Ion's association in soil and vadose zone of Azov-Black sea region

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Abstract. The assessment of soil and vadose zone as the drains for carbon sink, proper modelling of the effects and extremes of biogeochemical cycles in terrestrial biosphere are the key components to understand the carbon cycle, global climate system, aquatic and terrestrial systems uncertainties. Carbonate-calcium equilibrium causes saturation of solution with $CaCO_3$, determines its material composition, migration and accumulation of salts. In solution are formed electrically neutral ion pairs $CaCO_3°$, $CaSO_4°$, $MgCO_3°$, $MgSO_4°$. Charged ion pairs $CaHCO_3^+$, $MgHCO_3^+$, $NaCO_3^-$, $NaSO_4^-$, $CaOH^+$, $MgOH^+$ are developed the carbonate-calcium equilibrium algorithm, mathematical model and original software to calculate the real equilibrium forms of ions and determine the nature of carbonate-calcium balance in solution. An approach conducts the quantitative assessment of real ion forms of solution in solonetz soil and vadose zone of dry steppe taking into account the ions association at high ionic strength of saline soil solution. The concentration of free and associated ion form were calculated according to analytical ion concentration in real solution. In iteration procedure were used the equations of 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, the concentration constants of ion pair dissociation. The coefficient of ion association γ_e was determined as a ratio of ions free form to analytical content of ion $\gamma_e = C_{ass}/C_{an}$. 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-}, 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, 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, loss of carbon from soil through vadose zone.

1 Introduction

The problem of carbon sequestration is to be 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's improvement is proposed (Romanou et al., 2014). The chemical composition of soil and vadose zone water solution is influenced by 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 (Minkina

et al., 2012). Biosphere uncertainties, 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). The proper understanding is required of effects, drivers and extremes which altered the biogeochemical cycles of terrestrial biosphere, especially soil, vadose and saturation zone as a

5   continuum of salt's (including carbon) transfer.

The heterogeneity in carbon stream out of the soil and biosphere are 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), the function of vegetation (Melton and Arora, 2014). The CCE in water solution of soil,

10   vadose and saturation zones provides understanding of biogeochemical element cycles, models of anthropogenic emission of greenhouse gases (Peng et al., 2014), 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 (Wang et al., 2014), biogeochemical cycles (Caldararu et al., 2014).

15   The water solution is most mobile, volatile and active agent of soil, vadose and saturation zones, 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 is

20   ionic strength of the solution, the more ions pass to form of ions associates (Lewis and Randell, 1921; Adams, 1971; Sposito, 1984, 1989; Sparks, 1984). The fact is known for the waters of ocean and low mineralized waters of storage reservoirs (Levchenko, 1966). Ion's 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 of excess saturation of water with $CaCO_3$ is the ions association

25   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 solution are formed electrically neutral ion pairs $CaCO_3°$, $CaSO_4°$, $MgCO_3°$, $MgSO_4°$,

30   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 (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, interaction between soil solution and soil disperse system. The sampling of soil solution leads to destruction of its links to

35   disperse system of soil. So, the solution extracted from soil does not completely correspond to properties of native soil solution. On this reason the modelling of soil solution composition at different stages of water, salt and organic matter content in the soil, vadose, saturation zones to the some extend is more important than direct analyzing of extracted solution itself. Ionic strength of the soil solution, water solution of vadose, saturation zones 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), and it can be observed in rather short time period in the same discrete part of soil, vadose, saturation zones continuum. In some cases, the ionic strength of solution can be so high, as it is better to use the lows of quasicrystalline water structure, supercritical water (Johnston et al., 2010; Plugatyr et al., 2011) to describe the system properly.

5 The modern non-thermodynamic techniques are used for modelling 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), hybrid excitations in solution etc (Nicholson and Quirke, 2003; Reznikov and Shaposhnik, 2005; Maiti and Rogers, 2011; Lui et al., 2011; Farnum et al., 2011; Kielpinski, 2013). Recent years, the improved methods of direct ion pair study are used (Westerlund et al., 2011; Besser-Rogac et al., 2011; Wang et al., 2014).

10 For the most cases of water solution it is enough to use the lows of thermodynamics. The thermodynamics mathematical model and software of soil, vadose, saturation zones water solution equilibrium are proposed. The model was tested by experimental data.

2 Materials and methods

2.1 Study Area

15 The studied area is situated in South-East of the Russian Federation, Rostov region, and is named Lower Don.

Object of research is the dry steppe chestnut saline solonetzic soil of Southern Russia. The climate is arid, annual precipitation of 300-350 mm. The parent rocks are Carbonate and Carbonate-sulfate loess-like loam and clay. The landscape is semi-hydromorphic.

20 ### 2.2 Sampling and Analysis

The solonetz soil is moderately thick 0-40 cm, 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 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 25 to 2.0%.

Soil and vadose zone species were sampled from a section wall down to the depth of 1 m, samples from the deeper vadose zone layers were made by the soil auger, drill cup diameter 5 cm. During preparation the samples were crushed and sifted, openings 2 mm, than mixed with quartz sand in ratio 1:2 (Carter and Gregorich, 2007; Minkina et al., 2012). The mix from every soil and vadose zone layer was charged into 30 glass tube, inner diameter of 3.4 cm, length of 100 cm. At the bottom of the tube was mounted a solution draining off outlet. Soil solution was allocated by direct displacement method with ethyl alcohol poured on the top of 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 35 determined by thermostat 105°C method. pH was measured in thermostat (20±0,2°C) by 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

5 calculated as a difference. The sulfate was analyzed by $BaSO_4$ sedimentation method; 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).
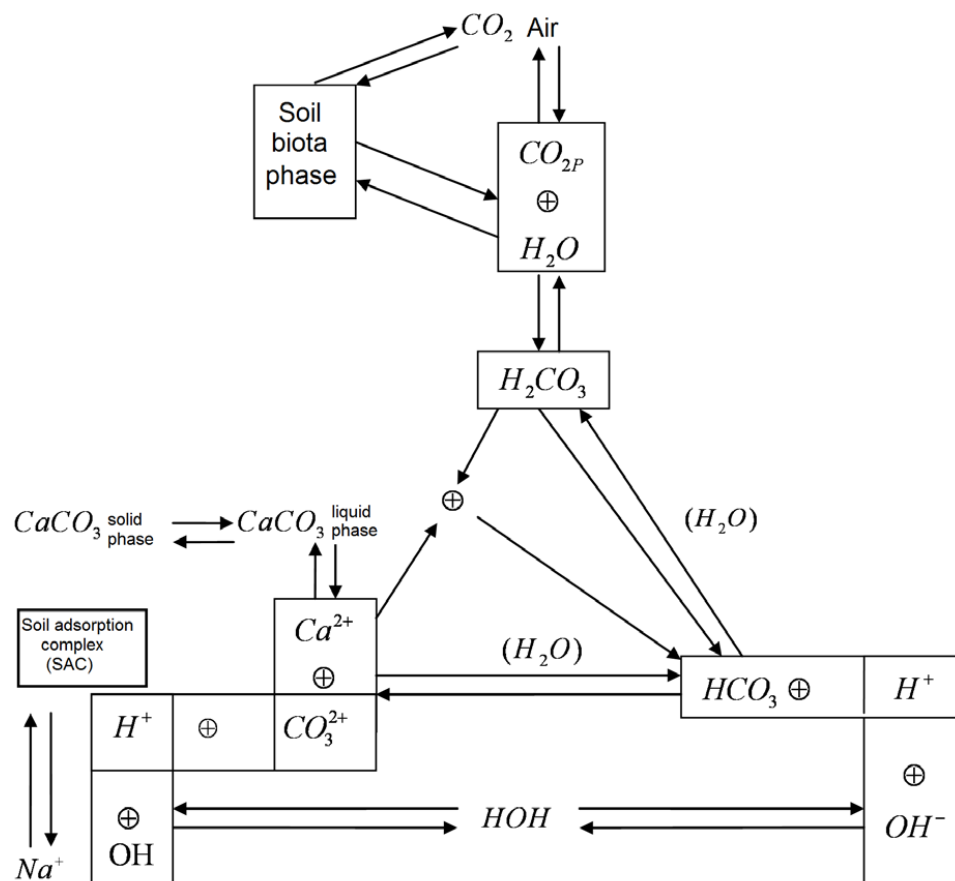
Figure 1. Calcium carbonate equilibrium system of soil solution

CCE system of soil solution is an adsorption-hydration balance between solution, gas phase, bioorganic phase, 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. The deposition or dissolution of $CaCO_3$ is caused by receipt or removal of Ca^{2+}, HCO_3^- and CO_3^{2-} from solution, carbonate

5   equilibrium shift, is influence by ionic composition of soil solution, and determine 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 solution is influenced by the high ionic strength and ion's association in soil and vadose zone solution.

10   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's association in the soil solution. The algorithm 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 own software the forms of main ions in the soil solution were calculated according the

15   Method of Ionic Pairs (MIP) (Adams, 1971): the law of initial concentration preservation, 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 ion's analytical concentration. To carry out the calculation were used: iteration to solve the system of algebraic equations of the material balance of ions; linear interpolation to calculate the values of tabulated equilibrium

20   constants according calculated data.

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

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

(1)

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

25

(2)

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

(3)

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

(4)

30    $$\sum HCO_3^{-} = \left[HCO_3^{-}\right] + \left[CaHCO_3^{+}\right] + \left[MgHCO_3^{+}\right]$$

(5)

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

(6)

where, $[Ca^{2+}]$, $[Mg^{2+}]$ – the equilibrium concentration of the free form of ion, $[CaCO_3^0]$, $[MgCO_3^0]$, – equilibrium concentration of ion in associated form (ion pair).

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

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

(7)

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

(8)

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

(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
15   transformed as follows. Equations (10-15):

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

(10)

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

(11)

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

20   (12)

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

(13)

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

(14)

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

(15)

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

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

(16)

where in K – concentration constant of dissociation of ionic couple; K^0 – the corresponding thermodynamic
10 constant; A – Debye-Huckel constant $0{,}5042$ at 20^0C; ΔZ^2 – the algebraic sum of squares of a charge of the particles in the equation of dissociation constant; I – ionic strength of solution.

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

Thermodynamic constants of dissociation as follows (Lurie, 1986;   Handbook of chemist 21;

15 Sposito G., 1989):

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

The formal ionic strength of soil solution was calculated on the data of analytical ion concentration. Equation (17):

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

20 (17)

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
25 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 (18):

$$I^* = 0.5 \begin{Bmatrix} 2^2[Ca^{2+}] + 2^2[Mg^{2+}] + [Na^+] + 2^2[CO_3^{2-}] + [HCO_3^-] + 2^2[SO_4^{2-}] \\ + [CaHCO_3^-] + [MgHCO_3^-] + [NaCO_3^-] + [NaSO_4^-] + [Cl^-] \end{Bmatrix}, mol/l$$

(18)

5 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 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

10 (19):

$$\gamma_e = C_{ass} / C_{an}$$

(19)

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

15 For calculation were used the software product , developed by the authors s (Endovitskii and Minkin, 1979; Endovitskii et al., M. B., 1985; Endovitskii et al., 2009).

4 Discussion

The equations 7-19 were used to model the association of ions at given analytical composition of solution

20 (Table 1).

The real equilibrium concentration of ion forms in soil solution and vadose zone depends on concentration and composition of soil solution (Table 2, 3). The higher salinity of the solution, the more ions are associated. In the form of ionic pairs in saline horizons of soil and vadose zone 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-}. In non-saline soil horizon 0-5 cm at soil

25 humidity of 22.4% the most of ions are in free form.

Due to ion association the mobility of dry steppe chestnut saline solonetzic soil and vadose zone water solution components is higher compared to previous estimates, especially for carbonates. In such circumstances the preference water fluxes in the soil and vadose zone causes the loss of soil mineral phase to deep soil horizons, then to vadose zone, saturation zone and landscape. The vertical and lateral salt

30 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 indicates the need for measures to reduce this seepage. The carbon sequestration theory is to be

understandable not as a carbon isolation, but 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, water saving. (El Marazky et al., 2011; Kalinichenko, 2014; Seitkaziev et al., 2015).

5   The nature of CCE in soils is a cause why using an analytical concentration of ions only the high calculated saturation degree of soil solutions with $CaCO_3$ is observed. Accounting processes of ion association reduces the supersaturation of soil solutions with $CaCO_3$ for 10 ... 50 times. The similar 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.

10 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, vadose and saturation zones, and landscapes concerning $CaCO_3$.

5 Conclusion

15 The result obtained in experiment and modelling shows the fundamental peculiarities of behaviour of calcium carbonate system in soil and vadose zone water solution taking into account the ion's association. At high ionic force in soil solution are formed electrically neutral ion pairs $CaCO_3°$; $CaSO_4°$, $MgCO_3°$, $MgSO_4°$, charged ion pairs $CaHCO_3^+$, $MgHCO_3^+$, $NaCO_3^-$, $NaSO_4^-$, $CaOH^+$, $MgOH^+$. The association of ions shows that the thermodynamic preconditions of $CaCO_3$ sedimentation in soil and vadose zone occur at much higher

20 concentration of Ca^{2+} and CO_3^{2-} ions in soil solution than it was considered previously. Therefore, there is a significant probability of high mobility of $CaCO_3$ in soil, vadose and saturation zones, and landscape, underestimated earlier.

The quantitative solving of water solution thermodynamic model shows that mobility of matter, especially carbon, in terrestrial system is much higher than in was known before. On this foundation the prediction of

25 soil, vadose and saturation zone, landscape evolution will be proper, soil and landscape management will be better and stable.

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 research fulfilled shows that the dangerous for biosphere uncertainty of terrestrial carbon sink from soil

30 through the vadose zone to the great extend is linked to high mobility of carbon in form of carbonates in the soil solution of dry steppe chestnut saline solonetzic soil of Southern Russia. Concerning preferable water flows (Shein et al., 2015), 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 drivers, promoting transformation of solution, excessive fluxes of carbon into soil, and loss of carbon from soil and biosphere to lithosphere and

35 other geospheres (Kalinichenko, 2014, 2015; Kalinichenko and Starcev, 2015; Kalinichenko et al., 2012, 2014; Sobgayda and Solodkova, 2015). Correction of carbon in soil, vadose and saturation zones, landscape stabilizes the biosphere (Glazko and Galzko, 2015; Yuan et al., 2014).

The soil is an important sink of atmosphere carbon, a resource of biological carbon for vadose zone lithosphere and other geospheres. The role of soil and vadose zone water solution as a biological and geosphere driver of terrestrial carbon sink is to be revised to higher rate on the idea of association of ions.

Author contribution. A.A. Batukaev, the head of investigation, designed the plan of research, organized the

5   study and data analysis, which were coordinated T.M. Minkina. The idea of ion's association in soil solution was by provided A.P. Endovitsky. He also gave the system of equations, and the mathematical model was developed by A.G. Andreev. This model was interpreted by V.P. Kalinichenko. S.N. Sushkova, V.A. Chapligin collected the field data, performed the statistical analysis. Z.S. Dikaev, T.M. Minkina, V.A. Chapligin S.S. and Mandzhieva carried out the experiment. All the authors contributed in writing of the

10   manuscript.

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1   Table 1. Soil solution of chestnut saline solonetz, mmol-eq/l.

Layer, cm	Moisture, %	Solid residue, g/l	pH	Ca^{2+}	Mg^{2+}
0-5	22,4±0,9	1,64±0,39	7,82±0,06	4,94±0,65	6,78±1,25
5-14	30,7±0,8	6,74±1,23	9,02±0,08	12,33±0,98	28,72±2,75
14-30	37,4±1,3	18,10±3,82	8,76±0,07	23,17±1,24	94,15±12,56
30-40	28,7±1,1	35,54±3,65	8,68±0,05	24,84±1,78	130,22±13,43
70-80	27,0±1,1	50,58±6,21	8,20±0,04	35,74±3,68	349,46±30,67
140-150	25,2±1,0	38,86±4,27	8,02±0,7	20,41±3,79	194,28±16,28
Layer, cm	Na^+	CO_3^{2-}	HCO_3^-	SO_4^{2-}	Cl^-
0-5	11,22±2,02	absent	4,75±1,36	10,44±2,28	7,75±0,95
5-14	60,21±7,42	1,95±0,88	8,64±1,99	59,45±4,58	31,22±2,02
14-30	165,73±14,65	0,99±0,71	8,31±1,45	184,31±13,22	89,44±5,24
30-40	400,27±21,21	0,82±0,68	7,74±1,82	358,32±25,69	188,45±13,89
70-80	444,42±20,33	absent	6,93±1,91	467,48±24,86	355,21±17,34
140-150	414,09±30,77	absent	7,15±2,38	327,28±24,12	294,35±18,01

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

Depth, cm	Calcium				Magnesium				Sodium		
	$[Ca^{2+}]$	$[CaCO_3^0]$	$[CaHCO_3^+]$	$[CaSO_4^0]$	$[Mg^{2+}]$	$[MgCO_3^0]$	$[MgHCO_3^+]$	$[MgSO_4^0]$	$[Na^+]$	$[NaCO_3^-]$	$[NaSO_4^-]$
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

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

Depth, cm	Sulfates				Hydrocarbons			Carbonates				Chlorides
	$[SO_4^{2-}]$	$[CaSO_4^0]$	$[MgSO_4^0]$	$[NaSO_4^-]$	$[HCO_3^-]$	$[CaHCO_3^+]$	$[MgHCO_3^+]$	$[CO_3^{2-}]$	$[CaCO_3^0]$	$[MgCO_3^0]$	$[NaCO_3^-]$	es
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