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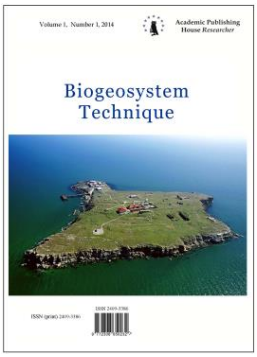
Published in the Russian Federation
Biogeosystem Technique
Has been issued since 2014.
ISSN: 2409-3386
E-ISSN: 2413-7316
Vol. 5, Is. 3, pp. 267-285, 2015

DOI: 10.13187/bgt.2015.5.267
www.ejournal19.com



UDC 631.41

Ion's Association in Soil Solution among the Drivers of Biogeosystem Dynamics

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Abstract

Biogeosystem change is linked to ion's association in soil solution. The concern of carbon sequestration problem is a soil as carbon sink drain. The carbonate calcium equilibrium (CCE) in soil solutions is important to characterize the degree soil solutions saturation with $CaCO_3$ as a factor of terrestrial system carbonate geochemical cycle. CCE depends on the state of the chemical composition, pH, Eh, buffering properties of soil liquid phase, dissolution, migration, precipitation of carbonates in the soil profile and landscape, ion exchange processes at the interface of solid and liquid phases. At high ionic force in soil solution are formed electrically neutral ion pairs $CaCO_3^o$; $CaSO_4^o$, $MgCO_3^o$, $MgSO_4^o$, charged ion pairs $CaHCO_3^+$, $MgHCO_3^+$, $NaCO_3^-$, $NaSO_4^-$, $CaOH^+$, $MgOH^+$.

The object of research – Southern Russia; saline chestnut soil, dry steppe zone; non-saline chernozem, steppe zone. The soil solution was extracted from soil layers 0-150 cm. Composition of soil solution was determined using standard analytical methods. The soil system is the object of mathematical thermodynamic modeling, because it is impossible to remove the solution from dry soil, on the other hand, the extraction of solution change the chemical equilibrium in solution. The approach to soil disperse system model is proposed as a discreet partially insulated form one another micro-water-basins on the internal surfaces of soil. This approach gives a new understanding of water-salt transfer, geochemical barrier functions and ecological properties of soil.

On the basis of CCE algorithm, the computer programs were developed to calculate the real equilibrium ion forms and determine the nature of carbonate-calcium balance in the soil solution. The mathematical model shows the real state of associated ions at different ionic strength of low saline and saline soil solution. The concentration of free and associated macro-ion forms were calculated in iteration procedure according analytical ion concentration considering ion material balance, linear interpolation of equilibrium constants, method of ionic pairs, laws of: initial

concentration preservation, operating masses of equilibrium system. Concentration constants of ion pairs dissociation were calculated following the law of operating masses. Were determined the quantity of ion free form and coefficient of ion association γ_e as a ratio of ions free form to its analytical contents $\gamma_e = C_{ass} / C_{an}$. The association of ions is higher in saline soil layers. Depending on composition and ionic force c of soil solution in the form of ionic pairs are: 11-52% Ca^{2+}; 22.2-54.6% Mg^{2+}; 1.1-10.5% Na^{+}; 3.7-23.8 HCO_3^-, 23.3-61.6% SO_4^{2-}, up to 85.7% CO_3^{2-}.

To interpret a behavior of heavy metal in soil solution an additional equation for microelements is proposed for the mathematical model of macro-ions.

The proposed thermodynamic calculation method for the real ion forms quantitative assessment in soil solution shows that in salted soils a chemical equilibrium in the soil solution causes a dissolved carbonate forms at high concentration of soil solution. It determines a high mobility of carbonates. Carbonate system of the soil solution is most important because on its state depends the nature of basic processes affecting formation and development of a certain type of soil. The nature of the calcium carbonate equilibrium soil is a cause why using an analytical concentration of ions only is observed the high calculated saturation degree of soil solutions with $CaCO_3$. The association of ions in soil solutions is one of the geochemical drivers promoting transformation of solution, salt and heavy metal migration and accumulation in disperse system, soil genesis, excessive fluxes of carbon into soil, carbon sink from soil and biosphere to lithosphere and other geospheres.

Keywords: soil solution, carbonate calcium equilibrium, ion's association, mathematical thermodynamic model, carbon sink.

Introduction

Biogeosystem change is linked to regularities of soil solution's formation, metamorphism, as well as its dissolution, saturation and precipitation in soil and lithosphere. The formation of chemical composition of soil solution is very complex process. One factor is a chemical equilibrium in soil solution – carbonate calcium equilibrium (CCE). CCE depend on the state of the chemical composition, pH, Eh, buffering properties of liquid phase, dissolution, migration, precipitation of carbonates in the soil profile and landscape, ion exchange processes at the interface of solid and liquid phases. On the contrary, to the great extend the CCE in its turn influence the soil pH, Eh and buffering properties.

The knowledge of CCE is a base for calculation of solubility $CaCO_3$ and other ingredients of soil solution [12, 28, 68, 70].

The uncertainties are found of aquatic and terrestrial systems physical and biogeochemical models, the need to improve these models is declared [91].

The carbon sequestration and climate engineering are to be based on assessment of the role of soil and soil solution as a carbon sink drain. Biosphere uncertainties, climate extremes are linked to geochemical cycles in the terrestrial biosphere soil [8], water systems [58]. It has a profound implication for society, biosphere and climate system [89, 93]. The heterogeneity in carbon stream is caused by landscape. The boreal landscape is known as an important source of dissolved organic carbon [2]. In the semiarid and arid catchments the soil solution equilibrium causes the carbon mobility into the soil. In these circumstances, the probability of uncontrolled carbon stream out of the soil and biosphere is high.

The data are obtained on increasing anthropogenic influence on the carbon cycle [9]. The biogeosystems are sensitive to change of carbon stocks [77]. The sinking of carbon is one of the leading components of the carbon cycle and global climate system [44]. The excessive saturation of water with $CaCO_3$ gives on adverse biogeochemical effect [30]. It is important to quantify the carbon source/sink nature, determine its drivers [105].

Soil solution equilibrium helps to represent properly the function of soil and vegetation [66]. CCE of water and terrestrial systems influences the growth of leading agents of biosphere – water and soil organisms [103]. Soil solution varies on temporal and spatial scales [67]. The meaning of qualified management of biosphere is great concerning dangerous anthropogenic influence on soils. The problem of carbon cycle is linked to release of entrapped methane when the soil is disturbed [78]. CCE provides understanding of key biogeochemical element cycles. The sinks and

sources of carbon are the key point for the proper assessment of terrestrial and aquatic ecosystem's drivers of atmospheric CO_2 concentration, biosphere functioning and climate models [84].

The problem of global climate changing drivers is discussed mainly in a framework of human activities, in particular anthropogenic emissions of CO_2 [96]. Nevertheless, the problem is not simple. For example, from the point of view of life conditions the sequestration of CO_2 on the Venus is urgent. But if the carbon sequester on the Earth will be endless, the life conditions will be lost because of carbon deficit. This deficit will appear locally and even commonly without measures to control the carbon and other elements migration, transformation, accumulation and loss form biosphere. This is a reason why there are significant uncertainties in understanding the role of soil mineral and organic carbon deposits in the global C cycle [108].

Unfortunately, there are real prospects to aggravate anthropogenic dangers by awkward efforts to "correct" the Nature. An opinion to mitigate the large-scale climate effects of human CO_2 using the Ocean as a large sink for anthropogenic CO_2 [44] is to bee discussed carefully and specially because due to this kind of artificial sink the carbon will be back into Biosphere only millions years later on.

Phenology is discussed as the way to understand the biogeochemical cycles and the climate system [15]. Unfortunately, there is obvious desire of scientific society part only to collect and analyze data, and do not take any action to maintain the biosphere situation properly.

The soil is an important part of terrestrial system. The water solution is an agent of soil properties. In every special case the soil solution as a carrier of soluble matter has a different structure, mineralization according to biogeosystem's properties. The soil solution is the most mobile, volatile and active part of the Pedosphere. Soil solution composition varies. In soil solution are observed the destruction and synthesis of organic substances, secondary minerals, organomineral compounds [5, 41, 107]. CCE of the soil solution is important for understanding the origin of soil and biogeosystems.

The mineralization of soil solution varies because of geological and biological composition of the local biogeosystem, regional and local water-mass-transfer, wetting and drying circles of the soil, biological process in the soil. CCE is important for proper modeling of heavy metals state and transfer in soil and landscape [6, *25*, 29, 85].

Important world problem is the soil anthropogenic heavy metal contamination and transfer [14, 18, 19, 33, 34, 37, 39, 40, 42, 43, 47, 54, 57, 59, 60, 63, 65, 75, 76, 80, 81, 88, 94, 101, 106, 112, 113, 116].

The properties and structure of water solution are the function of its chemical equilibrium [11, 13, 20, 21, 31]. The higher is ionic strength of solution, the more ions pass to the form of ions associates (1, 56, 82, 99]. The fact is known for the waters of ocean and low mineralized waters of storage reservoirs [55]. Ion's association in water calcium carbonate system helps to explain the natural water oversaturation with carbonates, migration and accumulation of carbonates [68]. The reason of excess saturation of water with $CaCO_3$ is the ions association to ionic mineral and organic complexes [69]. Carbonate system of water solution is under the influence of biological process, soil-atmosphere gas exchange, partial pressure and seasonal cycles of CO_2.

It should be noted that under natural conditions not content of HCO_3^-, CO_3^{2-} and H_2CO_3 in soil solution depends on pH, but namely the ratio of forms of CCE determines the pH value, buffering and redox properties of the soil solution, nature of ion exchange in the system "solid phase – solution", solubility of many mineral and organic compounds.

The precipitation or dissolution of $CaCO_3$ is linked to removal or reception of Ca^{2+}, HCO_3^- and CO_3^2. The ionic composition of the soil solution reflects the carbonate equilibrium, determines a type of migration and accumulation of various forms of carbonate formations in the soil profile.

An important characteristic of CCE is the degree of saturation of the soil solutions with $CaCO_3$. However, it does not give a clear answer to the question about the formation of $CaCO_3$. The studies of carbonate equilibrium in surface waters shows that saturation or supersaturation of natural waters with $CaCO_3$ reflects only the possibility to form a precipitate, but the $CaCO_3$ not always precipitates from supersaturated water solutions. The relationship between degree of saturation of solutions with $CaCO_3$ and its precipitation depends on physicochemical and biochemical processes, which controls $CaCO_3$ precipitation.

A cause of supersaturated $CaCO_3$ solution's sustainability varies relating the properties of calcium hydrocarbonate solution. The first is formation of a solid phase which chemical composition differs from the solution. The second – at extremely low concentration of CO_3^{2-} ions in

solution the spatial orientation of ion is required for onset of crystallization, which is probably hampered by the huge number of surrounding ions HCO_3^-. One more reason which determines the high degree of calculated saturation of soil solution with $CaCO_3$ is a complexation of Ca^{2+} with organic matter.

The soil solution determines the dynamics of its material composition, migration and accumulation of salts into the disperse system of soil continuum and landscape. The soil solution equilibrium plays important role in the genesis and evolution of soil. In the soil solution are formed electrically neutral ion pairs $CaCO_3^\circ$; $CaSO_4^\circ$, $MgCO_3^\circ$, $MgSO_4^\circ$, charged ion pairs $CaHCO_3^+$, $MgHCO_3^+$, $NaCO_3^-$, $NaSO_4^-$, $CaOH^+$, $MgOH^+$. Communications between the associated ions in soil solution are much more diverse comparing to water systems [41, 55, 82, 87, 102, 104, 115].

Another important property of soil solution is the strong dependence on soil moisture, interaction between soil solution and soil disperse system. The sampling of soil solution leads to destruction of its links to disperse system of soil. So the solution extracted from soil does not completely correspond to the properties of native soil solution. On this reason the modeling of soil solution composition at different stage of water, salt and organic matter content in the soil to the some extend is more important than direct analyzing of extracted soil solution itself.

Ionic strength of the soil solution varies form 0.05 (almost ideal chemical solution after rain in upper horizon of non-saline soil) to 0.5 and more (dry saline soil). Every variant can be observed in rather short time period in the same discrete part of soil continuum. In special cases the ionic strength of soil solution can be so high as it will be even better to use the lows of quasicrystalline water structure, supercritical water [46, 86] to describe the system properly. In recent years, the modern nonthermodynamic techniques are used for modeling the associated ion pairs in nanotubes [45, 62], ion pair association in supercritical water and other conditions [17, 86, 92], to develop the methods of computer modeling of ion pair formation in electrolyte, ion pair as a simulation of hybrid excitations in solution [53, 61, 64, 86, 87]. In recent years the improved methods of direct ion pair study are used [10, 109, 110). Of great importance are the possibilities of carbon nanotubes as a factor of soil minerals and soil solutions interaction, cation exchange on montmorillonite, nutrition, soil colloids stability, biodiversity concern, soil monitoring research [92, 104, 111, 115].

The mentioned data and models confirm the basic tenets of the theory of ion association solution and thermodynamic model of macro-processes of saturation in soil solution, transfer, metamofization and accumulation of salts in the three-dimensional soil continuum [74]. For the most cases of real soil solution it is enough to use the lows of thermodynamics.

The thermodynamics mathematical models of soil solution equilibrium is proposed. The models were tested on experimental empirical data.

Materials and methods

Study Area. The South-East of the Russian Federation.

Objects of research. The dry steppe chestnut saline solonetzic soil and chernozem of Southern Russia. The climate is semi-arid, arid. annual precipitation of 350-500 mm, the parent rocks are Carbonate and Carbonate-sulfate loess-like loam and clay. The solonetz soil is moderately thick, medium solonized, humus 2.6%, physical clay 47.7%, clay 29.5%, $CaCO_3$ 0.15% (up to 3-10% at the depth of 0,8-1,5 m), pH = 7.8, exchangeable cations: Ca^{2+} – 182 mmol/kg, Mg^{2+} – 65 mmol/kg, Na^+ – 34 mmol/kg. The chernozem common is thick, not solonized, humus 4.2%, physical clay 49.3%, clay 31.3%, $CaCO_3$ 0.14% (up to 3-6% at the depth of 1,3-1,6 m), pH = 7.8, exchangeable cations: Ca^{2+} – 342 mmol/ kg, Mg^{2+} – 27 mmol kg^{-1}, Na^+ – 6 mmol/kg.

The applied methods of field, analytical research and statistical methods are standard [7, 16, 36, 74, 107, Microsoft Excel 2010].

Modeling. The basic processes of soil formation and development depend on the CCE. CCE includes a number of dynamic equilibriums (Fig. 1).

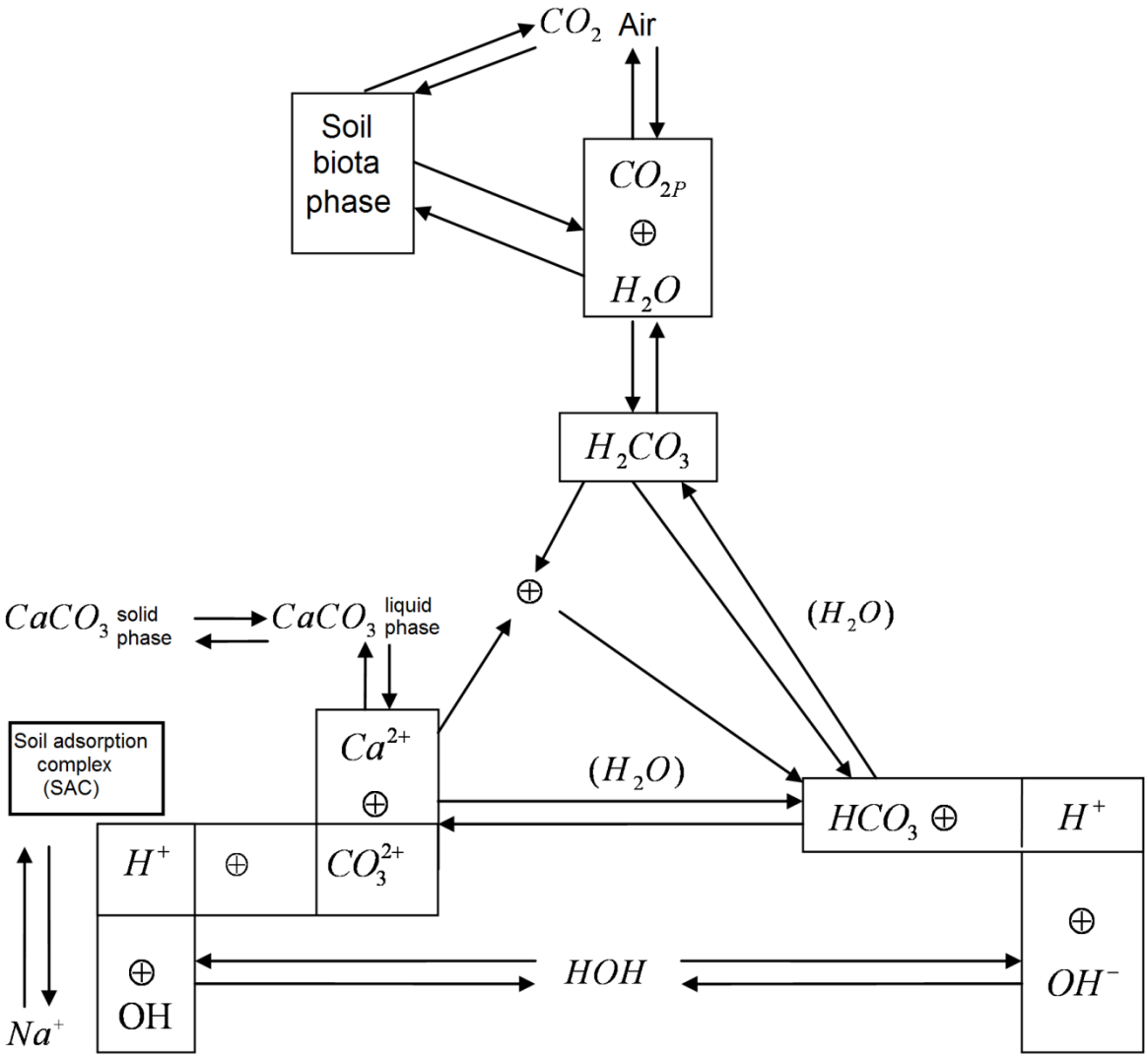

Fig. 1. Calcium carbonate equilibrium system of soil solution

CCE system of soil solution is an adsorption-hydration balance between solid, solution, gas and bioorganic phases. This balance includes step dissociation of carbonic acid; calcium carbonate-equilibrium between solution, soil absorbing complex, sediments of $CaCO_3$ and solid phase, the ion equilibrium of water, a degree of solution's saturation with $CaCO_3$. The deposition or dissolution of $CaCO_3$ caused by receipt or removal of Ca^{2+}, HCO_3^- and CO_3^{2-} from solution, as well as carbonate equilibrium shift, influence the ionic composition of the soil solution and determine the type of migration and accumulation of various forms of carbonate forms through the soil profile, thus – a certain soil type formation and development [3].

The dry residual of saline soil solution is rather high, the analytical composition is typical for dry steppe chestnut saline solonetzic soil of Southern Russia. The state of ions in such solution is influenced with high ionic strength and ion's association in soil solution.

The chernozem soil of Southern Russia is of rather high humidifying, so to its characteristic the water extract (1:5) was used.

The analytical composition of solution rather adequately characterizes the chemical system at a low concentration of the main ions in diluted solution. The measure of real participation of salts and separate ions in soil chemical reactions is their activity.

Was determined a real state of the main ions in soil solutions on the basis of ionic strength and ion's association. The models of soil solution equilibrium was proposed [23, 26, 27, 68, 72, 73].

On the basis of CCE algorithm the computer programs were developed to calculate the real equilibrium forms of ions and determine the nature of carbonate-calcium balance in the soil solutions.

Using analytical data the forms of main ions in soil solution are calculated, the Method of Ionic Pairs (MIP) [1].The components of algorithm are: the law of initial concentration preservation, the law of the operating masses of chemical equilibrium system.

The mathematical model includes the concentration of free and associated forms of ions calculation according to the sum of ion's analytical concentration. To carryout the calculation are applied: iteration to solve the system of algebraic equations of the material balance of ions; linear interpolation to calculate the values of tabulated equilibrium constants according calculated data.

The equations of main ions material balance are as follows. Equations (1-6):

$$\sum Ca^{2+} = \left[Ca^{2+}\right] + \left[CaCO_3^{\circ}\right] + \left[CaHCO_3^{+}\right] + \left[CaSO_4^{\circ}\right] \quad (1)$$

$$\sum Mg^{2+} = \left[Mg^{2+}\right] + \left[MgCO_3^{\circ}\right] + \left[MgHCO_3^{+}\right] + \left[MgSO_4^{\circ}\right] \quad (2)$$

$$\sum Na^{+} = \left[Na^{+}\right] + \left[NaCO_3^{-}\right] + \left[NaSO_4^{-}\right] \quad (3)$$

$$\sum CO_3^{2-} = \left[CO_3^{2-}\right] + \left[CaCO_3^{\circ}\right] + \left[MgCO_3^{\circ}\right] + \left[NaCO_3^{-}\right] \quad (4)$$

$$\sum HCO_3^{-} = \left[HCO_3^{-}\right] + \left[CaHCO_3^{+}\right] + \left[MgHCO_3^{+}\right] \quad (5)$$

$$\sum SO_4^{2-} = \left[SO_4^{2-}\right] + \left[CaSO_4^{\circ}\right] + \left[MgSO_4^{\circ}\right] + \left[NaSO_4^{-}\right] \quad (6)$$

where, $[Ca^{2+}]$, $[Mg^{2+}]$ – the equilibrium concentration of the free form of ion, $[CaCO_3^{o}]$, $[MgCO_3^{o}]$, – equilibrium concentration of ion in associated form (ion pair).

For groups of cation the concentration constants of ionic pair dissociation follow the law of operating masses. Equations (7-9):

$$K_{CaCO_3} = \frac{\left[Ca^{2+}\right]\left[CO_3^{2-}\right]}{\left[CaCO_3^{0}\right]};\ K_{CaHCO_3} = \frac{\left[Ca^{2+}\right]\left[HCO_3^{-}\right]}{\left[CaHCO_3^{+}\right]};\ K_{CaSO_4} = \frac{\left[Ca^{2+}\right]\left[SO_4^{2-}\right]}{\left[CaSO_4^{0}\right]} \quad (7)$$

$$K_{MgCO_3} = \frac{\left[Mg^{2+}\right]\left[CO_3^{2-}\right]}{\left[MgCO_3^{0}\right]};\ K_{MgHCO_3} = \frac{\left[Mg^{2+}\right]\left[HCO_3^{2-}\right]}{\left[MgHCO_3^{+}\right]};\ K_{MgSO_4} = \frac{\left[Mg^{2+}\right]\left[SO_4^{2-}\right]}{\left[MgSO_4^{0}\right]} \quad (8)$$

$$K_{NaCO_3} = \frac{\left[Na^{+}\right]\left[CO_3^{2-}\right]}{\left[NaCO_3^{-}\right]};\ K_{NaSO_4} = \frac{\left[Na^{+}\right]\left[SO_4^{2-}\right]}{\left[NaSO_4^{-}\right]}. \quad (9)$$

The equilibrium concentration of ionic pair was replaced in equations 1-6 with its value according to relevant dissociation constant from equations (7-9). The system of equations of material balance of ions was transformed as follows. Equations (10-15):

$$\sum Ca^{2+} = \left[Ca^{2+}\right]\left(1 + \frac{\left[CO_3^{2-}\right]}{K_{CaCO_3}} + \frac{\left[MgCO_3^{-}\right]}{K_{CaHCO_3}} + \frac{\left[SO_4^{2-}\right]}{K_{CaSO_4}}\right) \quad (10)$$

$$\sum Mg^{2+} = \left[Mg^{2+}\right]\left(1+\frac{\left[CO_3^{2-}\right]}{K_{MgCO_3}}+\frac{\left[HCO_3^{-}\right]}{K_{MgHCO_3}}+\frac{\left[SO_4^{2-}\right]}{K_{MgSO_4}}\right) \quad (11)$$

$$\sum Na^{+} = \left[Na^{+}\right]\left(1+\frac{\left[CO_3^{2-}\right]}{K_{NaCO_3}}+\frac{\left[SO_4^{2-}\right]}{K_{NaSO_4}}\right) \quad (12)$$

$$\sum CO_3^{2-} = \left[CO_3^{2-}\right]\left(1+\frac{\left[Ca^{2+}\right]}{K_{CaCO_3}}+\frac{\left[Mg^{2+}\right]}{K_{MgCO_3}}+\frac{\left[Na^{+}\right]}{K_{NaCO_3}}\right) \quad (13)$$

$$\sum CO_3^{-} = \left[HCO_3^{-}\right]\left(1+\frac{\left[Ca^{2+}\right]}{K_{CaHCO_3}}+\frac{\left[Mg^{2+}\right]}{K_{MgHCO_3}}\right) \quad (14)$$

$$\sum SO_4^{2-} = \left[SO_4^{2-}\right]\left(1+\frac{\left[Ca^{2+}\right]}{K_{CaSO_4}}+\frac{\left[Mg^{2+}\right]}{K_{MgSO_4}}+\frac{\left[Na^{+}\right]}{K_{NaSO_4}}\right) \quad (15)$$

According to Davies equation for constant the concentration constant of dissociation in equations (10-15) was recalculated. Equation (16):

$$pK = pK^0 - A\Delta Z^2\left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0,1I\right) \quad (16)$$

where in K – concentration constant of dissociation of ionic couple; K⁰ – the corresponding thermodynamic constant; A – Debye-Huckel constant 0,5042 at 20°C; Δz^2 – the algebraic sum of squares of a charge of the particles (ion or associate) in the equation of dissociation constant; I – ionic strength of solution.

The calculated with equation (16) value of pK corresponds to [11, 21, 31, 99, 100].

Thermodynamic constants of dissociation are as follows [11. 38. 100]:

$$pK^0_{CaCO_3} = 3,2; \quad pK^0_{CaHCO_3} = 1,26; \quad pK^0_{CaSO_4} = 2,31.$$
$$pK^0_{MgCO_3} = 3,4; \quad pK^0_{MgHCO_3} = 1,16; \quad pK^0_{MgSO_4} = 2,36.$$
$$pK^0_{NaCO_3} = 1,27; \quad pK^0_{NaSO_4} = 0,72.$$

The thermodynamic equilibrium constants were converted to the corresponding concentration constants using the activity coefficients (y) of free ions and associates. The activity coefficients were determined by Davis equation [20, *98]*:

$$-\lg y = Az^2\left(\frac{\sqrt{\mu^*}}{1+\sqrt{\mu^*}} - 0,2\mu^*\right) \quad (17)$$

where μ^* is the effective ionic strength of the solution.

The formal ionic strength of soil solution was calculated on the data of analytical ion concentration. Equation (18):

$$I = 0,5[2^2(Ca^{2+}) + 2^2(Mg^{2+}) + (Na^+) + 2^2(CO_3^{2-}) + (HCO_3^-) + 2^2(SO_4^{2-}) + (Cl^-)], mol/l \quad (18)$$

The equilibrium concentrations of ion's free forms were designated as unknown values of the equations system. The analytical concentration of all ion forms was used as a total value of every chemical element. The system was obtained of six equations with six unknown.

The iteration was used to find out the value of the equilibrium concentrations of free ions. The equilibrium concentrations of ion pairs were determined according equations for dissociation constants (7-9).

The effective ionic force of solution was calculated taking according the values of equilibrium concentration of all ion forms. Equation (19):

$$I^* = 0,5\{2^2[Ca^{2+}] + 2^2[Mg^{2+}] + [Na^+] + 2^2[CO_3^{2-}] + [HCO_3^-] + 2^2[SO_4^{2-}] + [CaHCO_3^+] + [MgHCO_3^+] + [NaCO_3^-] + [NaSO_4^-] + [Cl^-])\}, mol/l \quad (19)$$

As a result of the first step of iteration procedure were calculated the concentration constants of dissociation (16). The new system was obtained of equations of material balance. On the new set of the system ingredients made the next iteration of (10-15).

By the iteration sequence were calculated the ion forms in soil solution.

The coefficient of ion association γ_e proposed as a ratio of ion free form to its analytical content. Equation (20):

$$\gamma_e = C_{ass} / C_{an} \quad (20)$$

where, C_{ass} – calculated ion content in solution taking into account its association with another ions, C_{an} – analytical concentration of an ion.

The content of microelements in soil is many times less than contents of macro-ions, so there is no need to include the equation for Cd into the system of equations (10)-(15) for macro-ions – the quantity of microelement is insignificant as a contribution to total ionic force of soil solution. The obtained equilibrium concentrations of free anions $[CO_3^{2-}]$, $[HCO_3^-]$, $[SO_4^{2-}]$, $[Cl^-]$, and $[OH^-]$ can be used for the calculation of soluble microelements forms contents in water extracts from the mass balance equations [25]. The equation (21) is an example for Cd^{2+}:

$$Cd^{2+} = [Cd^{2+}]\{1+[CO_3^{2-}](K(CdCO_3))^{-1}+[HCO_3^-](K(CdHCO_3))^{-1}+ +[SO_4^{2-}](K(CdSO_4))^{-1}+ [Cl^-](K(CdCl))^{-1}+[OH^-](K(CdOH))^{-1}\}. \quad (21)$$

For calculation were used own software products [4, 23, 26].

Result and discussion

The procedures specified by equations 7-21 are proposed to calculate the quantity of associated ions in the soil solution in different soil horizons at the given soil moisture and soil solution analytical composition.

The calculation results are published [24, 27, 29, 68-70, 72, 73] and show that the association of ions varies in individual layers of soil. The real equilibrium concentration of ion forms in soil solution depends on concentration and composition of soil solution. The higher salinity of the soil

solution, the more ions are associated. In the form of ionic pairs in saline horizons of soil are: 11-52% Ca^{2+}; 22.2-54.6% Mg^{2+}; 1.1-10.5% Na^{+}; 3.7-23.8 HCO_3^-, 23.3-61.6% SO_4^{2-}, up to 85.7% CO_3^{2-}.

On the other hand, in the non-saline horizon 0-5 cm of the soil at the soil humidity of 22.4% the most of ions are in free form. This fact has good interpretation on example of water extract from chernozem soil [25]. In this case the quantity of bound to associates heavy metal Cd^{2+} is significant, influences the properties of the soil continuum, but is much less than in former mentioned case of saline horizon of soil.

A large amount of associated ions in the soil solution confirms the well-known similarity of soil and water systems of the biosphere. For the sea water system, water reservoirs with low salted water, groundwater the association of ions is known as an important factor in the carbonate system [55].

The principal difference of the soil from the water system is as follows:

- ✓ Continuum variety of properties of solid, liquid, gaseous phases of soil elements of the continuum as a drain or source of the material composition of the soil solution.
- ✓ Contact of the soil disperse continuum and disperse continuum of the soil water at the nanoscale.
- ✓ The inflow of water into the gravitational (preference downdrafts water flow respectively anisotropic properties of the soil continuum), capillary, vapor form.
- ✓ Selective drain of the soil solution within the continuum – the drain of the root system of plants, evaporation.
- ✓ Dynamics of the soil moisture and, accordingly, the dynamics of the soil solution concentration.
- ✓ Soil water steam flow.
- ✓ Transfer of the soil solution between the elements of the soil continuum according to gradient of the thermodynamic potential.

There is another aspect of the high mobility of ions in the soil solution linked to ions association.

The soil as a dispersed system is not simple crossing of the continuum of soil and water continuum. This simplified thermodynamic picture is useful only as a step of approximation. In fact these two continuums cross as a continuous only at high humidity of soil. Once the soil moisture content is decreasing, the soil solution is divided into the micro-basins within the soil continuum. Each of micro-basins is attached by capillary forces to the local film element(s) of soil structure. Micro-basin is stable in the space of the soil. When soil structure is disturbed during the passage of a growing root, resulting of soil swelling or any other causes, a separate micro-basin may move for some distance, but the overall picture of the distribution in the continuum soil micro-basins stable. From micro-basins there is water consumption for transfer and transpiration. In each micro-basin the process in soil solution goes in accordance to the laws of the spatial distribution of water. It's obvious that even at the small average soil water content there are local areas of soil continuum in which the soil solution has potentially movable ingredients. As soon as a stage of soil moisture comes, the micro-basins are linked, and their material migrates in accordance with the hydraulic flow lines, formed in the soil. The microbasins are an additional circumstance of the high intensity change of the soil material composition.

At the stage of soil formation it is favorable circumstance, ensuring the rapid evolution of soil to the quasi-stationary state of balance, or the same – reaching the stage of the genesis of which the soil corresponds to the regional conditions of soil formation. When the quasi-steady state is reached, then by the set of circumstances, the soil degradation is probable, loss of soil fertility, as a reflection of repeated cycles of wetting-drying which lead to the hydrolysis, destruction of the crystal lattice. The situation is complicated by excessive transport of material through the soil, as well as the aggressiveness of contained in a transferred soil solution material. Every micro-basin contains solution, which is sufficiently aggressive to mineral and organic phases of soil. It provides a process of soil transformation, even at relatively low humidity. In addition, it causes intensive migration of soil material, as in the initial phase of the soil wetting the micro-basins has the ready to migrate reserve of substances – the soil solution, which involves free and associated ions.

Due to ion association the mobility of dry steppe chestnut saline solonetzic soil solution components is higher compared to previous estimates, especially for carbonates. In such circumstances the preference descending water fluxes in the soil are extremely dangerous because

lead to the loss of soil mineral phase to deep soil horizons and lateral redistribution of salts. There is a danger of excessive carbonates loss from soil which influences the mechanical structure of soil, the calcium-carbon source for soil organisms and plants. Moreover, the migration ability of organic matter and mineral nutrients, which closely linked to soil carbonates, can be assumed significantly higher than it was previously thought because the association of ions and in soil the formation of complexes of carbonates with organic and inorganic matter are universal process for various chemicals.

In experiments, the soil solution removed from upper slightly saline soil horizon has been in diluted state. But sufficiently high soil moisture in the experiment is not always common in situ. Просто использованная нами методика вытеснения позволяет получить из этого горизонта почвы только такой почвенный раствор. При низкой влажности почвы любая известная методика извлечения почвенного раствора неработоспособна. But only this technique of displacement can be applied to obtain the soil solution. At lower soil moisture any known technique of extraction of the soil solution is unusable.

On the contrary, for the soils of southern dry regions the low soil moisture is typical. At this moisture the concentration of soil solution in the upper low saline soil horizons can be high. This means that the material composition of the soil solution of the upper layer of soil may be significantly influenced by association of ions in the way as it has been shown experimentally and by mathematical modeling for deep layers of soil. The soil system of upper layer is possible to describe in the model only, because there is no way to remove the solution from dry soil.

The microelemets at higher soil humidity are sufficiently bounded to ion pairs, this reduces their mobility [24, 25, 29].

Considering increase of soil solution concentration at low soil moisture, we have not touched upon the process of adsorption and precipitation of salts. The first process in soils of mainly mineral composition plays a subordinate role, the second stage occurs after the association becomes the subject of research. Obviously, at the used level of consideration, simplification of the processes in soil solution and the precipitation of the salts sorption evident even without direct accounting in model. Moreover, the procedure of the soil solution extraction alter the system "soil – salt – water" and affects its properties not less than assumptions, adopted in the model, as solution displacing is associated to significant impairment of the phenomena of dissolution and desorption. The destruction of the soil system distorts its properties, thus the method of mathematical simulation in the case discussed can be assumed as less distorting the regularities of the soil system.

The used simplified mathematical model system "soil – salt – water" allows the more wide range of possible states of pedosphere than it can be obtained in the model experiment. This basic feature of mathematical modeling is that the soil solution system is undisturbed.

The high mobility of the soil solution components is a prerequisite for the lateral redistribution of material within the soil continuum in the soil continuum at uneven moisture of soil areas. Is probable the depletion of the mineral composition of a donor soil and concentration in the acceptor soil. Both processes are unfavorable from the viewpoint of soil properties stability.

On the basis of calculations fulfilled it can be assumed that the low soil moisture to a certain limit is not an obstacle to the nutrient's transfer to the plant's roots. High soil moisture, which seeks, for example, at irrigation is not necessary from the point of view of plant nutrition. In this regard, we ought to note that in our experiments in the dry steppe chestnut soils without irrigation was obtained yields of winter barley 11.5 t/ha. This case reflects a large agronomic fortune. The soil moisture regime formed so that the humidity of plant's organogenesis in the spring-summer period from the conventional viewpoint has been relatively low, the soil moisture was not easy enough fro plants. But it appears to be the best for transfer nutrition ions and their associates to the to plant's roots. On the contrary, excessive soil humidity gives no advantage in plant nutrition. Although most of ions of soil solution time are in a free state, but at the same time the electrical conductivity of soil solution, which determines the intensity of the ion's flux in electric field to rhizosphere, is low. The ions are located far from each other and to extract them from soil the plant is forced to spend a lot of energy for transpiration, pumping large amounts of water. At the same time the negative role plays the diffusion of ions in solution. In conditions of high soil moisture diffusion rate is large, because the diffusion of ions essential nutrient can go opposite to the flow of the aqueous solution to the root hairs. The plant forces the rate of water flow, forms the excessive

transpiration. Water is a global deficit. The natural soil hydrology is difficult to control. But when the irrigation, from the viewpoint of soil solution's properties, to simulate natural alternation of high water content of the soil after precipitation and subsequent reduction of moisture during desiccation is wasteful in a view of discussed terms of excess water consumption. In addition, an excess of soil humidity results in flotation of soil units, their subsequent re-packaging and sealing in a phase of soil desiccation.

Association of ions promotes innovative solutions in the field of soil water regime, water saving, reduce the loss of nutrients, eliminate soil degradation. It is consistent in a view of the recent data on drawbacks of soil moisture sensors system, which correspond to the problem of true soil solution content determining [22[]. The soil moisture in artificial soil system and at the irrigation is too high from the point of view of ions association and soil solution migration [29, 48, 50, 71, *83, 95*].

The models proposed are applicable at I <1,0. At this ionic strength of soil solution the models outlines the nature of the studied object on the qualitative and quantitative level. In saline soil it is possible to have the conditions of significantly greater ionic strength of the soil solution in which the need to involve other instruments to describe the structure of concentrated solution will appear [79, 90]. Exotic models of this kind are very original, and in special circumstances, for which they are designed, remain the exceptional way of research because are the only method to describe the process. But for all their originality, for the object of our studies those models are redundant.

Yes, for part of the micro-basins of soil solution, linked to the ultra-thin nanotubes (capillaries) at very low soil moisture and, accordingly, a high concentration of the soil solution of sodium chloride structure, the model n^*NaCl^o quite efficient in terms of correct representing of NaCl migration. But at high ionic strength, which takes place in this case, no possibility for plants the use the nutrients exists, and in consequence, the absence of plant's roots gives no prerequisites for the soil biota development, which life is possible or preferable only in rhizosphere. The soil hydraulic conductivity low, mass transfer process almost stopped.

So to describe the leading transport phenomena of matter in the soil are necessary and sufficient the thermodynamic models operating at I <1.0.

The nature of CCE in soil is a cause why using an analytical concentration of ions only leads to the high calculated saturation degree of soil solutions with $CaCO_3$.

Accounting processes of ion association help to reduce the caculated supersaturation of soil solutions with $CaCO_3$ in 10 ... 50 times. Roughly, the same effect on soil solution has its ionic strength. In a view of complexation of Ca^{2+} with soluble organic substance the degree of calculated soil solution saturation with $CaCO_3$ reduces up to 1,5 ... 2,0 times [69].

The regularities of ion association process can help to explain the observed excess of ions concentration in the soil solution in comparison to ion thermodynamic solubility product.

The theoretical generalizations of thermodynamics of the soil solution and calculations give a new glance on the phenomena of ion association in water solution. Accounting association and activity of ions and calculating degree of soil solution saturation with chemicals provides the new understanding of migration and accumulation of chemical compounds in soils and landscapes concerning CaCO3.

Conclusion

Thus, the study of most important chemical equilibria and ionic structure of soil solution help to determine the formation and nature of chemical composition of saline soil. The approach proposed permits to consider the processes of migration and accumulation of salts, to predict the genesis, evolution and different methods of reclamation of soil and landscape systems.

The various experiment and mathematical modeling fulfilled show the calcium carbonate system in soil solution taking into account the ion association and without account of this phenomenon (). The association of ions helps to state that the thermodynamic preconditions of $CaCO_3$ oversaturation in saline soils occur at much higher concentration of Ca^{2+} and CO_3^{2-} ions in soil solution than considered previously.

At high ionic force in soil solution are formed electrically neutral ion pairs $CaCO_3^o$; $CaSO_4^o$, $MgCO_3^o$, $MgSO_4^o$, charged ion pairs $CaHCO_3^+$, $MgHCO_3^+$, $NaCO_3^-$, $NaSO_4^-$, $CaOH^+$, $MgOH^+$.

Therefore, there is a significant probability of high mobility of $CaCO_3$ in soil and landscape.

The completed research has significance not only from the point of view of theoretical foundation or accuracy of calculation procedures compliance to the details of natural phenomenon. The basic conclusion – the calculation suits the nature of the phenomenon of migration and accumulation of salts in soil. Thus, the association of ions in soil solution is important for knowledge of modern evolution of salted soils, use of the soils in a rain agriculture, irrigational agriculture, plant's nutrition.

The proposed scheme of soil solution system modeling is not highly instrumentally based, but nevertheless has more of high scientific and practical prospect than even compared up-to-date direct methods of soil solution research because the soil solution probing leads to the new state of soil solution after its extraction from the soil, this artificial system does not completely reflect the real soil solution system.

The shortcoming of research is the operation under the individual soil solutions from the layers of soil section. But soil continuum consists of series of vertical sections – one-dimension profiles. The layers of section and individual sections are interacting. The key problem of future research is not only to describe the state of soil solution system in individual part of soil volume at a particular moment of time but to explain the origin of metamorphisation of soil solution in time and through the soil continuum in accord to water-salt-mass transfer. On this foundation the prediction of soil evolution will be proper, soil management will be better and stable.

Next problem is modeling not only the soil solution macrosystem but taking into account disperse origin of the soil and soil solution. It is because the state of water in soil is not a continuous water amount crossed by solid soil phase continuum. It is a system of discreet insulated form one another micro-water-basins on the internal surfaces of soil. This approach gives the new understanding of water-salt transfer, geochemical barrier functions and ecological properties of soil.

The results of research are useable for plant nutrition, agriculture management of the soil, improving standard regional rain agriculture and irrigational agriculture.

The quantitative solving of soil solution thermodynamic model shows that mobility of matter, especially carbon, in terrestrial system is much higher than in was known before. On this reason the danger of carbon loss from the soil and biosphere is great. The task of carbon sequestration from biosphere by the way of transformation into deposits in aqueous or terrestrial system is false in conditions of transpiration reduction and shrinking of biosphere. The management of soil for growing plants needs to be focused on reducing soil moisture and reducing soil solution migration through the soil continuum and at the same moment increase the rate of biosphere production. It is necessary to ensure the delivery of nutrients directly to the roots of plants, in any case, delivery in closed compact zone of the soil continuum minimizing transit transport of substances through the soil.

Soil management can not be reduced to standard soil mechanical treatment in order to simulate natural weathering regime. Management of soil needs to be focused on preservation of the structure and composition of soil, reducing the destruction of the soil mechanical structure. Should be reduced an excessive soil mass transfer and migration of the soil solution within soil continuum to ensure the delivery of nutrients to the roots of plants without transport of these elements through the soil. On these principals the biogeosystem will lose some temporal and spatial uncertainty, become more stable and predictable. The heterogeneity in carbon and other material streams caused by landscape will be reduced. The excessive carbon and nutrients fluxes between terrestrial systems and to aquatic system will be excluded.

The idea of ions association in the soil solution helps to obtain a new glance on the processes in soil solution, soil and landscape, to consider quantitatively the equilibria model and its options for soil in vivo, undisturbed by procedures of physical modeling. The research fulfilled on example of dry steppe chestnut saline solonetzic soil of Southern Russia shows dangerous for biosphere uncertainty of terrestrial carbon sink from soil to the great extend is linked to high mobility of carbon in form of carbonates in the soil solution. Concerning preferable water flows [47, 94], the soil geochemical barriers for carbonates are probably less stable than in was known before.

The association of ions in soil solutions is one of the geochemical drivers promoting transformation of solution, salt and heavy metal migration and accumulation in disperse system, soil genesis, excessive fluxes of carbon into soil, carbon sink from soil and biosphere to lithosphere and other geospheres [28, 49-52]. According to the mathematical model of thermodynamic state of soil solution the excessive carbon sink from the soil to other parts of biosphere and geospheres is of high probability. On the base of research fulfilled it is obvious that correction of phases and

stages of carbon in soil is a challenging task to stabilize the soil, landscape, climate of the Earth [32, 35, 49-52, 97, 114].

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