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Ion association in water solution of soil and vadose zone of chestnut saline solonetz as a driver of terrestrial carbon sink

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Abstract. The assessment of soil and vadose zone as the drains for carbon sink and proper modeling of the effects and extremes of biogeochemical cycles in the terrestrial biosphere are the key components to understanding the carbon cycle, global climate system, and aquatic and terrestrial system uncertainties. Calcium carbonate equilibrium causes saturation of solution with $CaCO_3$, and it determines its material composition, migration and accumulation of salts. In a solution electrically neutral ion pairs are formed: $CaCO_3^0$, $CaSO_4^0$, $MgCO_3^0$, and $MgSO_4^0$, as well as charged ion pairs $CaHCO_3^+$, $MgHCO_3^+$, $NaCO_3^-$, $NaSO_4^-$, $CaOH^+$, and $MgOH^+$. The calcium carbonate equilibrium algorithm, mathematical model and original software to calculate the real equilibrium forms of ions and to determine the nature of calcium carbonate balance in a solution were developed. This approach conducts the quantitative assessment of real ion forms of solution in solonetz soil and vadose zone of dry steppe taking into account the ion association at high ionic strength of saline soil solution. The concentrations of free and associated ion form were calculated according to analytical ion concentration in real solution. In the iteration procedure, the equations were used to find the following: ion material balance, a linear interpolation of equilibrium constants, a method of ionic pairs, the laws of initial concentration preservation, operating masses of equilibrium system, and the concentration constants of ion pair dissociation. The coefficient of ion association γ_e was determined as the ratio of ions free form to analytical content of ion $\gamma_e = C_{\text{ass}}/C_{\text{an}}$. Depending on soil and vadose zone layer, concentration and composition of solution in the ionic pair's form 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-}, and up to 85.7 % CO_3^{2-}. The carbonate system of soil and vadose zone water solution helps to explain the evolution of salted soils, vadose and saturation zones, and landscape. It also helps to improve the soil maintenance, plant nutrition and irrigation.

The association of ions in soil solutions is one of the drivers promoting transformation of solution, excessive fluxes of carbon in the soil, and loss of carbon from soil through vadose zone.

1 Introduction

The problem of carbon sequestration is based on water solution in soil and vadose zone as the drains for carbon sink (Shein et al., 2014; Sammartino et al, 2015). Physical and biogeochemical model improvement is proposed (Romanou et al., 2014). The chemical composition of soil and vadose zone water solution is influenced by calcium carbonate equilibrium (CCE). CCE depends 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, and ion exchange processes at the interface of solid and liquid phases (Minkina et al., 2012b). Biosphere uncertainties and climate extremes are linked to biogeochemical cycles in the terrestrial biosphere (Bahn et al., 2015), which have profound implications for ecosystems, society and the climate system (Reichstein et al., 2013). Proper understanding is required of the effects, drivers and

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extremes which alter the biogeochemical cycles of terrestrial biosphere, especially soil, vadose and saturation zone as a continuum of salt (including carbon) transfer (Shein et al., 2015; Kalinichenko, 2014, 2015a, b; Kalinichenko and Starcev, 2015; Kalinichenko et al., 2012, 2014a, b; Sobgayda and Solodkova, 2015; Glazko and Glazko, 2015; Yuan et al., 2014).

The heterogeneity in carbon stream out of the soil and biosphere is caused by landscape (Ågren et al., 2014), anthropogenic influence on the carbon cycle (Berger et al., 2014), change of carbon stocks (Munir et al., 2014), sinking of carbon (Lima et al., 2014; Turi et al., 2014), saturation of water with CO_3^{2-} and Ca^{2+} (Evans et al., 2014), and the function of vegetation (Melton and Arora, 2014). The CCE in water solution of soil, vadose and saturation zones provides understanding of biogeochemical element cycles, models of anthropogenic emission of greenhouse gases (Peng et al., 2014), and anthropogenic CO_2 sink to the ocean (Ishii et al., 2014).

There are significant uncertainties in understanding the role of soil mineral and organic carbon deposits in the global C cycle and its models (Z. Wang et al., 2014) and biogeochemical cycles (Caldararu et al., 2014).

The water solution is the most mobile, volatile and active agent of soil, vadose and saturation zones, and landscape properties (Amakor et al., 2013; Hunenberger and Relf, 2011; Visconti and de Paz, 2012; Anisimov et al., 2015; Endovitskii et al., 2014; Endovitsky et al., 2012; Chaplygin et al., 2014).

The properties and structure of water solution are the function of its chemical equilibrium (Debye and Hückel, 1923; Bjerrum et al., 1958; Davies, 1962; Garrels and Christ, 1965; Butler, 1998). The higher the ionic strength of the solution is, the more ions pass to form ion associates (Lewis and Randell, 1921; Adams, 1971; Sposito, 1984, 1989; Sparks, 1984). This fact is known for the waters of ocean and low mineralized waters of storage reservoirs (Levchenko, 1966). Ion association in CCE helps to explain the natural water oversaturation with carbonates, migration and accumulation of carbonates (Minkin et al., 1977; Minkin and Yendovitskii, 1986). The reason for excess saturation of water with $CaCO_3$ is the ion association into the ionic mineral and organic complexes. The carbonate system of water solution is under the influence of biological process, soil–atmosphere gas exchange, partial pressure and seasonal cycles of CO_2. The soil solution determines the dynamics of its material composition, migration and accumulation of salts into the disperse system of soil continuum, vadose, saturation zones and landscape, genesis and evolution of biosphere. In soil solutions, electrically neutral ion pairs $CaCO_3^0$, $CaSO_4^0$, $MgCO_3^0$, and $MgSO_4^0$ are formed, as well as charged ion pairs $CaHCO_3^+$, $MgHCO_3^+$, $NaCO_3^-$, $NaSO_4^-$, $CaOH^+$, and $MgOH^+$. Communication between the associated ions in soil solution is much more diverse compared to water systems (Hunenberger and Relf, 2011; Stoyanov et al., 2011; Zhang et al., 2012; Tertre et al., 2011).

Another important aspect of soil solution is its strong dependence on the soil moisture and the interaction between soil solution and soil disperse system. The sampling of a soil solution leads to destruction of its links to disperse system of soil. So the solution extracted from soil does not completely correspond to properties of native soil solution. For this reason the modeling of soil solution composition at different stages of water, salt and organic matter content in the soil, vadose, saturation zones to the some extent is more important than the direct analysis of extracted solution itself. Ionic strength of the soil solution, water solution of vadose, and saturation zones varies from 0.05 (almost ideal chemical solution after rain in upper horizon of non-saline soil) to 0.5 and more (dry saline soil), and it can be observed in a rather short time period in the same discrete part of soil, vadose, saturation zone continuum. In some cases, the ionic strength of solution can be so high that it is better to use the lows of quasicrystalline water structure and supercritical water (Johnston et al., 2010; Plugatyr et al., 2011) to describe the system properly.

Modern non-thermodynamic techniques are used for modeling the associated ion pairs in nanotubes (Izgorodina et al., 2014; Luo et al., 2013), in supercritical water (Chialvo et al., 1995; Plugatyr et al., 2011), and hybrid excitations in solution (Nicholson and Quirke, 2003; Reznikov and Shaposhnik, 2005; Maiti and Rogers, 2011; Lui et al., 2011; Farnum et al., 2011; Kielpinski, 2013). In recent years, the improved methods of direct ion pair study have been used (Westerlund et al., 2011; Besser-Rogac et al., 2011; T. Wang et al., 2014).

For most cases of water solution, it is enough to use the lows of thermodynamics. A thermodynamic mathematical model and software of soil, vadose, saturation zone of water solution equilibrium have been proposed. The model was tested by experimental data.

2 Materials and methods

2.1 Study area

The studied area is situated in the southeast of the Russian Federation, Rostov Oblast, called Lower Don.

The subject of research is the dry steppe chestnut saline solonetzic soil of southern Russia. The climate is arid, with an annual precipitation of 300–350 mm. The parent rocks are carbonate and carbonate–sulfate loess-like loam and clay. The landscape is semi-hydromorphic.

2.2 Sampling and analysis

The solonetz soil is moderately thick at 0–40 cm, moderately 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, with exchangeable cations Ca^{2+} – 182 mmol kg^{-1},

Mg^{2+} – 65 mmol kg^{-1}, and Na^+ – 34 mmol kg^{-1}. The landscape is semi-hydromorphic; vadose zone under the solonetz soil is vast – the depth of ground water varying up to 7–10 m. Solid residual in vadose zone is up to 2.0 %.

Soil and vadose zone species were sampled from a section wall down to a depth of 1 m. Samples from the deeper vadose zone layers were taken by soil auger, with a drill cup diameter of 5 cm. During preparation the samples were crushed and sifted, with openings of 2 mm, and then mixed with quartz sand in a ratio of 1 : 2 (Carter and Gregorich, 2007; Minkina et al., 2012a). The mixture from every soil and vadose zone layer was put into glass tube with an inner diameter of 3.4 cm and a length of 100 cm. At the bottom of the tube an outlet was mounted to drain the solution. Soil solution was allocated by direct displacement method with ethyl alcohol poured on the top of the soil column. The volume of soil solution emitted from every soil column was 20–60 mL.

Soil and vadose zone solution was analyzed by standard methods (Carter and Gregorich, 2007; Visconti and de Paz, 2012). Moisture of soil was determined by thermostat 105 °C method. Dry residual of the soil was determined by thermostat 105 °C method. pH was measured in thermostat (20 ± 0.2 °C) by a pH meter with a glass electrode. The carbonate and bicarbonate anions were titrated directly by 0.01 M hydrochloric acid detecting titration, endpoint on color change of indicators – phenolphthalein and methyl orange. The chloride ion was detected by argentometric method with potassium chromate. The total content of Ca^{2+} and Mg^{2+} was measured by complexometric titration. In another aliquot Ca^{2+} was determined by complexometric. Mg^{2+} was calculated as a difference. The sulfate was analyzed by $BaSO_4$ sedimentation method and Na^+ by flame photometric detection. The experiment was performed in triplicate. All statistical calculations were performed using Microsoft Excel 2010.

3 Results

Carbonate system of soil solution includes dynamic equilibriums (Fig. 1).

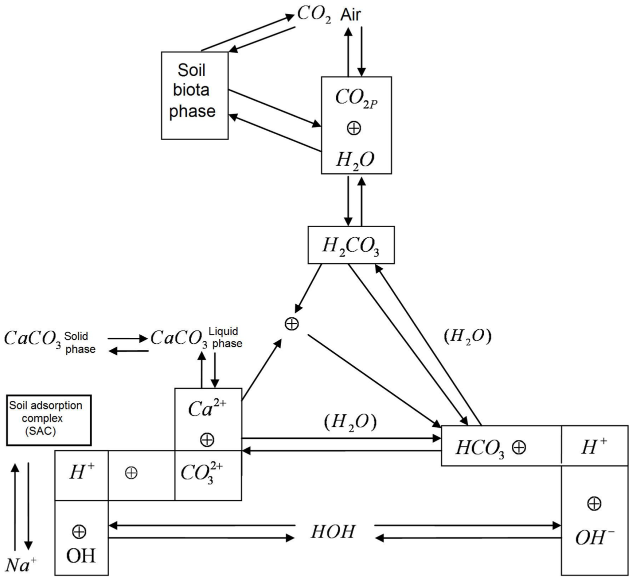

Figure 1. Calcium carbonate equilibrium system of soil solution.

CCE system of soil solution is an adsorption–hydration balance between solution, gas phase, and bioorganic phase, including step dissociation of carbonic acid, as well as calcium carbonate equilibrium between solution, soil absorbing complex, sediments of $CaCO_3$ and solid phase, and the ion equilibrium of water. The deposition or dissolution of $CaCO_3$ is caused by receipt or removal of Ca^{2+}, HCO_3^- and CO_3^{2-} from solution and carbonate equilibrium shift. It is influence by ionic composition of soil solution, and it determines the type of migration and accumulation of various forms of carbonate forms through the soil profile.

The dry residual of soil and vadose zone solution is rather high. Analytical composition is typical for dry steppe chestnut saline solonetzic soil of southern Russia (Table 1). The state of ions in such a solution is influenced by the high ionic strength and ion association in soil and vadose zone solution.

The measure of real participation of salts and separate ions in soil chemical reactions is their activity. The real state of the main ions in soil solutions was determined on the basis of ionic strength and ion association in the soil solution. Algorithms were proposed for soil and vadose zone solution equilibrium calculation (Endovitskii and Minkin, 1979; Endovitskii et al., 1985; Endovitskii et al, 2009). On the basis of analytical data (Table 1) using our own software, the forms of main ions in the soil solution were calculated according the method of ionic pairs (MIP) (Adams, 1971): the law of initial concentration preservation and the law of the operating masses of chemical equilibrium system.

The concentration was calculated of free and associated forms of ions according to the sum of the ion's analytical concentration. To carry out the calculation, the following was used: iteration to solve the system of algebraic equations of the material balance of ions and linear interpolation to calculate the values of tabulated equilibrium constants according calculated data.

The equations of main ions material balance are as follows:

$$\sum \mathrm{Ca}^{2+} = \left[\mathrm{Ca}^{2+}\right] + \left[\mathrm{CaCO}_3^0\right] + \left[\mathrm{CaHCO}_3^+\right] + \left[\mathrm{CaSO}_4^0\right], \tag{1}$$

$$\sum \mathrm{Mg}^{2+} = \left[\mathrm{Mg}^{2+}\right] + \left[\mathrm{MgCO}_3^0\right] + \left[\mathrm{MgHCO}_3^+\right] + \left[\mathrm{MgSO}_4^0\right], \tag{2}$$

Table 1. Soil solution of chestnut saline solonetz, measured in mmol-eq $\mathrm{L^{-1}}$.

Layer, cm	Moisture, %	Solid residue, $\mathrm{g\,L^{-1}}$	pH	Ca^{2+}	Mg^{2+}	Na^{+}	CO_3^{2-}	HCO_3^{-}	SO_4^{2-}	Cl^{-}
0–5	22.4 ± 0.9	1.64 ± 0.39	7.82 ± 0.06	4.94 ± 0.65	6.78 ± 1.25	11.22 ± 2.02	absent	4.75 ± 1.36	10.44 ± 2.28	7.75 ± 0.95
5–14	30.7 ± 0.8	6.74 ± 1.23	9.02 ± 0.08	12.33 ± 0.98	28.72 ± 2.75	60.21 ± 7.42	1.95 ± 0.88	8.64 ± 1.99	59.45 ± 4.58	31.22 ± 2.02
14–30	37.4 ± 1.3	18.10 ± 3.82	8.76 ± 0.07	23.17 ± 1.24	94.15 ± 12.56	165.73 ± 14.65	0.99 ± 0.71	8.31 ± 1.45	184.31 ± 13.22	89.44 ± 5.24
30–40	28.7 ± 1.1	35.54 ± 3.65	8.68 ± 0.05	24.84 ± 1.78	130.22 ± 13.43	400.27 ± 21.21	0.82 ± 0.68	7.74 ± 1.82	358.32 ± 25.69	188.45 ± 13.89
70–80	27.0 ± 1.1	50.58 ± 6.21	8.20 ± 0.04	35.74 ± 3.68	349.46 ± 30.67	444.42 ± 20.33	absent	6.93 ± 1.91	467.48 ± 24.86	355.21 ± 17.34
140–150	25.2 ± 1.0	38.86 ± 4.27	8.02 ± 0.7	20.41 ± 3.79	194.28 ± 16.28	414.09 ± 30.77	absent	7.15 ± 2.38	327.28 ± 24.12	294.35 ± 18.01

$$\sum \mathrm{Na^{+}} = \left[\mathrm{Na^{+}}\right] + \left[\mathrm{NaCO_3^{-}}\right] + \left[\mathrm{NaSO_4^{-}}\right], \tag{3}$$

$$\sum \mathrm{CO_3^{2-}} = \left[\mathrm{CO_3^{2-}}\right] + \left[\mathrm{CaCO_3^{0}}\right] + \left[\mathrm{MgCO_3^{0}}\right] + \left[\mathrm{NaCO_3^{-}}\right], \tag{4}$$

$$\sum \mathrm{HCO_3^{-}} = \left[\mathrm{HCO_3^{-}}\right] + \left[\mathrm{CaHCO_3^{+}}\right] + \left[\mathrm{MgHCO_3^{+}}\right], \tag{5}$$

$$\sum \mathrm{SO_4^{2-}} = \left[\mathrm{SO_4^{2-}}\right] + \left[\mathrm{CaSO_4^{0}}\right] + \left[\mathrm{MgSO_4^{0}}\right] + \left[\mathrm{NaSO_4^{-}}\right], \tag{6}$$

where $[\mathrm{Ca^{2+}}]$ and $[\mathrm{Mg^{2+}}]$ are the equilibrium concentrations of the free form of the ions, and $[\mathrm{CaCO_3^0}]$ and $[\mathrm{MgCO_3^0}]$ are equilibrium concentrations of ion in associated form (ion pair).

For groups of cations, the concentration constants of ionic pair dissociation follow the law of operating masses given via Eqs. (7)–(9):

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

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

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

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

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

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

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

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

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

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

According to Davies equation for constants, the concentration constant of dissociation in Eqs. (10)–(15) was recalculated:

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

where K denotes the concentration constant of dissociation of ionic couple, K^0 the corresponding thermodynamic constant, A the Debye–Huckel constant 0.5042 at 20 °C, AZ^2 the algebraic sum of squares of a charge of the particles in the equation of dissociation constant, and I the ionic strength of solution.

The calculated pK value with Eq. (16) corresponds to Bjerrum et al. (1958), Garrels and Christ (1965), Debye and Huckel (1923), and Sposito (1984).

Thermodynamic constants of dissociation are as follows (Lurie, 1986; Handbook of chemist 21; Sposito, 1989):

$$\begin{aligned} &pK^0_{\mathrm{CaCO_3}} = 3.2;\ pK^0_{\mathrm{CaHCO_3}} &&= 1.26;\ pK^0_{\mathrm{CaSO_4}} &&= 2.31.\\ &pK^0_{\mathrm{MgCO_3}} = 3.4;\ pK^0_{\mathrm{MgHCO_3}} &&= 1.16;\ pK^0_{\mathrm{MgSO_4}} &&= 2.36.\\ &pK^0_{\mathrm{NaCO_3}} = 1.27;\ pK^0_{\mathrm{NaSO_4}} &&= 0.72. \end{aligned}$$

The formal ionic strength of soil solution was calculated with the data of analytical ion concentration according to Eq. (17):

$$\begin{aligned} &I = 0,5[2^2(\mathrm{Ca}^{2+}) + 2^2(\mathrm{Mg}^{2+}) + (\mathrm{Na}^{+})\\ &+2^2(\mathrm{CO}_3^{2-}) + (\mathrm{HCO}_3^{-})\\ &+2^2(\mathrm{SO}_4^{2-}) + (\mathrm{Cl}^{-})],\ \mathrm{mol\,L^{-1}}. \end{aligned} \tag{17}$$

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

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 (Eqs. 7–9).

The effective ionic force of solution was calculated according to the values of equilibrium concentration of all ion forms according to Eq. (18):

$$\begin{aligned} &I^* = 0,5\left\{\begin{array}{l} 2^2\left[\mathrm{Ca}^{2+}\right] + 2^2\left[\mathrm{Mg}^{2+}\right] + \left[\mathrm{Na}^{+}\right]\\ +2^2\left[\mathrm{CO}_3^{2-}\right] + \left[\mathrm{HCO}_3^{-}\right] + 2^2\left[\mathrm{SO}_4^{2-}\right] \end{array}\right.\\ &+\left[\mathrm{CaHCO}_3^{+}\right] + \left[\mathrm{MgHCO}_3^{+}\right] + \left[\mathrm{NaCO}_3^{-}\right]\\ &+\left[\mathrm{NaSO}_4^{-}\right] + \left[\mathrm{Cl}^{-}\right])\},\ \mathrm{mol\,L^{-1}}. \end{aligned} \tag{18}$$

As a result of the first step of iteration procedure, the concentration constants of dissociation were calculated (Eq. 16). The new system of equations of material balance was obtained. On the new set of the system, components made the next iteration of Eqs. (10)–(15). By the iteration sequence calculated the ion forms in soil solution.

The coefficient of ion association γ_e is proposed as a ratio of ion free form to its analytical content:

$$\gamma_e = C_{\mathrm{ass}}/C_{\mathrm{an}}, \tag{19}$$

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

An activity coefficient is a factor used in thermodynamics to account for deviations from ideal behavior in a mixture of chemical substances. Activity coefficients may be determined experimentally, and it can be calculated theoretically using the Debye–Hückel equation and other models. The γ_e factor in Eq. (19) is not a result of direct determination or direct calculation, but rather it is an integral product of several stages of modeling taking into account laws of a solution's chemical thermodynamics and corresponding to Eqs. (1)–(18).

For calculation, the software product was used, developed by Endovitskii and Minkin (1979) and Endovitskii et al. (1985, 2009).

4 Discussion

Equations (7)–(19) were used to model the association of ions at a given analytical composition of solution (Table 1).

At high ionic strength of soil solution, the biological processes in plant and mass transfer in vadose zone are extremely slow. In this respect the modeling at soil solution ionic strength of more than 1.0 is excessive. The circumstance is significant for soil of medium salinity, where the solution in soil and aeration zone had an ionic strength of about 1.0 at low soil moisture, and it is not available to remove from dispersed systems without disturbing the structure and linkages with the solid and gas soil systems, and direct analytical composition determination.

A range of estimated ionic strength from 0.05 to 1.2 corresponds to the activity of ions useful for plants and moveable in vadose zone concentrated solutions. At higher ionic strength, the soil biological processes, plant growth and mass transfer in vadose zone are extremely slow.

To obtain the baseline data for thermodynamic model's testing, a standard physical modeling method was used. The method has drawbacks. Instead of proper soil, the substrate of soil and sand is used. Otherwise, the extraction of soil solution from the native soil of heavy structure and corresponding granulometric composition is impossible. The presence of sand in the substrate dramatically increases the hydraulic conductivity of the artificial system. It is distinguished from natural chestnut soil. The next lack of direct soil solution extraction methods is that links are broken in the system "solid–liquid phase".

Chestnut soil has low humidity. But at low soil moisture the soil solution displacement method is useless, so in the experiment the high soil moisture was applied. This leads to inadequate generalization of the object's simulation, but another version of the direct study of soil solution composition is not currently available. This disadvantage of method is a reason for thermodynamic model development. It allows for extrapolation of the solution's state in soil and vadose zone to the range of low humidity of soil complex components.

The real equilibrium concentration of ion forms in soil solution and vadose zone depends on concentration and composition of soil solution (Tables 2, 3). The higher the salinity of the solution, the more the ions are associated. In the form of ionic pairs in saline horizons of soil and vadose zone, there 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-}, and up to 85.7 % CO_3^{2-}. In non-saline soil horizon at 0–5 cm at soil humidity of 22.4 %, most of the ions are in free form.

Due to ion association, the mobility of dry steppe chestnut saline solonetzic soil and vadose zone water solution compo-

Table 2. Forms of ions (cations) in the soil solution of chestnut saline solonetz, % of the total ion content.

Depth, cm	Calcium				Magnesium				Sodium		
	$[\mathrm{Ca}^{2+}]$	$[\mathrm{CaCO}_3^0]$	$[\mathrm{CaHCO}_3^+]$	$[\mathrm{CaSO}_4^0]$	$[\mathrm{Mg}^{2+}]$	$[\mathrm{MgCO}_3^0]$	$[\mathrm{MgHCO}_3^+]$	$[\mathrm{MgSO}_4^0]$	$[\mathrm{Na}^+]$	$[\mathrm{NaCO}_3^-]$	$[\mathrm{NaSO}_4^-]$
0–5	78.96	absent	3.43	17.61	77.83	absent	2.69	19.48	98.91	absent	1.09
5–14	63.14	2.46	3.17	31.23	60.36	3.72	2.41	33.50	96.28	0.13	3.59
14–30	56.47	0.44	1.93	41.16	53.84	0.66	1.46	44.03	93.10	0.03	6.86
30–40	48.09	0.24	1.39	50.29	45.37	0.35	1.04	53.23	89.53	0.02	10.44
70–80	49.58	absent	1.11	49.31	46.87	absent	0.83	52.29	90.12	absent	9.88
140–150	53.78	absent	1.36	44.86	51.13	absent	1.02	47.85	91.47	absent	8.53

Table 3. Forms of ions (anions) in the soil solution of chestnut saline solonetz, % of the total ion content.

Depth, cm	Sulfates				Hydrocarbons			Carbonates				Chlorides
	$[\mathrm{SO}_4^{2-}]$	$[\mathrm{CaSO}_4^0]$	$[\mathrm{MgSO}_4^0]$	$[\mathrm{NaSO}_4^-]$	$[\mathrm{HCO}_3^-]$	$[\mathrm{CaHCO}_3^+]$	$[\mathrm{MgHCO}_3^+]$	$[\mathrm{CO}_3^{2-}]$	$[\mathrm{CaCO}_3^0]$	$[\mathrm{MgCO}_3^0]$	$[\mathrm{NaCO}_3^-]$	
0–5	76.69	8.33	12.65	2.33	96.30	1.78	1.92	absent	absent	absent	absent	100
5–14	70.07	6.48	16.19	7.27	93.73	2.26	4.00	21.65	15.54	54.84	7.97	100
14–30	59.99	5.17	22.49	12.34	89.02	2.69	8.29	15.36	10.28	63.14	11.21	100
30–40	53.83	3.49	19.35	23.33	89.01	2.23	8.76	14.32	7.20	56.44	22.03	100
70–80	38.35	3.77	39.09	18.79	76.13	2.86	21.01	absent	absent	absent	absent	100
140–150	47.22	2.80	28.40	21.58	84.17	1.93	13.90	absent	absent	absent	absent	100

nents is higher compared to previous estimates, especially for carbonates. In such circumstances the preferred water fluxes in the soil and vadose zone cause the loss of soil mineral phase to deep soil horizons, then to vadose zone, saturation zone and landscape. The vertical and lateral salt redistribution is high. The association of ions in saline carbonate water solution is a cause of high salt mobility through the vadose and saturation zones. It is dangerous in a view of biosphere carbon loss, and this indicates the need for measures to reduce this seepage. The carbon sequestration theory should not be understood as a carbon isolation but rather as the transformation of carbon gaseous phase to biological phase.

Association of ions in water solutions of soil and vadose zone promotes innovative solutions in the field of soil water regime and water saving (El Marazky et al., 2011; Kalinichenko, 2014; Seitkaziev et al., 2015).

The nature of CCE in soils is a reason why, using an analytical concentration of ions, only the high calculated saturation degree of soil solutions with $\mathrm{CaCO_3}$ is observed. Accounting processes of ion association reduces the supersaturation of soil solutions with $\mathrm{CaCO_3}$ for 10–50 times. The similar effect on soil solution has its ionic strength. In view of complexation of $\mathrm{Ca^{2+}}$ with soluble organic substance, the degree of calculated soil solution saturation with $\mathrm{CaCO_3}$ reduces up to 1.5–2.0 times.

Accounting association and activity of ions and calculating degree of soil solution saturation with chemicals provides new understanding of migration and accumulation of chemical compounds in soils, vadose and saturation zones, and landscapes concerning $\mathrm{CaCO_3}$.

Along with salt dynamics in soil profile, the lateral transfer of substances in landscapes and watersheds is important. The developed approach is closely linked to these objects due to the fact that, given the association of ions in the soil solution, assessment of the likelihood of substance mobility in landscape and watershed is significantly higher than previously thought.

The dynamics of solution composition is related to moisture of soil and aeration zone. According to the simulation, the transfer of substances in the soil and vadose zone is noticeable at low soil moisture. With this point of view, the transfer of a substance in disperse systems should be considered not only as the unbroken mass transfer flux but also taking into account the formation of micro-basins of solution. As the humidity reduces, the mass transfer zone of the actual transfer of water and dissolved substances becomes more discrete. The reason for discontinuity of the flow is the difference of water thermodynamic potential in individual capillaries, inner surfaces of soil, and water surface curvature variations. After subsequent wetting of soil, the agent of transfer does not pass the dissolution stage, but it quickly enters into a geochemical transfer process. The micro-basin formation, on the one hand, is useful as a source of plant nutrients, but, on the other hand, it is dangerous in terms of easy loss of useful substances from the soil and vice versa – the receipt of unwanted substances.

In agriculture, there is a danger of distortion of calcium carbonate system of soil and aeration zone. This determines a need for new findings in management of soil and aeration zone focused on reducing mobility of matter, especially for technological tools that will overcome an entrainment of useful substances from the soil, as well as receipt and accumulation of unfavorable substances at agriculture and irrigation.

5 Conclusions

The result obtained in experiment and modeling shows the fundamental peculiarities of behavior of calcium carbonate system in soil and vadose zone water solution taking into account the ion association. At high ionic force in soil solution, electrically neutral ion pairs $CaCO_3^0$, $CaSO_4^0$, $MgCO_3^0$, and $MgSO_4^0$ are formed, as well as charged ion pairs $CaHCO_3^+$, $MgHCO_3^+$, $NaCO_3^-$, $NaSO_4^-$, $CaOH^+$, and $MgOH^+$. The association of ions shows that the thermodynamic preconditions of $CaCO_3$ sedimentation in soil and vadose zone occur at a much higher concentration of Ca^{2+} and CO_3^{2-} ions in soil solution than was considered previously. Therefore, there is a significant probability of high mobility of $CaCO_3$ in soil, vadose and saturation zones, and landscape, which was underestimated earlier.

The quantitative solving of water solution thermodynamic model shows that mobility of matter, especially carbon, in terrestrial system is much higher than was known before. The prediction of soil, vadose and saturation zone,and landscape evolution will be properly carried out.

This research shows that uncertainty of terrestrial carbon sink from soil through vadose zone is linked to high mobility of carbon in the form of carbonates in the soil solution of dry steppe chestnut saline solonetzic soil of southern Russia. The soil geochemical barriers for carbonates are probably less stable than was known before. The association of ions in soil solutions is one of the drivers promoting transformation of solution, excessive fluxes of carbon into soil, and loss of carbon from soil and vadose zone.

The revealed regularities represent the evolution model of soil complexes under halogenesis on the global scale

Author contributions. Abdul-Malik A. Batukaev, the head of investigation, designed the plan of research and organized the study and data analysis, which were coordinated by Tatiana M. Minkina. The idea of ion association in soil solution was by provided by Anatoly P. Endovitsky, who also gave the system of equations. The mathematical model was developed by Andrey G. Andreev. This model was interpreted by Valery P. Kalinichenko. Svetlana N. Sushkova collected the field data and performed the statistical analysis. Zaurbek S. Dikaev, Tatiana M. Minkina and Saglara S. Mandzhieva carried out the experiment. All the authors contributed in writing of the paper.

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