

THE ASSOCIATION OF IONS IN THE SOIL SOLUTION OF SALINE SOILS

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ABSTRACT

The chemical equilibrium in the soil solution determines the dynamics of its material composition, migration and accumulation of salts. In the 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 calculation method proposed for quantitative assessment of real ion forms in the soil solution of solonetz taking into account the ions association. Determination of real condition of the main ions in soil solution is based on ion association and its influence on physical and chemical properties of solution. Were calculated the free and associated ion form concentration according to analytical ion concentration. Were used an iteration to solve the equations of ion material balance, a linear interpolation of equilibrium constants, a Method of Ionic Pairs including a law of initial concentration preservation, a law of the operating masses of equilibrium system, the concentration constants of ion pair dissociation following the law of operating masses. Upon completion of iterative procedure, was determined the quantity of ion free form and a coefficient of ion association γ_e as the ratio of ions free form to its analytical content $\gamma_e = C_{\text{ass}}/C_{\text{an}}$. For calculation procedure were used the own software products. The association of ions varies in individual soils and soil layers, increasing the soil solution salinity amplifies the ions association. Depending on concentration and composition of soil solution the ionic pairs are: 15-45% Ca^{2+} ; 16-49% Mg^{2+} ; 0,6-8,4% Na^+ ; 2,2-17,6% HCO_3^- , 16-51% SO_4^{2-} , up to 88% CO_3^{2-} . The proposed thermodynamic calculation method for quantitative assessment of real ion forms in the soil solution helps to explain the evolution of salted soils, maintain the soil, improve plant nutrition and irrigation.

Keywords: Soil Solution, Chemical Equilibrium, ION Association, Calculation Method

1. INTRODUCTION

Soil solution is the most mobile, volatile and active part of the soil. In soil solution occur destruction and synthesis of organic substances, secondary minerals, organomineral compounds (Amakor *et al.*, 2013; Hunenberger and Relf, 2011; Visconti and de Paz, 2012; Opfergelt *et al.*, 2014).

The chemical equilibrium in the soil solution determines the dynamics of its material composition, migration and accumulation of salts in soil, landscape and in supercritical water (Kar and Berenjian, 2013; Mari *et al.*, 2014;

Plugatyr *et al.*, 2011). This balance plays an important role in the genesis and evolution of soil. The important reason causing soil solution composition and high probability of its excess saturation with CaCO_3 are the association of ions, formation of ionic complexes (Maiti and Rogers, 2011; Lui *et al.*, 2011; Luo *et al.*, 2013).

In the 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^+ . Communications between the associated ions are not as strong as in the molecules, but diverse

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(Hunenberger and Relf, 2011; Stoyanov *et al.*, 2011; Raiteri *et al.*, 2012; Dave and Dikshit, 2011; Zhang *et al.*, 2012; Mandzhieva *et al.*, 2014; Tertre *et al.*, 2011).

The carbonate system of soil is not a completely open system. It is under the influence of biological process, extent of soil-atmosphere gas exchange, partial pressure and seasonal cycles of CO₂.

2. MATERIALS AND METHODS

2.1. Study Area

The South-East of the Russian Federation, Rostov region. Lower Don.

Object of research-the dry steppe solonetz. The climate is arid, annual precipitation of 300-350 mm. The parent rocks are Carbonate and Carbonate-sulfate loess-like loam and clay.

2.2. Sampling and Analysis of Soil

Solonetz is moderate thick, mediumsolonized. Properties: 2.6% of humus, 47.7% of physical clay, 29.5% of clay, 0.15% of CaCO₃ (up to 3-10% at depth of 0,8-1,5 m), pH = 7.8, the exchangeable cations: Ca²⁺ - 182 mmol/kg, Mg²⁺-65 mmol/kg, Na⁺ -34 mmol kg⁻¹.

The soil section 37 lays in an automorphic landscape. Soil was sampled down to the depth of 1 m from a section wall, deeper-with the soil auger, drill cup diameter 5 cm. In procedure of soil samples preparation the soil was crushed and sifted, openings 2 mm, than mixed with quartz sand in the ratio 1:2 (Mandzhieva *et al.*, 2014; Zhang *et al.*, 2012; Tertre *et al.*, 2011; Minkina *et al.*, 2013) charged into a glass tube, inner diameter of 3.4 cm, length 100 cm. At the bottom of a tube was an outlet for solution draining off. The direct allocation of soil solution with ethyl alcohol applied (Mandzhieva *et al.*, 2014; Zhang *et al.*, 2012; Tertre *et al.*, 2011). The extraction volume of soil solution emitted was 20-60 mL⁻¹ from single soil column.

Soil solution analysis as follows (Visconti and de Paz, 2012; Opfergelt *et al.*, 2014; Kar and Berenjian, 2013; Mari *et al.*, 2014). Moisture by thermostat 105°C method. pH was measured in thermostat (20±0,2°C) by pH-meter using a glass electrode. The carbonate and bicarbonate ions were titrated directly by 0.01 M hydrochloric acid detenting titration, endpoint on color change of indicators phenolphthalein and methyl orange. The chloride ion was determined by argentometric method with potassium chromate. The total content of Ca²⁺ and Mg²⁺ was determined with complexometric titration. In another aliquot Ca²⁺ was determined in

complexometric too, Mg²⁺ calculated by difference. The sulfate was determined with BaSO₄ sedimentation method. Na⁺ was determined with flame photometric.

3. RESULTS

We formulated methodic bases of calculation of the main ions state in the soil solution taking into account ideas of association of ions in soil solutions and for the first time made an approach to a quantitative assessment of ions forms in soil solutions of saline solonetzic soils. The concept and approach are the basis of given research.

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. The analytical composition of the studied soil solution is in **Table 1**.

Determination was made of real condition of the main ions in soil solutions taking into account the ions association and its influence on physical and chemical properties of solution.

Calculation was made of free and associated ion form concentration according to the sum of analytical ion concentration. Were used the following methods: Iteration to solve the system of algebraic equations of the material balance of ions, linear interpolation to calculate the values of tabular form of equilibrium constants.

The basis of calculations is the Method of Ionic Pairs (MIP) (Visconti and de Paz, 2012; Opfergelt *et al.*, 2014; Kalinichenko *et al.*, 2011; Kar and Berenjian, 2013; Mandzhieva *et al.*, 2014): The law of initial concentration preservation, the law of the operating masses of equilibrium system. The equations of main ions material balance are as follows Equation (1-6):

$$\Sigma \text{Ca}^{2+} = [\text{Ca}^{2+}] + [\text{CaCO}_3^{\circ}] + [\text{CaHCO}_3^+] + [\text{CaSO}_4^{\circ}] \quad (1)$$

$$\Sigma \text{Mg}^{2+} = [\text{Mg}^{2+}] + [\text{MgCO}_3^{\circ}] + [\text{MgHCO}_3^+] + [\text{MgSO}_4^{\circ}] \quad (2)$$

$$\Sigma \text{Na}^+ = [\text{Na}^+] + [\text{NaCO}_3^-] + [\text{NaSO}_4^-] \quad (3)$$

$$\Sigma \text{CO}_3^{2-} = [\text{CO}_3^{2-}] + [\text{CaCO}_3^{\circ}] + [\text{MgCO}_3^{\circ}] + [\text{NaCO}_3^-] \quad (4)$$

$$\Sigma \text{HCO}_3^- = [\text{HCO}_3^-] + [\text{CaHCO}_3^+] + [\text{MgHCO}_3^+] \quad (5)$$

$$\Sigma \text{SO}_4^{2-} = [\text{SO}_4^{2-}] + [\text{CaSO}_4^{\circ}] + [\text{MgSO}_4^{\circ}] + [\text{NaSO}_4^-] \quad (6)$$

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

The next group of equations-the concentration constants of ionic pair dissociation following law of operating masses, grouped according cations Equation (7-9):

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

$$; K_{CaSO_4} = \frac{[Ca^{2+}][SO_4^{2-}]}{[CaSO_4^0]}$$

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

$$K_{MgSO_4} = \frac{[Mg^{2+}][SO_4^{2-}]}{[MgSO_4^0]}$$

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

Equilibrium concentration of ionic pairs in equations 1-6 replaced their values according to relevant dissociation constants (7-9). The transformed system of the equations of material balance of ions is as follows Equation (10-15):

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

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

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

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

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

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

The concentration constants of dissociation in equations were recalculated according Davies equation for constant Equation (16):

$$pK = pK^0 - A\Delta Z^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0,11 \right) \quad (16)$$

where in K-a concentration constant of dissociation of ionic couple; K^0 -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 in the equation of dissociation constant; I-ionic strength of solution.

Values of thermodynamic constants of dissociation:

$$pK_{CaCO_3}^0 = 3,2; \quad pK_{CaHCO_3}^0 = 1,26; \quad pK_{CaSO_4}^0 = 2,31$$

$$pK_{MgCO_3}^0 = 3,4; \quad pK_{MgHCO_3}^0 = 1,16; \quad pK_{MgSO_4}^0 = 2,36$$

$$pK_{NaCO_3}^0 = 1,27; \quad pK_{NaSO_4}^0 = 0,72$$

Was calculated the formal ionic strength of the solution on the data of analytical ion concentration Equation (17):

$$I = 0,5[4(Ca^{2+}) + 4(Mg^{2+}) + (Na^+) + 4(CO_3^{2-}) + (HCO_3^-) + 4(SO_4^{2-}) + (Cl^-)], \text{mol/l} \quad (17)$$

The value of pK rather adequately follows from the equation (16). At the ionic force of 0.1 mol/L an error is less than 3%, at 0.5 mol/l-less than 8%.

Was used the equilibrium concentration of a free form of ions as the unknown values X_{Ca} , X_{Mg} . Was used the total value of all ion forms as the analytical concentration. The system was obtained of six equations with six unknown.

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

Taking into account values of equilibrium concentration of all ion forms was calculated the effective ionic force of solution Equation (18):

Table 1. The composition of the soil solution steppe solonetz, mmol-eq/l

| Layer (sm) | Moisture (%) | Solid resedual (g/L) | Ph | Ca ²⁺ | Mg ²⁺ | Na ⁺ | CO ₃ ²⁻ | HCO ₃ ⁻ | SO ₄ ²⁻ | Cl ⁻ |
|------------|--------------|----------------------|------|------------------|------------------|-----------------|-------------------------------|-------------------------------|-------------------------------|-----------------|
| 0-12 | 25,4 | 0,80 | 7,74 | 2,45 | 2,87 | 6,19 | absent | 4,15 | 4,52 | 2,84 |
| 13-21 | 33,7 | 1,67 | 8,22 | 5,11 | 4,35 | 14,95 | absent | 6,47 | 10,41 | 7,53 |
| 55-65 | 29,8 | 37,74 | 8,15 | 30,21 | 207,28 | 372,60 | absent | 3,12 | 328,52 | 278,45 |
| 80-90 | 20,4 | 31,86 | 7,78 | 29,58 | 120,25 | 358,43 | absent | 2,40 | 280,42 | 225,44 |
| 180-190 | 18,7 | 25,58 | 8,74 | 31,06 | 100,04 | 258,01 | 1,20 | 8,24 | 244,33 | 135,34 |
| 250-260 | 17,8 | 27,92 | 8,85 | 19,45 | 155,03 | 270,42 | 1,44 | 8,88 | 274,35 | 160,23 |

$$I^* = 0,5 \left\{ \begin{aligned} &4[Ca^{2+}] + 4[Mg^{2+}] + [Na^+] \\ &+ 4[CO_3^{2-}] + [HCO_3^-] + 4[SO_4^{2-}] + \\ &+ [CaHCO_3^+] + [MgHCO_3^+] + [NaCO_3] \\ &+ [NaSO_4^-] + [Cl^-] \end{aligned} \right\}, \text{mol/l} \quad (18)$$

Thereafter, was calculated the concentration dissociation constants (16) and constituted a new system of material balance equations. On the new set of ingredients of system of equations (10-15) was solved the next iteration approach.

Calculate ion forms in soil solution.

Upon completion of iterative procedure, was determined the quantity of ion free form.

The coefficient of ion association γ_e as the ratio of the ions free form to its analytical content Equation (19):

$$\gamma_e = C_{\text{ass}} / C_{\text{an}} \quad (19)$$

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

For calculation procedure were used the own software products (Kalinichenko *et al.*, 2012a; Mandzhieva *et al.*, 2014; Visconti and de Paz, 2012; Wiatrak, 2014).

4. DISCUSSION

According to data of a **Table 1**, the association of ions in the soil solution was calculated in procedures specified by equations 7-18.

Association coefficient γ_e was calculated according to ion species as the ratio of the calculated amount of the ion in the free form to its analytical content in **Table 1** (19). The results of calculation are in **Table 2**.

The association of ions varies. The variability observed in individual soils and layers. Increasing the soil solution salinity amplifies the ions association.

The real equilibrium concentration of various ion forms in soil solution is calculated. Depending on concentration and composition of soil solution in form of ionic pairs are: 15-45% of Ca²⁺; 16-49% of Mg²⁺; 0,6-8,4% of Na⁺; 2,2-17,6% of HCO₃⁻, 16-51% of SO₄²⁻. The ion CO₃²⁻ is most associated. Its share of the associated ion form makes up to 88%.

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

On the theoretical generalizations of thermodynamics of the soil solution, the research fulfilled, justifications and calculations proposed, it is possible to claim the following. Accounting of association and activity of ions and calculating degree of soil solution saturation by chemicals provides a new understanding of migration and accumulation of chemical compounds in soils and landscapes, especially concerning CaCO₃.

In recent years, the modern nonthermodynamic techniques are used for modeling the associated ion pairs in nanotubes (Izgorodina, 2011; Izgorodina *et al.*, 2014; Kalinichenko *et al.*, 2012a; Luo *et al.*, 2013; Zhang *et al.*, 2012), ion pair association in supercritical water and other conditions (Sushkova *et al.*, 2013; Saito, 2013), to develop the methods of computer modeling of ion pair formation in electrolyte, ion pair as a simulation of hybrid excitations in solution (Raiteri *et al.*, 2012; Maiti and Rogers, 2011; Lui *et al.*, 2011; Farnum *et al.*, 2011; Plugatyr *et al.*, 2011; Kielpinski, 2013). In the recent years the improved methods of direct ion pair study are used (Westerlund *et al.*, 2011; Bester-Rogac *et al.*, 2011; Wang *et al.*, 2014; Shatti *et al.*, 2011). 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 (Zhang *et al.*, 2012; Tertre *et al.*, 2011; Wiatrak, 2014; Jiang *et al.*, 2012; Saito, 2013; Minkina *et al.*, 2012; 2013; Sushkova *et al.*, 2013).

Table 2. Forms ions in the soil solution of steppe solonetz, % of the total ion content

| Depth (sm) | I | pH | Calcium | | | | Magnesium | | | | Sodium | | | Chlorides |
|----------------|-------|------|----------------------------------|-----------------------------------|------------------------------------|-----------------------------------|----------------------------------|------------------------------------|------------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------|
| | | | [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 ⁻] | |
| Cations | | | | | | | | | | | | | | |
| 0-12 | 0,016 | 7,74 | 84,08 | Her | 3,81 | 12,11 | 83,50 | Her | 3,00 | 13,50 | 99,40 | Her | 0,60 | |
| 13-21 | 0,035 | 8,22 | 77,73 | Her | 4,59 | 17,68 | 76,80 | Her | 3,60 | 19,60 | 98,88 | Her | 1,12 | |
| 55-65 | 0,893 | 8,15 | 54,47 | Her | 0,59 | 44,94 | 51,70 | Her | 0,44 | 47,86 | 91,56 | Her | 8,44 | |
| 80-90 | 0,723 | 7,18 | 54,67 | Her | 0,48 | 44,85 | 51,88 | Her | 0,37 | 47,75 | 91,65 | Her | 8,35 | |
| 180-190 | 0,577 | 8,74 | 53,65 | 0,45 | 1,71 | 44,19 | 50,95 | 0,68 | 1,29 | 47,09 | 91,82 | 0,04 | 8,14 | |
| 250-260 | 0,670 | 8,85 | 53,44 | 0,42 | 1,75 | 44,38 | 50,75 | 0,63 | 1,32 | 47,29 | 91,64 | 0,04 | 8,33 | |
| | | | Sulphates | | | | Hydrocarbons | | | | Carbonates | | | |
| Depth (sm) | I | pH | [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 ⁻] | |
| Anions | | | | | | | | | | | | | | |
| 0-12 | 0,016 | 7,74 | 83,21 | 6,57 | 8,57 | 1,65 | 97,84 | 1,12 | 1,04 | - | - | - | - | 100 |
| 13-21 | 0,035 | 8,22 | 79,92 | 8,68 | 8,19 | 3,21 | 96,98 | 1,81 | 1,21 | - | - | - | - | 100 |
| 55-65 | 0,893 | 8,15 | 46,52 | 4,13 | 30,20 | 19,15 | 82,47 | 2,84 | 14,69 | - | - | - | - | 100 |
| 80-90 | 0,723 | 7,18 | 53,45 | 4,73 | 20,48 | 21,34 | 87,84 | 2,99 | 9,17 | - | - | - | - | 100 |
| 180-190 | 0,577 | 8,74 | 57,91 | 5,62 | 19,28 | 17,19 | 88,95 | 3,22 | 7,82 | 15,49 | 11,66 | 56,54 | 16,31 | 100 |
| 250-260 | 0,670 | 8,85 | 53,72 | 3,15 | 26,72 | 16,41 | 86,52 | 1,92 | 11,56 | 12,51 | 5,69 | 68,24 | 13,56 | 100 |

Carbonate calcium equilibrium means much for proper modeling of heavy metals state and transfer in soil (Kalinichenko *et al.*, 2012b; Mandzhieva *et al.*, 2014). These researchs are of high importance. They give a new glance on the phenomena of ion association in water solution.

The data and models confirm the basic tenets of the theory of ion association in solution and justify the thermodynamic model of macroprocesses of saturation in soil solution, the transfer, metamofization and accumulation of salts in soil. There are data on drawbacks of soil moisture sensors systems which corresponds to the problem of true soil solution content determining (El Marazky *et al.*, 2011).

Those researches corresponds to the origin and results of research fulfilled. So there is productive cooperation of different kind of approach on the matter of discussed complicated problem (Visconti and de Paz, 2012).

Computer programs are available for different soil and environment conditions to speed up the process of ion association calculation.

5. CONCLUSION

On the ideas of ions association in the soil solution in rather accurately outlined framework of solution ionic strength range and ionic composition, there is an opportunity to obtain a new glance on processes in soil solution, soil and landscape (Visconti and de Paz, 2012; Minkina *et al.*, 2014). To consider quantitatively the options of equilibria models for soil in vivo, undisturbed by procedures of physical modeling.

The results obtained show the fundamental differences in behavior of calcium carbonate in soil solution taking into account the ion association and without account of this phenomenon. The association of ions shows that the thermodynamic preconditions of CaCO₃ sedimentation in saline soils occur at much higher concentration of ions Ca²⁺ and CO₃²⁻ in soil solution than considered previously. Therefore, there is a significant probability of high mobility of CaCO₃ in soil and landscape, earlier underestimated.

The completed research has significance not only from the point of view of theoretical foundation or accuracy of calculation procedures compliance to phenomenon details. The basic conclusion – the calculations executed correspond to the nature of the phenomenon of migration and accumulation of salts in soil. Therefore, the association of ions in soil solution matters for knowledge concerning the modern evolution of salted soils. use of soils in a standard regional rain agriculture, irrigational agriculture, plant nutrition.

The modelling of soil solution system proposed is not high instrumentally based, but nevertheless has more scientific and practical prospect than even uptodate direct methods of soil solution research because the soil solution probing leads to new state of soil solution after its extraction from the soil. So this system is not completely corresponds to the real soil-solution system.

The short cut of research is operation under the individual soil solutions from the layers of soil section. But soil continuum consist of many vertical sections-vertical 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 carbonate calcium system in individual part of soil volume at some time but to use this result for explaining of metamorphisation of soil solution in time and through the soil continuum in conditions of water salt mass transfer. It will permeates the proper prediction of soil evolution, better and stable soil management.

Another key problem is to model not only soil solution macrosystem but to take into account its disperse origin because the state of water in soil is not a water continuum crossed by solid soil phase but the system of individual insulated form one another micro water basins on the internal surface of soil continuum.

It will permeate to get new understanding of water-salt transfer, geochemical barriers and ecological functions of soil. The research fulfilled are useable to improve the soils in a standard regional rain agriculture, irrigational agriculture, plant nutrition, agriculture management.

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