\tau_B} - q_w B_s, \quad (13)$$

$$\frac{dD_s}{dt} = \frac{B_s}{\tau_B} - \frac{D_s}{\tau_D} - V_{sed}^{B_s} D_s - q_w D_s, \quad (14)$$

$$G^s = G_{\max}^s f_T^s(T) \cdot \frac{m_1}{K_{m1}^s + m_1} \cdot \frac{m_2}{K_{m2}^s + m_2} \cdot \frac{m_7}{K_{m7}^s + m_7} \quad (15)$$

where $K_{m7}, K_{m1}^s, K_{m2}^s, K_{m7}^s$ are the Michaelis-Menten constants. We assume the flows $V_{sed}^B D$ and $V_{sed}^{B_s} D_s$ output to kerogen.

Let ξ be the fraction of skeleton in the biomass of the second phytoplankton type (in molCaCO₃/molC), then

$$\frac{dm_1}{dt} = q_w^in m_1^in - q_w m_1 - \xi G^s, \quad (16)$$

$$\frac{dm_2}{dt} = q_w^in m_2^in - q_w m_2 - \xi G^s, \quad (17)$$

where q_w^in and q_w is the water inflow and outflow, m_i^in are the concentrations of corresponding ions and molecules in the input flow. It is obvious that the other equations are

$$\frac{dm_i}{dt} = q_w^in m_i^in - q_w m_i, \quad i = 3, 4, 5, 6. \quad (18)$$

Let consider the calcite balance. We assume that the calcite, which contains within dead cells, participates in chemical reactions, and, on the contrary, the calcite, which contains within living cells, does not. Since the living cells, which leave the system, cannot survive in another environment, we include them into a special flow of calcite to the next reservoir (ocean). Then

$$\frac{dm_0}{dt} = q_0 + \frac{\xi B_s}{\tau_B} - q_w \xi D_s - V_{sed}^{B_s} \xi D_s - V_{sed}^0 m_0, \quad (19)$$

where $1/V_{sed}^0$ is the mean time of sedimentation of inorganic calcite, q_0 is the input of calcite from an external source. And finally,

$$\begin{aligned} \frac{dm_7}{dt} &= k_w(p_a - m_7) + (q_w^in m_7^in - q_w m_7) - \\ &\quad - (G^s - r_s B_s - \frac{D_s}{\tau_D}) - (G - rB - \frac{D}{\tau_D}) + q_{juv}. \end{aligned} \quad (20)$$

Here $k_w = k_w(T)$ is the coefficient of exchange between the atmosphere and the reservoir, p_a is the partial pressure of CO_2 in the atmosphere, q_{juv} is the flow of juvenile CO_2 through the bottom of "pot".

Using all these equations we can calculate dC^0/dt and dC^β/dt and substitute their expressions into the equations of chemical kinetics. Their solution gives the dynamics of all chemical variables, and, in particular, the dynamics of atmosphere carbon depended on biological processes in the Zavarzin pot. In this case the Zavarzin pot can be a sink of the atmosphere carbon.

It is interesting that the system can have multiple equilibria.

5. CYANOBACTERIAL MATS AND ZAVARYIN'S BIOSPHERE

Let us consider our planet at early stages of his history (2 - 3 aeons ago) when single large and flat continent was surrounded by mountains (Zharkov, [2000]), so there was not any contact between the continent and the slightly acid ($\text{pH} = 4 - 5$) ocean. This entire "pot" was fulfilled by shallow water-body systems of intercontinental seas, which were ideal niches for *Cyanobacter* microbial mats (CBM) ("Zavarzin's pots"). All this forms a special type of active cover, which consists of photosynthesising prokaryotic communities: CBM. This system can be considered as some first stage of the biosphere succession: the biosphere of CBM or Zavarzin's biosphere (Zavarzin [1984]). Namely this system has a predecessor of the contemporary Phanerozoic biosphere and atmosphere. If assuming that contemporary CBM are analogues of those ancient ones then the CBM were optimally adapted to their ecological niche. In accordance with Gerasimenko and Zavarzin [1994]) the following properties were adaptive.

1. *Their productivity was very high (as by contemporary tropical rain forest)*. For instance, under sub-optimal conditions (salinity $\sim 16-21\%$, $t^\circ \sim 40-45^\circ\text{C}$), the annual gross production and destruction of CBM is equal to 1.6kgC/m^2 and 1.1kgC/m^2 . Their difference is equal to 0.5kgC/m^2 . Although the destruction in CBM is mostly anaerobic but the production of oxygen by photosynthesis is proportional this difference so that one square meter CBM produces $1,3\text{kgO}$ per year.
2. *CBM were covered by mucopolysaccharide film ("mucus")*. A sandwich from 2m of water and 2mm of mucus guaranteed practically the full defense from UV radiation. Mucus fibers within CBM are very good light-conductors,

due to this the light is transported to the whole volume of CBM.

3. *Due to the high species diversity of organisms, which form the mat*, a full use of visible spectrum was attained.
4. *CBM creates conditions for CaCO_3 formation*, since over a mat the $\text{pH} = 8.4 - 9.6$ and the concentration of HCO_3^- is equal to 280 mg/l , while under a mat the pH decreases down to 7 and the concentration of HCO_3^- is equal to 915 mg/l .

CBM has a perfect structure organisation: light conductors, calcium and gypsum quasi-skeleton, Their "shark skin" adjusted external water flows increasing the nutrients transport, etc.

Considering the scenario in which the area of intercontinental seas covered by CBM was 10^7 km^2 ($\sim 6\%$ of the contemporary continental area). We assume that all water, which was degassed from the mantle, is concentrated in the contemporary hydrosphere, $1.64 \cdot 10^{24}\text{ g}$. All degassing nitrogen is concentrated in the atmosphere, $4.1 \cdot 10^{21}\text{ g}$. If we test the composition of volcanic gases of the different origin (Voitkevich, Bessonov, [1986]) then the best approximation will be the emission of Iceland geysers and fumaroles: $99.4\% \text{ H}_2\text{O}$, $0.33\% \text{ C}$ in the form of CO_2 , $0.05\% \text{ N}_2$. In accordance with these assumptions we get the estimations for N_2 : $0.825 \cdot 10^{21}\text{ g}$, and for carbon (in the form of CO_2): $5.445 \cdot 10^{21}\text{ g}$. In order to "suck" all this carbon dioxide 10^7 m^2 of CBM have to work one million years. $1.45 \cdot 10^{22}\text{ g}$ oxygen will be produced by photosynthetic mats. The most part of oxygen is spent for the oxidation of FeO , CO , SO_2 and H_2 . The contemporary atmosphere contains $1.1 \cdot 10^{21}\text{ g}$.

Certainly, this is some extreme estimation under conditions very closed to optimal ones. Substantively, the process of the atmosphere CO_2 "grazing" by CBM occurred much slower.

In accordance with Ronov's estimation (Budyko et al. [1985]) the stratosphere contain $9.8 \cdot 10^{22}\text{ gC}$. This value is 18 times higher than the estimation, which was mentioned above. In order to get a better consistency of these estimations we have to increase either the percentage of N_2 (~ 5 times) and C (~ 18 times) in volcanic emanations or the total amount of degassed water.

Let us consider the following thermodynamic model: a flow of mixed gases with the concentrations corresponding to volcanic emanations passes through an active membrane with properties of CBM. The process is isothermal and isobaric: $t^\circ = 50^\circ\text{C}$, pressure = 5atm. Using the methods of non-linear thermodynamics we calculated the equilibrium atmosphere, which was established behind membrane: 1% of CO_2 and 8% of O_2 .

When as a result of intensive orographic processes the depth of intercontinental seas has begun to increase, this was a reason of massive ruin of CBM since their density was $\approx 1.39 \text{ g/cm}^3$. The biosphere of the CBM has been replaced by the contemporary Phanerozoic biosphere of vascular plants.

6. GLOBAL CARBON CYCLE IN THE VASCULAR BIOSPHERE

This cycle can be described by the following equations:

$$\frac{dC_a}{dt} = -G\sigma_s - Q_{as} + Q_{res} - Q_{ao} + Q_{vol}, \quad (21)$$

$$\frac{dB}{dt} = G\sigma_s - r_L B_L - r_R B_R - \frac{B}{\tau_B}, \quad (22)$$

$$\frac{dD}{dt} = \frac{B}{\tau_B} - \frac{D}{\tau_D} - k_{ker} D, \quad (23)$$

$$\frac{dC_s}{dt} = \left(\frac{D}{\tau_D} + r_R B_R\right)\sigma_s - Q_{weath} + Q_{as}, \quad (24)$$

where C_a and C_s are the total amounts of CO_2 in the atmosphere and soil, respectively, σ_s is the soil area, B_L and B_R are the densities of above ground and roots biomasses, r_L and r_R are the respiration coefficients for them, τ_B and τ_D are the residence times of carbon in living and dead organics, G is the gross annual production. It is obvious that $B = B_L + B_R$. If assuming that $k_B = B_L / B = \text{const}$ that the total respiration is defined as $rB = r_L B_L + r_R B_R$ where $r = r_R + k_B(r_L - r_R)$. The value $k_{ker} D$ is the kerogen outflows, the exchange between the ocean and the atmosphere, Q_{ao} , is described in any standard way, the flux of volcanic CO_2 , Q_{vol} , is given in the form of scenario, $Q_{res} = rB$. The CO_2 flux from the soil air to water reservoirs (lakes, seas, etc.), Q_{weath} , caused by the rain-water weathering, is described by the model of Section 3. The problem is how to describe the exchange between the atmosphere and soil.

Usually the model of turbulent diffusion is used. However, if applying it then there is not any gradient of CO_2 concentration between the atmosphere and soil. The point is that any soil with plants is covered by a litter, which plays a role of semi-penetrated membrane and destroys the turbulence. Therefore, a model of molecular diffusion is more suitable for description of the exchange. Then $Q_{as} = D_{diff}(c_a - c_s)(\sigma_s / \Delta z_s)$ where c_a and c_s are the concentrations of CO_2 in

the atmosphere and soil, Δz_s is the membrane (soil layer) thickness, D_{diff} is the coefficient of molecular diffusion,

$$D_{diff} = D_0 \cdot \left(\frac{T}{273}\right)^2 \cdot \left(\frac{M_{atm}^0}{M_{atm}}\right), \quad D_0 = 0.138 \frac{\text{cm}^2}{\text{sec}}.$$

M_{atm} is the mass of atmosphere and M_{atm}^0 is its current value. The concrete calculations are shown that in the biosphere of vascular plants the weathering accelerates the rate of carbon evacuation from the atmosphere by 8-10 times (in comparison with purely chemical process).

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