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Association of Ions in the Soil Solution of Saline Soil's Landscape

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Abstract: *Soil up-to-date study and management are crusial in a circular economy implementation. A soil solution material composition, migration and accumulation dynamics is determined by soil solution chemical equilibrium. The soil solution contains the associated electrically neutral ion pairs* $CaCO_3^0$*;* $CaSO_4^0$*,* $MgCO_3^0$ *and* $MgSO_4^0$ *and charged ion pairs* $CaHCO_3^+$*,* $MgHCO_3^+$*,* $NaCO_3^-$*,* $NaSO_4^-$*,* $CaOH^+$*, and* $MgOH^+$*. A soil solution chemical equilibrium calculation method is proposed for quantitative assessment of real ion forms in the soil solution of Kastanozem soil complex and Haplic Chernozem. Ions association varies in individual soils and soil layers increasing soil solution salinity and amplifying ions association. In an ionic pair form in soil solution are presented: 11.8–53.8% of* Ca^{2+}*; 9.4–57.3% of* Mg^{2+}*; 0.7-11.9% of* Na^+*; 2.2–22.3% of* HCO_3^-*, 11.8–62.7% of* SO_4^{2-}*.*

An associated form CO_3^{2-} *ion share is up to 92.7%. The ion association coefficient as a ratio of the ion free form to its analytical content is proposed* $\gamma_e = C_{ass} / C_{an}$.

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A Cd thermodynamic state in Haplic Chernozem in conditions of soil reclamation with phosphogypsum in doses of 10, 20, and 40 t ha^{-1} *was assessed concerning a chemical equilibrium in soil solution. Based on carbonate-calcium equilibrium (CCE) algorithm, computer programs ION–2 and ION–3 were developed to calculate the real equilibrium ion forms in soil solution. The ions association was calculated in an iteration procedure according to the data on a water soil extract analytical ion concentration considering the ion material balance accounting the equilibrium constants linear interpolation, method of ionic pairs, initial concentration preservation law, equilibrium system operating masses law and ion pair concentration constants of dissociation. To characterize a* Cd^{2+} *ion binding into associates in soil solution, a coefficient of heavy metal ion's association* k_{as} *is proposed. The phosphogypsum application increases a* Cd^{2+} *free form soil content by 57.1%.*

The BGT methodology was developed to implement a circular economy as a system of the non-standard technical means and technologies for a long-term optimization of the soil geophysical, chemical, water, biological properties and productivity.*

The long-term field experiment in the Kastanozem soil zone showed that a 20–45 cm layer intra-soil milling methodology provides a rhizosphere uniform development in the whole processed soil profile at a rate of 2.2 roots per cm^{-2} *in 0–20 cm and of 1.7 roots per* cm^{-2} *in 20–40 cm. An intra-soil milling machine new active drive design provides five times less traction resistance, 80% increased reliability, and halving energy costs.*

The BGT based intra-soil pulse sequential-discrete unmanned system provides soil watering and simultaneous stimulants and/or other substances supply to the soil and a soil solution equilibrium control, a humic substances and polymicrobial biofilms synergy, a high rate soil biological process, a plant phytopathogens resistance and a soil productivity. Intra-soil pulsed sequential-discrete humidification methodology is capable in reducing a plants heavy metals consumption providing a high level control of soil additives and plant stimulants supply. THe BGT* methodology ensures an ecosphere and human health in a circular economy.*

Keywords: Soil Solution, Chemical Equilibrium, Ion Association, Programs Ion–2 and Ion–3, Biogeosystem Technique

10.1. Introducton

Soil vulnerability combined natural and anthropogenic effects hinder a circular economy principals' implementation (Duanyang Xu et al. 2024) and a natural capital expanded technological reproduction (Brander et al. 2024; Kalinitchenko et al. 2024; Mao and Jiao 2024; Seidl et al. 2024). The soil is an important ecosphere ingredient providing a humans and planet health (Kopittke et al. 2024), and the soil restoration and soil solution correct management are needed (Smith et al. 2021; Yadav et al. 2023).

Soil solution is an active part of the soil influencing its properties (Amakor et al. 2013; Endovitskii et al. 2009a, 2017; Hunenberger, Relf 2011; Visconti and de Paz 2012). A soil solution chemical equilibrium determines migration and accumulation of salts in soil, landscape and in other chemical systems (Adams 1971; Kar and Berenjian 2013; Minkin and Endovitskii 1978; Plugatyr et al. 2011). This balance plays an important role in the genesis and evolution of soil (Kalinichenko et al. 2021; Lui et al. 2011; Luo et al. 2013).

In the soil solution are formed electrically neutral ion pairs $CaCO_3^0$; $CaSO_4^0$, $MgCO_3^0$, $MgSO_4^0$ and charged ion pairs $CaHCO_3^+$, $MgHCO_3^+$, $NaCO_3^-$, $NaSO_4^-$, $CaOH^+$, $MgOH^+$. Interactions between associated ions are not as strong as in molecules, but diverse (Endovitsky et al. 2014; Minkina et al. 2012a; Tertre et al. 2012).

Phosphogypsum, a by-product of phosphorus fertilizer production, contains pollutants flowing from a phosphogypsum disposal area to the environment (Pérez-López et al. 2016). At the same time, phosphogypsum is an important substance for the soil reclamation and remediation, especially for the Solonetz soil (Minkin et al. 1992; Robinson et al. 2023). However, the phosphogypsum, as well as phosphorus fertilizer contain the adverse and dangerous substances, in particular, heavy metals (HMs) (Robinson et al. 2023). The natural and anthropogenic HMs, including pollutant of the first hazard class – Cd as well, badly influence the biosphere (Adriano 2001; Minkina et al. 2012b; Motuzova et al. 2014; Sparks 2003; Xiong et al. 2014), causes the conflict of biosphere and agroecosystem (Glazko, Galzko, 2015), unhealthy soil (Kopittke et al. 2024) and geochemical cycle and climate uncertainty (Kalinitchenko et al. 2024). A Cd water-diluted form is the most dangerous because of its high availability to plants (Batukaev et al. 2017; Robinson et al. 2023).

A Cd total and water-soluble forms content in the soil depends on its geographical location, an ionic composition of the soil solution, and the soil genesis. A Cd content in environment is limited (Land contamination 2015; McGahren et al. 2024). In Russia, a Cd total content generally does not exceed 1 mg kg^{-1} soil dry weight (DW) in the soils under agriculture or in urban conditions; its concentration in contaminated area is up to 3 mg kg^{-1} soil DW (Endovitskii et al. 2014; Batukaev et al. 2017). Russia's Maximum permissible concentrations (MPC) Cd total content in the soil is of 2 mg kg^{-1} DW (Maximum permissible concentrations of chemical substances in soil 2006**)**.

The EU risk assessment report gives a predicted no-effect concentration value for Cd in the soil of 1.1 mg kg^{-1} DW based on an ecotoxicity for plants, invertebrates and micro-organisms while 0.9 mg kg^{-1} DW based on a secondary poisoning. However, a spatial distribution of the samples with a concentration of Cd above 1 mg kg^{-1} DW gives an evidence that a large number of samples exceed this threshold (Ballabio et al. 2023). The maximum in the world recommended limit of Cd in the soil is 5 mg kg^{-1} DW (Snakin et al. 2001).

An anthropogenic Cd pollution by phosphate fertilizers strongly depends on the origin of phosphate rocks (Suciu et al. 2022). Phosphogypsum, the waste of phosphate fertilizer production – a wet phosphate rock sulphuric acid digestion technology, contains Cd and more than 60 chemical elements (Goswami, Nand 2015). Applying for the soil reclamation, the phosphogypsum is a source of an additional HMs input into the soil (Minkin et al. 1992; Mays and Mortvedt 1984). A HMs potential accumulation in the soil after application of phosphogypsum was noted by some authors (Tayibi et al. 2009), but significant changes in the natural contents of HMs were not observed at application of phosphogypsum at the recommended doses around 10 t ha^{-1} both immediately after reclamation, and in the long-term sequence of soil reclamation (Kalinitchenko et al. 2020; Robinson et al. 2023; Sukovatov 2009).

In the Russian Federation, a phosphate fertilizer is produced from apatite of the Kovdor phosphate rock deposit. The Kovdor apatite is of a high environment quality (Lapin, Lyagushkin, 2014), almost nonradioactive (Gázquez et al. 2014), and its ingredients are authorized to be used as the feed additives for livestock. Therefore, the phosphogypsum from the Kovdor apatite is radioactively safe for the soil reclamation purposes. An important feature of Kovdor apatite is a lowest Cd total content (Lapin and Lyagushkin 2014). Commonly used models to predict metal bioavailability consider the free ion as the major bioavailable species. Dissolved trace metals are present in the environment as free ions and as complexes. Ion association and complex ions formation decrease Cd mobility in soil and thus its availability to enter the plant root system. The degree of HMs passivation into the soil is conjugated to its activity according ion association in soil solution. This circumstance is substantiated on the base of theoretical thermodynamics of electrolytes (Endovitsky et al. 2014).

A chemical equilibrium of soil solution is important for understanding the origin of soil. A formation of the soil solution chemical composition is very complex process. The soil solution composition varies causing the destruction and synthesis of organic substances, secondary minerals and organomineral compounds. One of the factors is most important chemical equilibrium in soil solutions – carbonate calcium equilibrium (CCE) (Minkina et al. 2012a). CCE depend on, and, in its turn, influences 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. A CCE study is a basis for $CaCO_3$ solubility calculation at given conditions.

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 (Anisimov et al. 2015; Endovitsky et al. 2014). At a higher ionic strength of soil solution, more ions pass to the form of ions associates. A carbonate system of water solution is under an influence of the biological process, soil-atmosphere gas exchange, partial pressure and seasonal CO_2 cycles.

A Cd^{2+} transfer rate of to the plant depends on the content of carbonates in soil as well as on the pH value. The thermodynamic activity of Cd^{2+} free ions decreases because the Cd^{2+} ion bound into associates with other ions. In the soil solution of alkaline calcareous solonetzic soil, the molar fraction of active concentration (activity) of Cd^{2+} ion does not exceed 4.0%, in water extract the activity of Cd^{2+} is low too – 11.2% (Endovitsky et al. 2014).

Not only the soil chemical properties, but also the soil geophysical properties, specifically its architecture as a continuum for physicochemical processes and rhizosphere development are of high importance. The standard soil ploughing and soil reclamation technologies based on a passive soil structure loosening diminishing soil productivity and stability are not acceptable anymore because are incapable in a fine soil macro-aggregates formation. The long-term field experiment in the Rostov region Kastanozem soil zone was focused on a 20–45 cm layer intra-soil milling methodology justification. After intra-soil milling, the rhizosphere developed uniformly in the whole processed soil profile: 2.2 roots per cm^{-2} in 0–20 cm; 1.7 roots per cm^{-2} in 20–40 cm (Mishchenko et al. 2009). An intra-soil milling machine active drive new design provides five times less traction resistance and 80% increased reliability, halving energy costs.

An important condition of plants development in a steppe zone is a soil humidification. The standard irrigation leads to the water loss and soil degradation, not providing the sustained plant growth and productivity (El Marazky et al. 2011;

McDermid et al. 2023). On a Biogeosystem Technique (BGT*) methodology basis, an intra-soil pulse sequential-discrete humidification unmanned system was developed. The system provides a simultaneous stimulants and/or other substances supply to the soil, a humic substances and polymicrobial biofilms synergy, a high rate soil biological process and soil productivity. Intra-soil pulsed sequential-discrete humidification methodology is capable of reducing a plants HMs consumption and provides the soil additives and plant stimulants supply high level control (Kalinitchenko et al. 2024).

The aims of this chapter were focused on: a soil solution thermodynamics and a Cd^{2+} forms in a soil water extract; an intra-soil milling prospects in the soil architechture improving and phosphogypsum environmentally safe recycling; an intra-soil pulse sequentially-discrete humidification potential in the plants HMs consumption reducing and soil additives and plant stimulants supply.

10.2. Materials and methods

10.2.1. Study area

The study area is situated in the Russian Federation South-West part in the Rostov Region (Lower Don) and Krasnodar Territory (Kuban) and is a part of a wider Eurasian steppe belt extending for thousands of miles in an east-west direction across most of the Eurasian continent. Terrain is a plains-type watershed for the Don and Kuban’ rivers. The soils of the area are formed on the Carbonate and Carbonate-sulfate loess-like loam and clay parent rocks. The Rostov Region climate is continental and arid with annual precipitation of 300–350 mm. The Krasnodar Territory climate is temperate continental and semiarid with annual precipitation of 450–500 mm.

10.2.2. Objects of research

The objects of research are the dry steppe Kastanozem (Rostov Region) and the steppe Haplic Chernozem (Krasnodar Territory).

Kastanozem is moderate thick, medium solonized. However, the properties of Kastanozem complex are laterally differentiated according to the dry steppe parent rock, climate and microrelief: The soil complex properties in general are as follows: a humus content – 2.6%, a physical clay content – 47.7%, a clay content – 29.5%, a $CaCO_3$ content – 0.15% (up to 3–10% at a depth of 0.8–1.5 m), a pH=7.8, the exchangeable cations content is Ca^{2+} – 182 mmol kg^{-1}, Mg^{2+} – 65 mmol kg^{-1} and Na^{+} – 34 mmol kg^{-1}.

The Haplic Chernozem non-saline slightly frozen calcareous of the southern European facies spreads in northern geographical zone of Krasnodar Territory. The Haplic Chernozem is thick, a humus content – 4.2%, a particles size <10 µm content – 49.3%, a calay content (the particles size <1.0 µm) – 31.3%, a $CaCO_3$ content in the upper soil horizon – 0.14% (and up to 3–6% at a depth of 1.3–1.6 m), a pH=7.6, the exchangeable cations content is Ca^{2+} – 342 mmol kg^{-1}, Mg^{2+} – 27 mmol kg^{-1} and Na^{+} – 6 mmol kg^{-1}.

The field studies in the dry steppe Kastanozem zone were conducted on the key plots established at different the areas: key plot 1324 has been laid down in the dry steppe automorphic laterally differentiated Kastanozem soils complex of the components: Solonetz steppe, Kastanozem solonetzic soil and Kastanozem dark in a microrelief depression. Key plot 1325 has been laid down in the dry steppe hydromorphic Kastanozem complex, a studied soil component was the Kastanozem solonetz meadow.

The field studies in the Haplic Chernozem zone were conducted in Kanevskaya in the large-scale production experimental trial.

For the both objects of research were conducted a thermodynamic modelling of soil solution and soil paste water extract focusing on a HMs intra-soil passivation, an optimized intra-soil mechanical processing development, and a methodology substantiation of phosphgypsum intra-soil application to the soil while its intra-soil milling.

The thermodynamic state of main ions of salt composition in a soil system before and after apply of phosphogypsum neutralized to pH 5.0–5.3 was studied in a model experiment. Phosphogypsum was applied to the soil at rates of 10, 20, and 40 t ha^{-1}. Phosphogypsum is a by-product of the phosphorus fertilizer production by sulfuric acid technology from apatite of the Kovdor raw material deposit at the Belorechensk chemical plant. A Cd^{2+} total content in phosphogypsum – 2.76 mg kg^{-1}, a Cd^{2+} water-soluble form content – 0.33 mg kg^{-1}. The contents of total and water-soluble Cd^{2+} forms in the original soil are correspondingly 0.240, 0.0348 mg kg^{-1} soil DW (Endovitsky et al. 2014).

The mathematical modelling methodology has been applied (Kalinichenko et al. 2018).

A heuristic nonstandard approach to mechanical systems synthesis was used in an intra-soil milling processing machine and intra-soil pulse sequentially-discrete watering unmanned system development (Kalinitchenko et al. 2024; Okolelova et al. 2022).

The experiments were performed in triplicate. All statistical calculations were performed using Microsoft Excel 2010.

10.2.3. Soil sampling and analysis

10.2.3.1. Soil sampling

In Rostov Region, the Kastanozem was sampled from a soil cross section wall down to a 1 m depth and deeper with a soil auger with a drill cup diameter 5 cm. In the sample preparation procedure, the soil was crushed and sifted through a sieve with the 2 mm openings then mixed with the quartz sand in a ratio 1:2 and charged into a glass tube of the inner diameter 3.4 cm and length 100 cm. At a bottom of the tube there was an outlet for the solution draining off. A soil solution direct allocation with the ethyl alcohol was applied. An extraction volume of the soil solution emitted was 20–60 mL from a single soil column (Endovitsky et al. 2014).

In Krasnodar Territory, the Haplic Chernozem was sampled from the 0–20 and 20–40 cm layers. The studied soil layers appointed in a view of the illuvial soil horizon need for reclamation. This methodological approach avoids an aeolian distribution of waste after its standard utilization in the upper soil layer, excludes an anthropogenic Heavy Metals (HMs) excess in this soil layer and provides the soil architecture and physicochemical properties improvement.

10.2.3.2. Soil analysis

The soil solution and soil water extract were analyzed using standard methods (Carter and Gregorich 2008; Shtiza and Swennen 2011). The soil moisture was determined by a thermostat 105°C method. The soil dry residue content was determined by an oven drying at 105 °C. A pH was measured at 20°C using an ion meter with a glass electrode (TITAN, Tom Analit Ltd., Russia). Carbonate and bicarbonate ions were titrated directly by 0.01 M hydrochloric acid with an endpoint determined by a color change of standard indicators phenolphthalein and methyl orange. A Cl^- ion was determined by an argentometric method with a potassium chromate. The Ca^{2+} and Mg^{2+} total content was determined with a complexometric titration. In another aliquot, Ca^{2+} was determined in a complexometric, and Mg^{2+} was calculated by difference. A sulfate content was determined with a $BaSO_4$ sedimentation method. A Na^+ content was measured using a flame photometer PFP7 (JENWAY, UK).

Additionally, in the Chernozem soil of Krasnodar Territory (Kanevskaya large-scale production experimental trial), we measured a water-soluble HMs concentration. As an example, we focused on Cd because it is one of the most hazardous HMs.

A Cd total soil content was determined by an X-ray fluorescence method on the X-ray fluorescent scanning spectrometer “SPECTROSCAN MAKC-GV”. This method is listed by producer and included into a register of methods approved for the state and industrial environmental monitoring in the Russian Federation (PND F 16.1.42-04). The XRF measurements analytical quality was controlled according the reference standard soil sample “Chernozem” no. 29107. Duplicates and reagent blanks were also used as a part of the quality control.

A water soluble Cd concentration in soil solution was determined by an atomic absorption spectrophotometry (AAS) using the atomic absorption spectrophotometer (KVANT 2-AT, Russia). The X-ray fluorescent method and AAS method allowed deviation in a soil HMs determination less than 10–15%.

Each experiment was performed in triplicate, and the data were used to test the developed mathematical models.

10.2.3.3. Soil solution main ions state calculation methodological bases

We first formulated a soil solution main ions state calculation methodology taking into account an ions association in soil solution and developed an approach to a quantitative assessment of ion forms in soil solution. The methodology and approach are a basis of given paper (Endovitsky et al. 2014, 2017; Minkina et al. 2012a; Nicholson and Quirke 2003; Wright 2007).

Calcium carbonate system (CCE) is an important complex chemical system of soil solution because it influences a nature of many basic processes in a soil formation and a certain soil type evolution (Lisetskii et al. 2016, 2018). CCE includes a number of dynamic equilibriums (Stoyanov et al. 2011) (Fig. 10.1).

A soil solution CCE is an adsorption-hydration balance between the solution, gas phase, bioorganic phase. This balance includes a step dissociation of carbonic acid; CCE between the soil solution, soil absorbing complex and $CaCO_3$ sediments and solid phase; and water ions equilibrium. An important characteristic of the CCE is a soil solution saturation with $CaCO_3$ degree. The $CaCO_3$ deposition or dissolution caused by the receipt or removal of a Ca^{2+}, HCO_3^- and CO_3^{2-} from solution, as well as carbonate equilibrium shift, change an ionic composition of soil solution. Thus a type of carbonates migration and accumulation in soil profile becomes special.

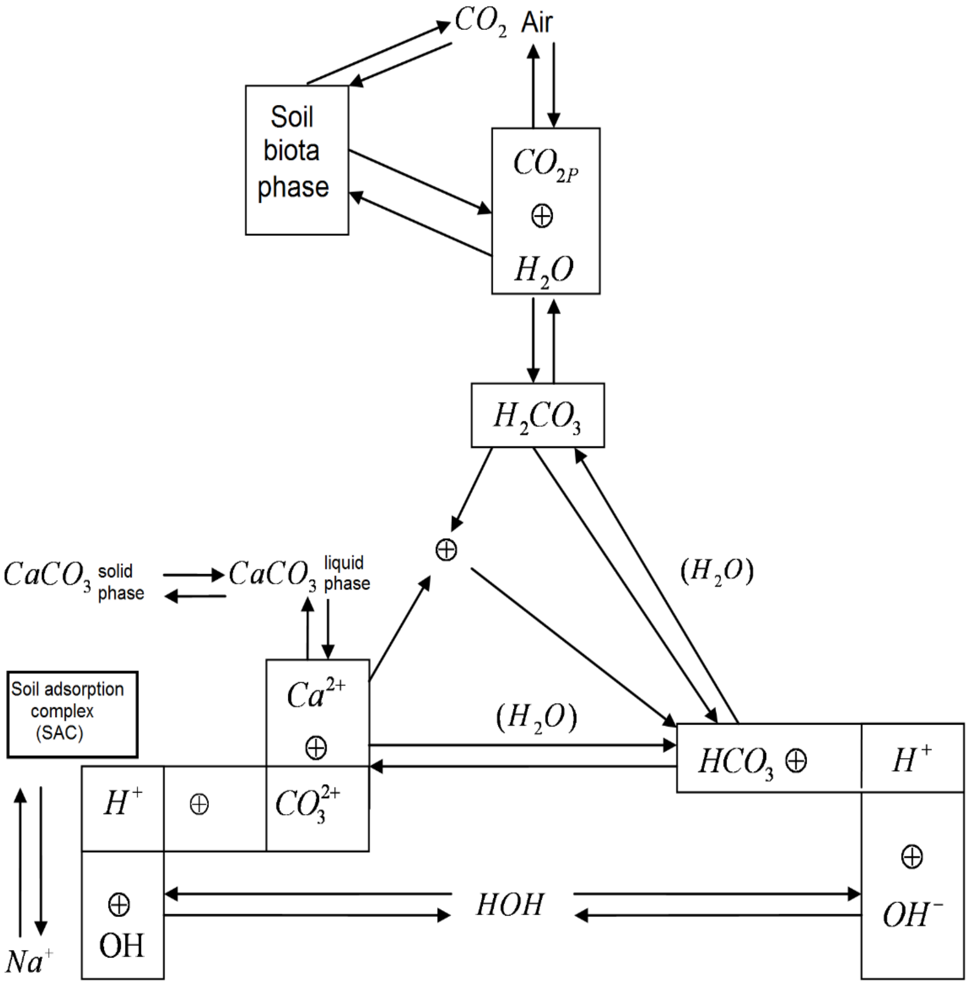

Fig. 10.1. Calcium-carbonate system of the soil solution
Сл. 10.1. Калцијум-карбонатни систем у раствору земљишта

An analytical composition of soil solution determines soil solution properties correctly at a low concentration of main ions only. In reality, a measure of soil solution properties and function is the ions activity. The analytical composition of the studied soil solutions is presented in Tab. 10.1 below.

A real state of the main ions in soil solution was determined taking into account the ions association and ion activity influence on the physical and chemical properties of soil solution.

A free and associated ion form concentration calculation was conducted according a sum of ion analytical concentration. The following methods were used: an ions material balance algebraic equations system solving iteration methodology, a linear interpolation in calculation of the equilibrium constants tabular form values.

10.2.3.4. Mathematical model of soil solution carbonate calcium equilibrium

In the study, a natural waters hydrochemistry classification based on the soil solution main ions macroconcentration relationships was applied. An ion equilibrium calculation in soil solutions was based on the physical chemistry concepts and began from an analytical ion concentration. An ion pairs method was applied (Adams 1971; Endovitsky et al. 2014; Minkin and Endovitskii 1978) which accounts the laws of initial concentration and operating masses preservation in a chemical equilibrium system.

The total concentrations of CO_3^{2-} and HCO_3^- ions were found by calculation from the total alkalinity Alk_Σ, pH, and carbonic acid $K^0(HCO_3)$ second-step dissociation constant, Eqs. (1), (2):

$$(CO_3^{2-})_A = 0{,}94Alk_\Sigma 10^{-3}/(2+aH^+ + y''(K^0(HCO_3)\,y'\,)^{-1}), \qquad (1)$$

$$(HCO_3^-)_A = 0{,}94Alk_\Sigma 10^{-3} - 2(CO_3^{2-})_A, \qquad (2)$$

where 0.94 is the coefficient accounting the contribution of carbonate alkalinity to the total alkalinity (Minkina et al. 2012a); y' is a singly-charged particle activity coefficient (free ion or its associate); and y'' is a double-charged particle activity coefficient.

After phosphogypsum apply, a Cd^{2+} soil content was determined as a sum of a corresponding metal form in original soil content and a Cd additional content according the phosphogypsum application dose.

The soil solution and water extract main ionic forms equilibrium composition at 25 °C was calculated using ION–2 and ION–3 programs (Endovitskii et al. 2009a; Minkina et al. 2016). The algorithm was realized basing on a mass balance equation system for main ions using concentration stability constants for associates $CaCO_3^0$, $CaHCO_3^+$, $CaSO_4^0$, $MgCO_3^0$, $MgHCO_3^+$, $MgSO_4^0$, $NaCO_3^-$, and $NaSO_4^-$ (Endovitsky et al. 2014).

A concentration was calculated of free and associated forms of ions according to the ions analytical concentration sum. An iteration was used to solve the ions material balance algebraic equations system. A linear interpolation was used to calculate the tabulated equilibrium constant values according intermediate calculated data.

The soil solution mass balance equation system is given in Eqs. (3)–(8):

$$\sum \mathrm{Ca}^{2+} = [\mathrm{Ca}^{2+}] + [\mathrm{CaCO}_3^0] + [\mathrm{CaHCO}_3^+] + [\mathrm{CaSO}_4^0] \quad (3)$$

$$\sum \mathrm{Mg}^{2+} = [\mathrm{Mg}^{2+}] + [\mathrm{MgCO}_3^0] + [\mathrm{MgSO}_4^0] \quad (4)$$

$$\sum \mathrm{Na}^{2+} = [\mathrm{Na}^{2+}] + [\mathrm{NaCO}_3^-] + [\mathrm{NaSO}_4^-] \quad (5)$$

$$\sum \mathrm{CO}_3^{2-} = [\mathrm{CO}_3^{2-}] + [\mathrm{CaCO}_3^0] + [\mathrm{MgCO}_3^0] + [\mathrm{NaCO}_3^-] \quad (6)$$

$$\sum \mathrm{HCO}_3^- = [\mathrm{HCO}_3^-] + [\mathrm{CaHCO}_3^+] + [\mathrm{MgHCO}_3^+] \quad (7)$$

$$\sum \mathrm{SO}_4^{2-} = [\mathrm{SO}_4^{2-}] + [\mathrm{CaSO}_4^0] + [\mathrm{MgSO}_4^0] + [\mathrm{NaSO}_4^-] \quad (8)$$

where $\sum \mathrm{Ca}^{2+}$, $\sum \mathrm{Mg}^{2+}$ and other cations and anions symbols are the total concentration of ions; $[\mathrm{Ca}^{2+}]$, $[\mathrm{Mg}^{2+}]$, and others cations and anions symbols are the equilibrium concentrations of ion free forms; and $[\mathrm{CaCO}_3{}^0]$, $[\mathrm{MgCO}_3{}^0]$, and others ion associates symbols are equilibrium concentrations of ion associated forms (ion pairs).

The ionic pair concentration dissociation constants K for cation group were determined with Eqs. (9)–(11):

The ionic pair concentration dissociation constants K for Ca

$$\mathrm{K}_{\mathrm{CaCO}_3} = \frac{[\mathrm{Ca}^{2+}][\mathrm{CO}_3^{2-}]}{[\mathrm{CaCO}_3^0]};\ \mathrm{K}_{\mathrm{CaHCO}_3} = \frac{[\mathrm{Ca}^{2+}][\mathrm{HCO}_3^-]}{[\mathrm{CaHCO}_3^+]};\ \mathrm{K}_{\mathrm{CaSO}_4} = \frac{[\mathrm{Ca}^{2+}][\mathrm{SO}_4^{2-}]}{[\mathrm{CaSO}_4^0]} \quad (9)$$

The ionic pair concentration dissociation constants K for Mg

$$\mathrm{K}_{\mathrm{MgCO}_3} = \frac{[\mathrm{Mg}^{2+}][\mathrm{CO}_3^{2-}]}{[\mathrm{MgCO}_3^0]};\ \mathrm{K}_{\mathrm{MgHCO}_3} = \frac{[\mathrm{Mg}^{2+}][\mathrm{HCO}_3^-]}{[\mathrm{MgHCO}_3^+]};\ \mathrm{K}_{\mathrm{MgSO}_4} = \frac{[\mathrm{Mg}^{2+}][\mathrm{SO}_4^{2-}]}{[\mathrm{MgSO}_4^0]} \quad (10)$$

The ionic pair concentration dissociation constants K for Na

$$\mathrm{K}_{\mathrm{NaCO}_3} = \frac{[\mathrm{Na}^{+}][\mathrm{CO}_3^{2-}]}{[\mathrm{NaCO}_3^-]};\ \mathrm{K}_{\mathrm{NaSO}_4} = \frac{[\mathrm{Na}^{2+}][\mathrm{SO}_4^{2-}]}{[\mathrm{NaSO}_4^-]} \quad (11)$$

Using the dissociation constant K in Eqs. (9)–(11) and thermodynamic equilibrium constant K^0 according to Sposito (1989), the equation system of ions material balance in Eqs. (3)–(8) was transformed as follows to directly represent the ion form (Eqs. (12)–(17):

$$\sum \mathrm{Ca}^{2+} = [\mathrm{Ca}^{2+}]\left(1 + \frac{[\mathrm{CO}_3^{2-}]}{\mathrm{K}_{\mathrm{CaCO}_3}} + \frac{[\mathrm{MgCO}_3^-]}{\mathrm{K}_{\mathrm{CaHCO}_3}} + \frac{[\mathrm{SO}_4^{2-}]}{\mathrm{K}_{\mathrm{CaSO}_4}}\right) \quad (12)$$

$$\sum Mg^{2+} = [Mg^{2+}]\left(1 + \frac{[CO_3^{2-}]}{K_{MgCO_3}} + \frac{[HCO_3^-]}{K_{MgHCO_3}} + \frac{[SO_4^{2-}]}{K_{MgSO_4}}\right) \quad (13)$$

$$\sum Na^{2+} = [Na^{2+}]\left(1 + \frac{[CO_3^{2-}]}{K_{NaCO_3}} + \frac{[SO_4^{2-}]}{K_{NaSO_4}}\right) \quad (14)$$

$$\sum CO_3^{2-} = [CO_3^{2-}]\left(1 + \frac{[Ca^{2+}]}{K_{CaCO_3}} + \frac{[Mg^{2+}]}{K_{MgCO_3}} + \frac{[Na^+]}{K_{NaCO_3}}\right) \quad (15)$$

$$\sum HCO_3^- = [HCO_3^-]\left(1 + \frac{[Ca^{2+}]}{K_{CaHCO_3}} + \frac{[Mg^{2+}]}{K_{MgHCO_3}}\right) \quad (16)$$

$$\sum SO_4^{2-} = [SO_4^{2-}]\left(1 + \frac{[Ca^{2+}]}{K_{CaSO_4}} + \frac{[Mg^{2+}]}{K_{MgSO_4}} + \frac{[Na^+]}{K_{NaSO_4}}\right) \quad (17)$$

The thermodynamic equilibrium constants for Eqs. (3)–(17) were recalculated into the concentration dissociation constants by Davies via Eq. (18):

$$pK = pK^0 - A\Delta z^2\left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.2I\right), \quad (18)$$

where К denotes the concentration constant of dissociation of the ionic pairs; $К^0$ is a corresponding thermodynamic constant; A is Debye and Hückel (1923) constant 0.5085 at 25°C; Δz^2 is the algebraic sum of the squares of individual particle's charge (ion or associate); and I is the solution ionic strength.

A calculated with Eq. (16) pК value error at the solution ionic strength of 0.1 mol L^{-1} is less than 3%, and at the 0.5 mol L^{-1} – less than 8%.

At the first iteration step, the soil solution formal ionic strength (I) was calculated using the data on analytical ion concentration via Eq. (19):

$$I = 0.5(2^2(Ca^{2+}) + 2^2(Mg^{2+}) + (Na^+) + 2^2(CO_3^{2-}) + (HCO_3^-) + 2^2(SO_4^{2-}) + (Cl^-), \mathrm{mol\ L^{-1}} \quad (19)$$

A system of six equations with six unknowns was obtained as follows: the free equilibrium concentration forms of every ion listed in Eqs. (3)–(8) were designated as the unknown values, and the analytical concentration of all ion forms was used as a total value of every chemical element.

The value of free ion equilibrium concentrations was calculated in an iteration procedure with Eqs. (12)–(17) according to dissociation constants from Eqs. (9)–(11).

At the next iteration step, the soil solution effective ionic strength I* was calculated using the ion equilibrium concentration via Eq. (20):

$$I^* = 0.5(2^2[Ca^{2+}] + 2^2[Mg^{2+}] + [Na^+] + 2^2(CO_3^{2-}) + (HCO_3^-) + 2^2(SO_4^{2-}) + [CaHCO_3^-] + [MgHCO_3^-] + [NaCO_3^-] + [NaSO_4^-] + [Cl^-]), \mathrm{mol\ L^{-1}} \quad (20)$$

For the next iteration step, the dissociation concentration constants were recalculated via Eqs. (7)–(9), using the calculated soil solution effective ionic strength I* value.

The coefficient of activity (y) of free ions and associates (the last term in Eq. (18) right-hand side, with the opposite sign) was calculated via Eq. (21):

$$-\lg y = Az^2\left(\frac{\sqrt{I^*}}{1+\sqrt{I^*}} - 0.2I^*\right) \qquad (21)$$

where I* is the soil solution effective ionic strength (I is the soil solution ionic strength in the first iteration step).

The next step of iteration sequence for the material balance equation system (12–17) was fulfilled using the recalculated K values for every ion by the Eqs. (18), (21).

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

The coefficient of ion association γ_e was calculated as the ratio of the ion free form to its analytical content in Eq. (22):

$$\gamma_e = C_{ass} / C_{an} \qquad (22)$$

wherein, C_{ass} – a calculated ion content in the solution taking into account its association with other ions, C_{an} – an analytical ion concentration.

10.2.3.5. Soil solution saturation

A procedure of ions association in soil solution calculation according to Eqs. (3)–(22) was presented in details in our previous publications (Kalinitchenko et al. 2020, 2021a).

To understand better the processes in soil solution of the salted soil, a degree of soil solution saturation is of a high importance.

A soil solution saturation degree was determined for each ion as a ratio of a calculated associated ion quantity and a thermodynamic solubility product of corresponding chemical compound. Stages of calculation and equations are given below.

A solubility product S^0 for ideal diluted solution was taken into account.

The soil solution saturation degree at the first step of approximation is K_1.

The solubility product of directly determined analytical ion concentrations is S_1, Eq. (23):

$S_1=C_c\,C_a$, (23)

wherein C_c – analytical cation concentration and C_a – analytical anion concentration in both charged or electrically neutral ion associate.

K_1 is calculated via Eq, (24):

$K_1=S_1/S^0$. (24)

The degree of saturation of soil solution in the second approximation step is K_2.

A product of directly determined analytical ion concentrations multiplied by the ion association coefficient of each ion is S_2, Eq. (25):

$S_2=C_c\,\gamma_{ec}\,C_a\,\gamma_{ea}$, (25)

wherein C_c, and C_a – see above, γ_e – coefficient of association of cation and anion respectively.

K_2 is calculated via Eq, (26):

$K_2= S_2/S^0$. (26)

The degree of saturation of soil solution in the third approximation step is K_3.

In the third approximation step, the molar coefficient of ion activity y was determined by Debye-Huckel equation in modification of E.A. Guggenheim – C.W. Davies with a linear polarization coefficient value of 0.2, Eq. (21).

A product of directly determined analytical ion concentrations multiplied by the ion association coefficient of each ion and ion activity coefficient accounting the effective ionic force I*, Eq. (20), is S_3, Eq. (27):

$S_3=C_c\,\gamma_{ec}\,y_c\,C_a\,\gamma_{ea}\,y_a$, (27)

wherein, C_c, C_a, γ_{ec}, γ_{ea} – see above, y – ion activity coefficient, respectively, cation and anion.

K_3 is calculated via Eq (28):

$K_3= S_3/S^0$. (28)

Self-developed software products ION–2 and ION–3 were used.

10.3. Results

10.3.1. Soil solution saturation degree in Kastanozem soil complex

Research fulfilled showed an influence of main ions association in soil solution on the Kastanozem soil complex and landscape. An origin of landscape differentiation is closely connected to the hydrological regime of landscape. The soils of dry steppe are of loamy-clay composition and have low water resistance. Because of the soil properties, even at a low precipitation level, a lateral differentiation of hydrological regime of landscape appears. It causes the differences in individual soils salinization reflected in the Tab. 10.1.

On the Tab. 10.1 data, a calculation of ions association γ_e in a soil solution of the Kastanozem key plots 1324, 1325 and Haplic Chernozem was fulfilled. The calculation has been made according to the methodologically based procedures of the main ions state in soil solution determination, the results of calculation are presented in the Tab. 10.2–10.6.

The association coefficient γ_e was calculated for ion species as a ratio of a calculated ion free form to its analytical content presented in the Tab. 10.1. The results of calculation are presented in the Tab. 10.2.

Table 10.1. Soil solution composition in Kastanozem soil complex, mmol-eq L^{-1}

Таб. 10.1. Састав раствора земљишта у комплексу кастанозема, mmol-eq l^{-1}

Layer (cm)	Moisture (%)	Dry residue (g L^{-1})	pH	Ca^{2+}	Mg^{2+}	Na^{+}	CO_3^{2-}	HCO_3^{-}	SO_4^{2-}	Cl^{--}
Key plot 1324										
Kastanozem Solonetz steppe										
0-10	27.1	1.29	7.71	4.24	3.98	9.01	0	5.74	7	4.49
10-27	29.3	2.88	8.32	8.53	10.99	22.05	1.6	10.33	15.91	13.73
40-50	22.1	38.46	7.98	69.35	138.51	388.43	0	10.33	323.74	262.22
70-80	19.2	33.97	8.72	64.32	172.13	299.12	3.02	11.48	277.95	243.12
Kastanozem solonetzic soil										
0-28	31.4	3.3	8.1	6.83	8.57	32.71	0	6.84	16.41	24.86
60-70	29.8	21.89	8.2	89.35	119.32	128.21	0	8.61	218.42	109.85
90-100	26.9	24.53	8.35	27.2	126.61	226.35	0.42	13.72	203.85	162.17
Kastanozem dark soil of depression										
0-15	37.7	1.3	7.6	6.92	3.56	5.43	0	9.33	4.53	2.05
40-70	34.2	1.2	7.8	6.98	4.53	3.87	0	7.92	4.11	3.35
90-110	32.6	2.62	7.9	15.2	12.36	7.66	0	14.42	14.53	6.27
130-160	31.3	4.3	8.4	30.21	20.21	13.24	0.95	10.84	30.54	21.33
Key plot 1325										
Kastanozem Solonetz meadow										
0-15	32.1	4.2	8.7	8.53	14.88	38.19	2.87	11.65	16.41	30.67
40-50	33.9	5.9	8.9	10.82	19.38	59.83	3.85	10.37	14.04	61.77
60-70	33.7	41.78	9.04	48.54	218.42	403.82	4.33	18.76	248.55	399.14
90-100	25.3	51.58	8.55	29.8	226.06	578.53	0.9	7.96	363.56	461.97

Table 10.2. Ion association in soil solution, % of the total ion content

Таб. 10.2. Асоцијација јона у раствору земљишта, % од укупног садржаја јона

Layer (cm)	Ca^{2+}	Mg^{2+}	Na^{+}	CO_3^{2-}	HCO_3^{-}	SO_4^{2-}	Cl^{-}
Key plot 1324							
Kastanozem Solonetz steppe							
0-10	14.9	17.8	0.7	0	4.2	18.2	0
10-27	26.5	28.9	2.4	0	6.2	24.5	0
40-50	53.8	57.3	11.9	0	15.5	58.6	0
70-80	50.2	55.8	10.5	87.8	14	52.5	0
Kastanozem solonetzic soil							
0-28	18.5	22.8	1.3	0	4.2	24.7	0
60-70	45.7	53.7	7.7	0	5.2	51.8	0
90-100	49.5	51.2	3.2	88.2	18.1	63.2	0
Kastanozem dark soil of depression							
0-15	11.8	9.4	1	0	2.5	13.2	0
40-70	12.7	10.8	0.8	0	2.2	11.8	0
90-110	19.5	15.6	1.2	0	8.4	13.2	0
130-160	38.2	43.3	2.5	82.2	15.8	22.7	0
Key plot 1325							
Kastanozem Solonetz meadow							
0-15	29.1	34.5	3.6	68.7	3.8	19.9	0
40-50	31.1	35.3	3.9	73.8	4.7	42.2	0
60-70	43.2	48.8	6.6	88.1	6.7	57.2	0
90-100	40.1	49.9	5.8	92.7	22.3	62.7	0

10.3.2. Cd^{2+} thermodynamics in Haplic Chernozem methodology

In natural waters and in the soil, the HMs can bind in associates and hydroxocomplexes (Endovitskii et al. 2014; Sposito 1989). An ion's binding degree depends on the compound thermodynamics instability constant value and main ions concentration.

The Belorechensk chemical plant by-product – phosphogypsum – recycling was fulfilled in a Haplic Chernozem 20-40 cm layer in the doses from 10 to 40 t ha^{-1} according to Patent USSR №1704070 (Minkin et al. 1992). Phosphogypsum recycling is closely linked to a thermodynamic chemical equilibrium of ions in soil solution. In the soil solution are formed associated and complex HMs ions. Model ION–3 has been applied to reveal a Cd^{2+} ion thermodynamic state in Haplic Chernozem. With the free anion and ion pair equilibrium concentrations $[CO_3^{2-}]$, $[HCO_3^-]$, $[SO_4^{2-}]$, $[Cl^-]$ and $[OH^-]$, a Cd^{2+} soluble form content in water extract was calculated from the mass balance Eq. (29) (Endovitsky et al. 2009b; Minkina et al. 2016):

$$Cd^{2+}=\left[Cd^{2+}\right]\left(1+\frac{\left[CO_3^{2-}\right]}{K_{CdCO_3}}+\frac{\left[HCO_3^{-}\right]}{K_{CdHCO_3}}+\frac{\left[SO_4^{2-}\right]}{K_{CdSO_4}}+\frac{\left[Cl^{-}\right]}{K_{CdCl}}+\frac{\left[OH^{-}\right]}{K_{CdOH}}\right) \qquad (29)$$

The Eq. 29 was written out of the main equation system (10)–(15) . Because a Cd soil content and a Cd concentration in soil extract is much less compared to the macroions content. Consequently, a Cd contribution to the formal and effective soil solution ionic strength values is insignificant, and the Eq. (29) was not added to the Equation system (12)–(17). The Eq. (30) written in general form provides free and associated ions form mobile fraction calculation allowing higher level approximation of the HMs in soil because the Equation system is not overloaded with an additional equation for Cd.

A set of associates in the Eq. (29) was considered accounting associated ions stability. The unstable associates were not considered because their influence on the ion association process and thus on the calculation result is insignificant.

In the soil, a potentially hazardous HM thermodynamic state in the soil solution and water extract can be characterized using an association coefficient $k_{as(HM)}$ (Kalinitchenko et al. 2021a).

Ion's binding into associates and complexes can be characterized with a HM ion's association degree ratio by the Eq. (30):

$$k_{as(HM)} = \sum_{i=1}^{n}[An_i]\left(K_{HMAn_i}\right)^{-1} \qquad (30)$$

Association coefficient k_{as} is considered in an electrolytes and surface waters thermodynamics framework on a vast basis of *in vitro* and *in situ* experimental data (Endovitskii et al. 2014).

Given the $k_{as(HM)}$, a final version of the HM model is as follows, Eq. (31):

$$C_{(HM)} = (1 + k_{as(HM)})\,[C_{(HM)}] \tag{31}$$

where $C_{(HM)}$ is the total concentration of microelement in the solution, and $[C_{(ME)}]$ is the equilibrium concentration of free microelement ion.

The HM ions association degree ratio value for Cd^{2+} was transformed from the Equation (30) to the form of Eq. (32):

$$k_{as(Cd)} = \frac{\left[CO_3^{2-}\right]}{K_{CdCO_3}} + \frac{\left[HCO_3^{-}\right]}{K_{CdHCO_3}} + \frac{\left[SO_4^{2-}\right]}{K_{CdSO_4}} + \frac{\left[Cl^{-}\right]}{K_{CdCl}} + \frac{\left[OH^{-}\right]}{K_{CdOH}} \tag{32}$$

Using the coefficient of ion association, the molar fractions of free and bounded Cd^{2+} can be calculated as follows:

$$\nu_{free} = 1/(1 + k_{as(HM)})\cdot 100\% \tag{33}$$

$$\nu_{bound} = 100 - \nu_{free} \tag{34}$$

$$\nu_{Cd} = 100/(1 + k_{as(Cd)}),\ \% \tag{35}$$

$$\nu_{Cd(as)} = 100 - \nu_{Cd},\ \% \tag{36}$$

10.3.3. Cd^{2+} state in Haplic Chernozem calculation results

The results of Cd^{2+} state in Haplic Chernozem calculation according the experimental data and mathematical models ION–2 and ION–3 are presented in the Tab. 10.3–10.6 and discussed below.

Table 10.3. Analitical composition of main ions of soil water extract (in the ratio 1:5) before and after of phosphogipsum appling, cmol(+/–) L^{-1}

Таб. 10.3. Аналитички састав главних јона у воденом екстракту земљишта (у односу 1 : 5) прије и послије примјене фосфогипса, cmol(+/–) l^{-1}

Option of experiment	pH	Total alkalinity (Alk_Σ), cmol(+/–) L^-	Ca^{2+}	Mg^{2+}	Na^+	SO_4^{2-}	Cl^-	$(CO_3^{2-})_A$	$(HCO_3^-)_A$
					$\cdot 10^{-1}$			$\cdot 10^{-4}$	$\cdot 10^{-2}$
Control (original soil)	7.89	44	0.35	0.10	0.012	0.086	0.30	1.492	4.106
After application of 10 t ha^{-1} phosphogypsum	7.72	40	1.90	0.45	0.013	2.005	0.30	1.217	3.736
After application of 20 t ha^{-1} phosphogypsum	7.61	36	2.75	0.50	0.013	2.880	0.35	0.885	3.366
After application of 40 t ha^{-1} phosphogypsum	7.63	36	4.50	0.75	0.013	4.925	0.30	0.877	3.366

Table 10.4. Equilibrium concentrations of main ions, cmol (+/–) L– (above), and molar fractions, %, (below), of free forms of the main ions in soil solution

Таб. 10.4. Равнотежне концентрације главних јона, cmol (+/–) l– (горе), и моларне фракције, %, (доље), слободних облика главних јона у раствору земљишта

Option of experiment	Effective ionic strength, μ*	Coefficient of ion activity, γ'/γ''	$[Ca^{2+}]$	$[Mg^{2+}]$	$[Na^{+}]$	$[SO_4^{2-}]$	$[Cl^{-}]$	$[CO_3^{2-}]_A$, $\cdot 10^{-4}$	$[HCO_3^{-}]_A$, $\cdot 10^{-2}$	$[OH^{-}]$, $\cdot 10^{-5}$
			$\cdot 10^{-1}$							
Control (original soil)	0.001814	0.9537	0.343	0.0986	0.01199	0.0806	0.30	1.079	4.081	8.141
		0.8272	98.00	98.60	99.92	93.72	100.00	72.32	99.39	
After application of 10 t ha^{-1} phosphogypsum	0.007702	0.9115	1.627	0.380	0.01292	1.672	0.30	0.454	3.648	5.759
		0.6902	85.63	84.44	99.38	83.39	100.00	37.30	97.64	
After application of 20 t ha^{-1} phosphogypsum	0.01036	0.8997	2.277	0.4065	0.01292	2.324	0.35	0.296	3.265	4.292
		0.6551	82.80	81.30	99.38	80.69	100.00	33.45	97.00	
After application of 40 t ha^{-1} phosphogypsum	0.01715	0.8826	3.518	0.6111	0.01289	3.818	0.30	0.309	3.235	4.833
		0.6069	78.18	81.48	99.15	77.52	100.00	35.23	96.11	

Table 10.5. Cd^{2+} total and water-soluble form soil content, mg kg^{-1} DW

Таб. 10.5. Укупни и водорастворни облик садржаја Cd^{2+} у земљишту, mg kg^{-1} DW

Option of experiment	Cd^{2+} total content	Cd^{2+} water-soluble form content	Cd^{2+} water-soluble weight fraction, % Cd^{2+} total content
Control (original soil)	0.240	0.0348	14.500
After application of 10 t ha^{-1} phosphogypsum	0.2505	0.03605	14.392
After application of 20 t ha^{-1} phosphogypsum	0.2610	0.0373	14.296
After application of 40 t ha^{-1} phosphogypsum	0.2819	0.0398	14.123

Table 10.6. Cd^{2+} water soluble form concentration in soil water extract

Таб. 10.6. Концентрација водорастворног облика Cd^{2+} у воденом екстракту земљишта

Option of experiment	Concentration, cmol (+/–) L^{-1}			Molar fraction, %							Association coefficient, $k_{as(Cd)}$
	Cd^{2+} total content	$[Cd^{2+}]$ equilibrium content	$\alpha[Cd^{2+}]$ active content	$\alpha[Cd^{2+}]$	$[Cd^{2+}]$	$[CdCO_3^0]$	$[CdHCO_3^+]$	$[CdSO_4^0]$	$[CdCl^+]$	$[CdOH^+]$	
	$\cdot 10^{-6}$										
Control (original soil)	6.192	3.2272	2.6695	43.118	52.119	0.657	3.208	0.370	1.451	42.195	0.919
After application of 10 t ha^{-1} phosphogypsum	6.415	3.8801	2.6780	41.746	60.485	0.223	2.776	6.207	1.405	28.904	0.656
After application of 20 t ha^{-1} phosphogypsum	6.639	4.3296	2.8363	42.722	65.214	0.142	2.543	8.379	1.678	22.044	0.533
After application of 40 t ha^{-1} phosphogypsum	7.085	4.4505	2.7010	38.123	62.815	0.122	2.248	11.380	1.283	22.150	0.592

10.4. Discussion

10.4.1. Main ions association in Kastanozem landscape soil solution

In result of calculation different soil solution saturation levels were revealed.

A soil solution supersaturation degree K_1 was calculated as an analytical ion concentration solubility product S_1 to thermodynamic solubility product S^0 ratio by Eqs. (23) and (24). It was revealed that a substantial part of studied soil solutions is supersaturated, especially regarding $CaCO_3$.

A real equilibrium concentration of various ion forms in soil solution was calculated. Depending on the soil solution concentration and composition in an ionic pairs form are presented: Ca^{2+} – 11.8–53.8%; Mg^{2+} – 9.4–57.3%; Na^+ – 0.7–11.9%; HCO_3^- – 2.2–22.3%; and SO_4^{2-} – 11.8–62.7%. A CO_3^{2-} ion associated form share is up to 92.7%.

The ion association process explains an excess ions concentration in soil solution in comparison to ion thermodynamic solubility product S^0 in many different modelling systems (Endovitsky et al. 2014; Izgorodina 2011; Izgorodina et al. 2014; Kalinichenko et al. 2024; Luo et al. 2013). In particular, it is important for an ion pairs association in a supercritical water and other conditions (Chialvo et al. 1995; Plugatyr et al. 2011; Sushkova et al. 2013), in a simulation of ion pairs hybrid excitations in solution (Kielpinski 2013), and it is crucial in a methods of ion pair formation in electrolyte computer modeling developing (Lui et al. 2011; Raiteri et al. 2012; Shatti et al. 2011). In the recent years, the improved methods of a direct ion pairs study are aplied (Westerlund et al. 2011; Besser-Rogac et al. 2011; Wang et al. 2014).

The ions association varies by the soil layers. A soil solution salinity increase amplifies the ions association. The ions association in soil solution varies in landscape at a soil complex components level in a lateral soil cover structure (SCS) framework. The most common dry steppe Kastanozem soil complex SCS components are represented in the key plot 1324.

The key plot 1325 has a feature. This keyplot is laterally separated from the key plot 1324 to reveal the special properties of Kastanozem Solonetz meadow soil, which is less common. The Kastanozem Solonetz meadow soil appears only in the Kastanozem saline plain local depressions. However, a knowledge about this type soil is vital because it represent the most unfavorable component of soil cover in terms of teh plant growth conditions. In the key plot 1325 Kastanozem Solonetz meadow soil solution there is a pH high value and soda is presented. Therefore, according to the calculations, in this soil a significant part of ions, especially CO_3^{2-}, are in an associated state.

A soil solution saturation degree K_2 value was calculated by Eqs. (26) as a ratio of the electrically charged ions, ion pairs and molecules form concentration solubility product accounting the ion association S_2 to the thermodynamic solubility product S^0. To account the ion association, the solubility product of ion analytical content in an ion, ion pair and molecule form was multiplied by the ion association coefficient constituting the associates, Eqs. (25).

The soil solution saturation degree K_2 is significantly less compared to the first embodiment of saturation K_1.

On the Tab. 10.1 data, the ion activity coefficient y was calculated via Eq. (21) – the third approximation of Debye-Huckel equation by Guggenheim and Davies with a linear Guntelberg polarization coefficient.

The coefficient K_3 is the third embodiment of soil solution saturation calculation. The calculated soil solution saturation in Eq. (28) is a ratio of the analytical content of ion pairs in soil solution solubility product multiplied by an ion association coefficient γ_e and an ion activity coefficient y S_3 (Eq. (27)) to the thermodynamic solubility product S^0.

Calculations show that in the third embodiment when the ion association and activity were taken into account the calculated soil solution saturation degree K_3 was significantly lower compared to K_1 and K_2.

Given the ions association and ions activity, the calculated soil solution supersaturation K_3 in most cases did not exist, even for $CaCO_3$, though it was often believed that the natural water and soil solution are supersaturated with $CaCO_3$ (Amakor et al. 2013; Kalinitchenko et al. 2018).

According to the K_3 value, a soil solution supersaturation appeared only in a Kastanozem Solonetz meadow key plot 1325 – $K_3 \approx 2–5$. In this soil, an organic matter content in soil solution is relatively larger than in other soils ensuring the ion complexes with organic matter formation. Very complicated phenomenon of organic complexes formation in the soil solution was a subject of a former publication (Kalinitchenko et al. 2018, 2024). However, this intricate problem is waiting for the new special messages.

On the soil solution thermodynamics theoretical generalization basis, and the studies and calculations conducted it can be argued that the ions association and ion activity cause the soil solution saturation degree with various compounds providing a fundamentally new picture of the chemicals migration and accumulation in the soils and landscapes, especially regarding the $CaCO_3$ patterns.

10.4.2. Influence of main ions association in soil solution on Kastanozem soil complex and landscape

The layers of individual soil profile and soils in landscape are interacting. A soil solution carbonate calcium system state in an individual small part of the soil continnum can be characterized at an exact time by the developed mathematical models. In addition, the calculation explains a soil solution metamorphisation on a time pattern and through the soil continuum under the water salt mass transfer.

In saline landscape, the salinity of soil continuum is linked to a high ion mobility in tsoil solution. Geochemical barriers in landscape down the soil profile and between soils are weak, and salts freely migrate into the soil continuum and constantly influence the soil evolution. On this cause, an origin of SCS is stable and its forecast concerning an agriculture success is unfavorable. The natural Kastanozem soil complex watering is insufficient for a plant growth. However, if a general soil moisture of Kastanozem soil complex will be increased, this will be not a positive circumstance for the soil fertility. Under a higher soil watering, a salts migration through the soil continuum will increase, and a Kastanozem soil complex as a whole will be under increased negative influence of salts. A causes of a phenomenon are the vertical and lateral water salt transfer, and metamofization and second accumulation of salts in soil. This probable result fully accords to the proposed thermodynamic models of salt transfer macroprocesses, including the ions association, compexation and saturation in soil solution.

The model shows that a salt transfer in a Kastanozem soil complex is a significant feature of the object of research. Thus, a prediction of a Kastanozem soil complex evolution in conditions of salinization is unfavorable. To sustain the soil, there is a need to correct the hydrological regime of landscape, maintain a proper soil solution equilibrium and a total and partial salt content, apply additional water in proper quantities to a proper part of soil profile to avoid outdated irrigation and other soil management practices adverse current consequences. It is important because of soil degradation, which is probable under the known conventional methods of landuse. Calculations fulfilled showed that a soil degradation scenario taking into account the ion association in soil solution and soil spatial differentiation throughout SCS is much more probable and dangerous compared to the previous assessments.

Calculations fulfilled show the soil solution composition dependence on the ion association and ion activity. On the ideas of ion association in soil solution, there is a possibility of a new glance on the processes in soil solution, soil and landscape. A $CaCO_3$ sedimentation in saline soil occurs at a much higher concentration of Ca^{2+} and CO_3^{2-} ions in the soil solution than it was considered previously. Consequently, a significantly high $CaCO_3$ mobility in soil and landscape is probable. The same is highly probable for other ions too. The salinity of soils in a Kastanozem complex landscape is laterally differentiated, and some soils salinity is higher than a Kastanozem general level salinity. However, some other soils salinity, on the contrary, is less general level. It is caused by soil local excessive periodic temporal moistening under influence of Kastanozem complex micro-relief, and soil solution becomes extremely mobile laterally. This cause a salt forms lateral redistribution between Kastanozem complex soils.

An ion association in soil solution knowledge matters in understanding a modern evolution of salted soils as well as in these soils use.

The research fulfilled shows that a linked to CCE behavior of ions in soil solution of soil horizons and then in Kastanozem landscape helps to characterize the origin and level of different soils coordination in Kastanozem complex and landscape. There is a need to account a CCE phenomenon in a Kastanozem soil complex management.

For the dry steppe saline laterally differentiated Kastanozem soil complex sustainable management there is a need to understand better an origin of vertical and lateral water salt transfer, metamofization and secondery accumulation of salts in different soils. It is important to reduce the ion mobility and obtain more stable geochemical barriers in landscape and soil to prevent or at least reduce a negative influence of salts on SCS and an uncontrolled transfer of salts including polutants.

A soil and landscape productivity can be increased accounting the CCE, ions association, ions activity and SCS. CCE provides the soil and water-salt environmental transfer functions and geochemical barriers new understanding.

This will help to decide a main task of soil management – achieve a goal of a high plant productivity and thereby indirectly increase a plant resistance to phytopathogens.

10.4.3. Ion association thermodynamic model in Haplic Chernozem

An original Haplic Chernozem soil water extract of calcium chloride composition (Tab. 10.3) Ca > Mg > Na (calcium water group) was the same both before and after the phosphogypsum application. After the phosphogypsum application, a water extract pH decreased by 0.23–0.26 units, a soil solution composition changed to the sulfate class and became the calcium sulfate. A real state of the main ions in soil solution was determined on a basis of ionic strength and ion association in soil solution according the soil solution equilibrium model (Endovitskii et al. 2009b).

The thermodynamic properties of soil solution depend on association of its main ions. The result of ion association is a significant decrease of the concentration of ion free forms and ionic strength of solution (μ). The activity coefficients of single-charged (γ′) and double-charged (γ″) ions increase. As a result, the stability constants of associates and complexes in soil solution also change.

The forms of main ions in a Haplic Chernozem soil solution were calculated according analytical data (Tab. 10.3) via the Eqs. (1)–(22). A main ion form associates shore is to a significant degree lower than that in solonetz soil (Tab. 10.4). The molar fractions of calcium and magnesium associates are 2.0–6.1% [Ca^{2+}] and 1.4–6.6% [Mg^{2+}] against 13.1–19.2 and 15.7–23.5% respectively in solonetz (Endovitskii et al. 2009b).

In soil solution of Haplic Chernozem a cation molar fraction was 21.8–20.6% Ca^{2+} and 18.5–22.4% Mg^{2+} correspondingly, a sulfate ion association was 6.3–12.9%, and a carbonate associate fraction – 64.7–78.2% (Endovitskii et al. 2009b).

Along with main ions, the soil contains different microelements, including the potentially harmful HMs (Alloway 1995; Anisimov et al. 2015; Minkina et al. 2014). The total background contents of Cd^{2+} in soil is of 0.24 mg kg^{-1} DW (Robinson et al. 2023; US Environmental Protection Agency, 2020). Accordingly, a Cd^{2+} total content in soil was taken in a Cd^{2+} forms calculation. The free and associated ions molar fractions are a universal characteristic of a microelement or HM thermodynamic state in soil solution. The water extract data were used for calculation, a water-soluble Cd^{2+} weight fraction was taken as 14.5% in the model approximation.

The Cd soil content is many times less than that of macro ions and has a little influence on the soil solution ionic strength and thermodynamic constant value. There is no need to include an equation for Cd into the system of equations for macro ions. The obtained equilibrium concentrations of free anions [CO_3^{2-}], [HCO_3^-], [SO_4^{2-}], [Cl^-], and [OH^-] from the mass balance equations were used for calculation the soluble Cd^{2+} form content in water extract (Batukaev et al. 2017; Endovitsky et al. 2014). The calculation of free and associated Cd^{2+} mobile fractions in the soil water extract was made by Eq. (29).

The thermodynamic equilibrium constants of associates $CdCO_3^0$ and $CdHCO_3^+$ were taken according to Sposito (1989):

$pK^0(CdCO_3) = 4.23$; $pK^0(CdHCO_3) = 2.261$, $pK^0(CdSO_4) = 2.11$; $pK^0(CdCl) = 2.05$; $pK^0(CdOH) = 6.08$

Concerning the soil organic matter proton complexes with salt cations, if taken into account in Eq. (30) this will reduce a free Cd^{2+} ion calculated concentration, and the calculated Cd^{2+} association and complexation will be lower. A Cd^{2+} total concentration is given in the Eqs. (37–40) left part. After phosphogypsum application, the main ions and Cd^{2+} concentration in Eqs. (38–40) change accordingly, and a Cd^{2+}equilibrium form concentration as well.

Water extract before application of phosphogypsum:

$6.192{\cdot}10^{-6} = [Cd^{2+}](1+10^5[CO_3^{2-}]/8.5567+10^3[HCO_3^-]/6.6308 +10^3[SO_4^{2-}]/$

$/11.3436+10^3[Cl^-]/10.7749+10^7[OH^-]/10.0556)$ (37)

After application of 10 t ha^{-1} phosphogypsum:

$6.415{\cdot}10^{-6} = [Cd^{2+}](1+10^5[CO_3^{2-}]/12.2907+10^3[HCO_3^-]/7.9470 +10^3[SO_4^{2-}]/$

$/16.2938+10^3[Cl^-]/12.9136+10^7[OH^-]/12.0516)$ (38)

After application of 20 t ha^{-1} phosphogypsum:

$6.639{\cdot}10^{-6} = [Cd^{2+}](1+10^5[CO_3^{2-}]/13.6431+10^3[HCO_3^-]/8.3728 +10^3[SO_4^{2-}]/$

$/18.0867+10^3[Cl^-]/13.6056+10^7[OH^-]/12.6973)$ (39)

After application of 40 t ha^{-1} phosphogypsum:

$7.085{\cdot}10^{-6} = [Cd^{2+}](1+10^5[CO_3^{2-}]/15.8962+10^3[HCO_3^-]/9.0377 +10^3[SO_4^{2-}]/$

$/21.0736+10^3[Cl^-]/14.6861+10^7[OH^-]/13.7057)$ (40)

The total and water-soluble Cd^{2+} forms contents in soils were calculated with the above referenced Equations, the result of calculation is presented in Tab. 10.5 and Tab. 10.6. A Cd^{2+} soil total and water-soluble forms content increases corresponding to a phosphogypsum dose value (Tab. 10.6). A maximum Cd^{2+} total and water-soluble form is at a 40 t ha^{-1} dose.

The maximum Cd^{2+} coefficient of association was 0.919 in original soil. Most Cd^{2+} ion is bound into the hydroxo-complexes $CdOH^+$ (molar fraction 42.2–46.4%). A smaller Cd^{2+} ion amount is bound into the hydrocarbonate associate $CdHCO_3^+$ (3.2%) or chloride associate $CdCl^+$ (4.5%). A free Cd^{2+} ion active molar fraction concentration is 38.3% (Endovitsky et al. 2014). Compared to the original soil, a phosphogypsum apply reduces a Cd^{2+} associates molar fraction. At the phosphogypsum dose of 20 t ha^{-1}, Cd^{2+} free molar fraction content increases by 13.1%, and an active concentration fraction decreases by 2.0%.

At the maximum dose of phosphogypsum, the Cd^{2+} hydroxo complexes are prevailing compounds by 23.4% and sulfate associates make up 9.8%. A Cd^{2+} association coefficient is of 0.533 decreasing by 1.43 times.

The Cd^{2+} total content and water soluble form content in original soil and in the soil after the phosphogypsum application of 10–40 t ha^{-1} did not exceed a limit of Cd content in soil. This fact indicates no hazard of the phosphogypsum application to the soil and environment.

The soil solution is diluted and its ionic strength is low in non-saline Haplic Chernozem (Tab. 10.3). A soil solution ionic strength is higher than that in a water extract from the same soil, and a real Cd^{2+} passivation degree is higher in the soil solution (Endovitskii et al. 2009b). However, *in vitro* both a water extract and a soil solution extracted by the standard method are diluted compared a typical low water content of 9–16% DW in the steppe soil in a period of plant ontogenesis. A real soil solution concentration is 30–100 times higher than water extract data shown in the Tab. 10.3, and effective ionic strength of soil solution *in situ* can be assessed up to $I^{*}=0.2–0.6$. A calculated Cd^{2+} association coefficient can be extrapolated to be 10–30 units. It means that in Krasnodar Territory a plant ontogenesis is reliably protected from a Cd^{2+} ion transfer through the root system to plant tissues because of a Cd^{2+} ion passivation in soil solution according to a revealed soil solution thermodynamics pattern.

The more hydromorphic is landscape and higher the soil humidity, the higher is the Cd^{2+} and other HMs danger for the plant and environment (Kalinichenko et al. 2024; Kwasniewska 2014). The problem of Cd^{2+} content in the soil is closely linked to the problem of matter leaching from the soil. The landscape of Krasnodar Territory is prematurely automorphic. This is an additional reason to use the phosphogypsum for the Chernozem Haplic reclamation without the Cd^{2+} environmentally adverse effects because of a rather high ionic strength and corresponding ions association in a concentrated soil solution (Visconti and De Paz 2012; Amakor et al. 2013).

The studied phosphogypsum doses of 10–40 t ha^{-1} are environmentally substantiated from the thermodynamic point of view. To implement the research results, an improved soil layer 20–40 cm architecture is needed providing the phosphogypsum uniform dispersed distribution at a concentration lower than Clark (Rules and Regulations, 2001; McGahren et al. 2024) and safe utilization without an uncontrolled redistribution. The phosphogypsum intra-soil recycling excludes the phosphogypsum stacks and ponds providing the landscape recreational appearance, ensures a higher soil biological productivity and the plant better development and resistance to phytopathogens. The new technical solutions and technology in soil reclamation are proposed (Kalinichenko 2020, 2021a, 2021b, 2024).

10.4.4. Environmentally safe plant biological production in circular economy

At all the ontogenesis stages *in vitro, ex vitro, in situ*, a plant development is determined by environmental conditions. Besides, it is important to overcome the limitations of ontogenesis imposed by the use of outdated technologies for controlling both the processes of planting material production and cultivation of plants in open ground (Silva et al. 2021). The substrate, fertilizers, microfertilizers and growth stimulants determine the root system development and features of a plant nutritional regime. The soil moisture is important that in standard conditions in vitro or ex vitro is maintained high and therefor an excessively high water matrix potential is formed. This is due to a defect in the cultivation protocol that does not provide for the modern possibilities to control a moisture regime of substrate or the soil *ex vitro* and *in situ* causing an intense hydrodynamic and static destruction of substrate and soil due to a weak stability of their structure and architecture in conditions of an excessive moisture (Kalinitchenko and Rykhlik 2019).

A plant growing *ex vitro* at a high humidity of substrate causes a subsequent deteriorated plant acclimatization *in situ*. In addition, a high humidity of substrate leads to a HMs free penetration into plant tissue. The same adverse effects are observed when the standard irrigation or greenhouse technology are applied for plant watering *in situ*. In order to reduce a plant HMs intake and increase productivity, a transcendental Biogeosystem Technique (BGT*) approach to the soil and water management has a prospect.

A “transcendental” means rejection of a direct copying of natural phenomena as it is in a case of standard irrigation and other imitational technologies (McDermid et al. 2023). Instead of a direct copying, a transcendental methodology ensures a new priority environmental niche for plant development. This is achieved using a combination of natural water transfer in a fine-aggregate system or substrate phenomenon and new technical solutions of water transfer control developed on a basis of a Biogeosystem Technique (BGT*) heuristic qualified intuition methodology (Kalinichenko 2020, 2021a, 2021b, 2024). The BGT* methodology was developed as a system of non-standard technical means and technologies for a long-term optimization of the soil geophysical, chemical, water, biological properties, plant phytopathogens protection and crop productivity in circular economy.

The standard soil processing is incapable to overcome a soil dead-end porosity that value under agriculture can reach an incredible level of 99% (Granstrand, Holgersson

2020; Jensen et al. 2020; Shein et al. 2021). Fig. 10.2 shows illuvial and transition horizons blocks that remain intact on a long-term after standard three-tier PTN–40 plowing being an obstacle in root development.

Fig. 10.2. Solonetz profile in a cross section wall at a depth of 20–35 cm 40 years after PTN-40 plowing

Сл. 10.2. Профил солонца у попречном пресјеку зида на дубини 20–35 cm, 40 година након орања методом PTN–40

An intra-soil milling methodology was developed and the devices for methodology implementation were created (Fig. 10.3) (Kalinichenko 2021c).

The device (Fig. 10.3) is equipped with a moldboard section 3 for the soil upper layer of 0–20 cm standard plowing. The device had a mechanical drive 1 connected to the power take-off shaft. The chisel for preliminary soil loosening 2 formed a slit for the passive ripper 5 equipped with a closed housing for the transmission drive gearing placement. The drive gearing transmits the torque to the milling ripper 4. The milling cutters diameter of 250 mm are installed vertically with a spacing of 80 mm along the milling ripper 4 horizontal shaft processing the soil layers of 20–45 cm in the illuvial and transitional horizons. The speed of rotation is of 500 rpm.

The homogenous soil layer 20–45 cm after PMS–70 intra-soil processing is presented in Fig. 10.4. The soil structure and architecture become favorable for a root development in the whole soil profile, the soil cross-section wall is riddled with roots.

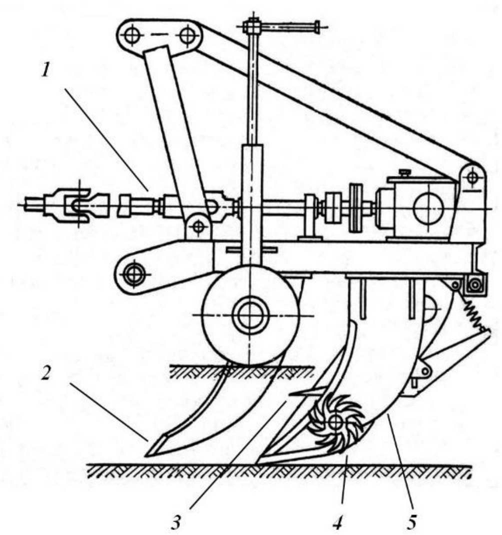

Fig. 10.3. Mechanical scheme of intra-soil milling device
Сл. 10.3. Механичка шема уређаја за унутарземљишно мљевење

Mechanical drive 1, chisel for preliminary soil loosening 2, moldboard section 3, soil illuvial and transitional horizons milling ripper 4, passive ripper with a closed gearing housing 5.

Fig. 10.4. Solonetz soil profile wall at a depth of 25–40 cm (40 years after PMS–70 processing)
Сл. 10.4. Профилни зид солонца на дубини 25–40 cm (40 година након обраде методом PMS–70)

The X-ray photo (Fig. 10.5) of barium sulfate scattering visualize the soil crumbling and mixing after intra-soil milling (Kalinitchenko et al. 2021b).

Fig. 10.5. Barium sulfate particles X-Ray diffraction after PMS–70 intra-soil processing

Сл. 10.5. Честице баријум-сулфата након унутарземљишне обраде методом PMS–70, дифракција рендгенских зрака

Along with a positive function of the PMS-70 intra-soil milling concerning soil geophysical properties, there was a mechanical problem of a high passive traction resistance of the chisel for preliminary soil loosening 2 and passive ripper 5 (Fig. 10.3).

Based on a heuristic nonstandard approach to the mechanical system synthesis, new gear drive is designed that provide an intra-soil processing machine traction resistance reduction (Kalinitchenko et al. 2021b) (Fig. 10.6). Intra-soil milling machine new technical solution maintains the former design benefits while increasing a device reliability, reducing an intra-soil processing cost and providing an efficient land-use.

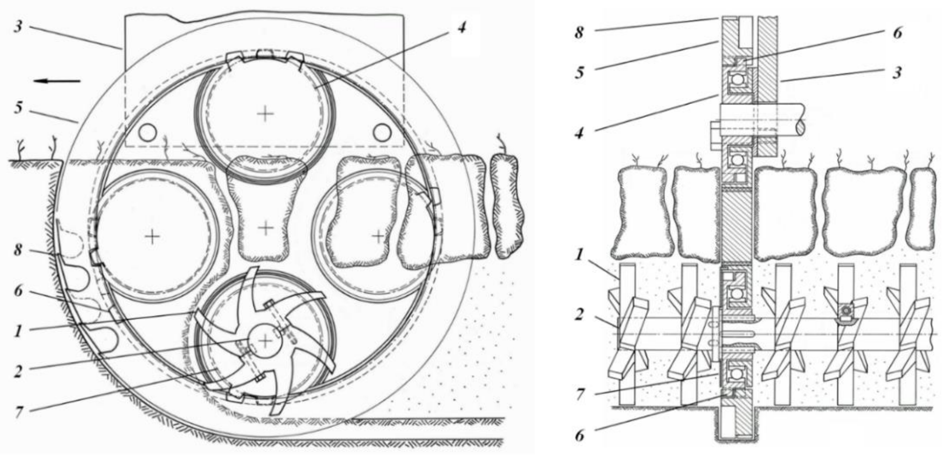

Fig. 10.6. Intra-soil milling machine PMS–280, (**a**) side view, (**b**) front view
Сл. 10.6. Машина за мљевене земљишта PMS–280, (a) бочни приказ, (b) предњи приказ

Mills 1; shaft 2; frame 3; driving gear 4; ring cogwheel 5; internal gearing 6; driven gear 7; external cutter 8.

An intra-soil milling machine active drive new design provides five times less traction resistance and 80% increased reliability, halving energy costs. A new device heuristic essence is a drive unit system 4–8 design that provide a system movement along the slit without traction resistance (Kalinichenko 2021c). The device is capable to supply the phosphogypsum and other substances in dispersed, pulp or liquid form to a processing soil layer of 20-45 cm (up to 40–70 cm). This improves the soil architechture and physicochemical properties excluding an uncontrolled eolian spread and transfer of unsafe substances in the environment (Kalinichenko 2010a).

Plant growth-promoting rhizobacteria stimulate plant by multiple mechanisms (Matilla and Krell 2018). The plant ontogenesis and productivity have the soil-biological limitations of development in the rhizosphere. Currently, the soil geophysical system structure and architecture (Lin 2012; Totsche et al. 2018) are inappropriate for rhizobacteria and organic matter synthesis (Roth et al. 2019), soil humeome (Piccolo et al. 2019) and plant growth. The soil compaction and illuviation are a biological stress-factor instigating plant weak stress tolerance. The soil layer of 20–45 cm intra-soil milling provides a fine multilevel soil aggregate system (Kharitonova et al. 2018; Shein et al. 2017) and improves the soil biological capabilities (Kalinitchenko 2021b). New abundant soil interfaces ensure a high rate soil biological process in the multilevel soil architecture system (Kalinitchenko 2016; Kalinitchenko et al. 2024; Nayak et al. 2011; Røder et al. 2019) and increase the soil quality (Bünemann et al. 2018).

A biological potential of soil amendments and other additives will become higher on intra-soil milling background.

A development in a framework of the BGT* methodology is an intra-soil pulse sequential-discrete watering paradigm (Kalinitchenko and Rykhlik, 2019). An unmanned intra-soil pulse sequential-discrete watering system provides water economy and high plant productivity. Simultaneously, different substances could be supplied: Plasmolite H_2O_2 (Belov et al. 2020), Selenium nanoparticles as fertilizer (Gudkov et al. 2020), activated potassium phosphate fertilizer (Konchekov et al. 2021), soil structurizers, fertilizers, plant protection biological preparations (Chaplygin et al. 2022) and other. The H_2O_2 different functions in plant still require examination (Belov et al. 2020; Niu and Liao 2016), especially accounting BGT* methodology. A seed and plant stimulation is of high importance because signaling crosstalk between H_2O_2 and NO, H_2O_2 and Ca^{2+} is crucial for plant development and physiological processes on every stage of a plant ontogenesis.

After intra-soil pulse sequential-discrete watering including simultaneous additional substances supply, the soil matrix potential is of −0.2 to −0.4 MPa. The potential is much less than that at the standard irrigation, but at the same time forms the priority conditions for the plant and soil biome ontogenesis. We proposed the BGT* methodology (Kalinitchenko et al. 2024) to provided synergetic technological application of plant additives for a soil-biological process stimulation. The BGT* methodology is vital for Plasmolite H_2O_2 and other additives function because: a) there will be no need for excess H_2O_2 because water loss from soil is excluded; b) water supply plant stress-factor is limited, and Plasmolite H_2O_2, Selenium nanoparticles, activated potassium phosphate fertilizer stimulation is optimal. Intra-soil pulse sequential-discrete unmanned watering is of a high importance for the soil matter turnover because ensures strict control of water spread throughout the soil. Implementation of the intra-soil pulse sequential-discrete unmanned watering and simultaneous additives supply is presented in the Fig. 10.7. Our patent (Kalinichenko 2010b) is a basis of the proposed soil watering, plant and soil stimulation and plant protection system.

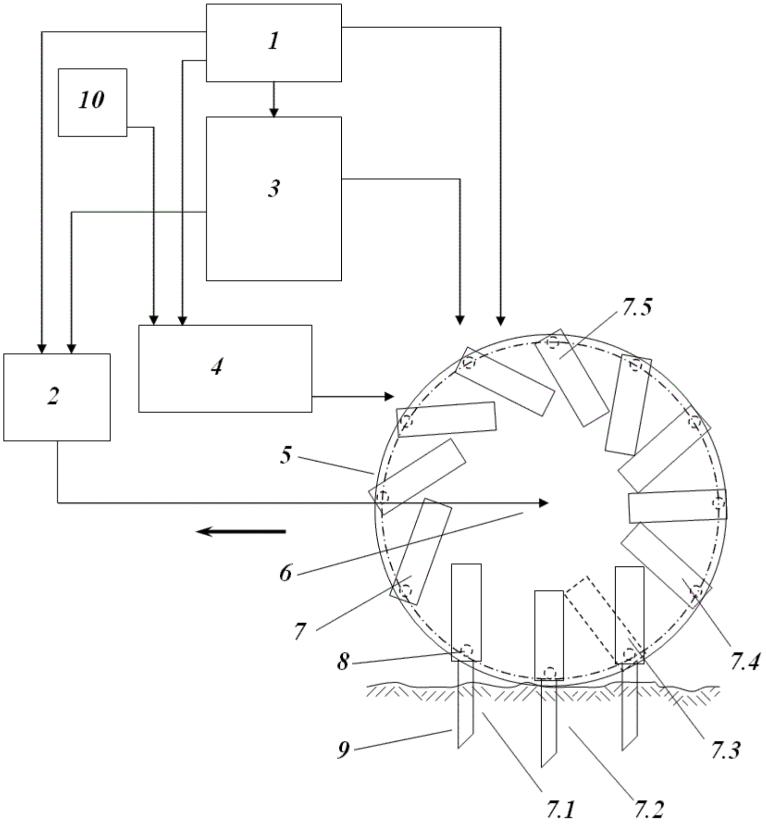

Fig. 10.7. Unmanned intra-soil pulse sequential-discrete plant watering and simultaneous Plasmolite H_2O_2 supply to the soil device
Сл. 10.7. Беспилотни уређај за пулсно секвенцијално-дискретно наводњавање биљака и додавање Plasmolite H_2O_2 *у земљиште*

Power supply unit 1, wheel chassis unit 2, control unit 3, water supply unit 4, disc 5, axis 6, syringe element 7, syringe element positions 7.1–7.5, flexible supply coupling 8, retractable syringe 9, substances supply unit 10.

Unmanned intra-soil pulse sequential-discrete plant watering and simultaneous substance supply to the soil system comprises the remote controlled devices (Fig. 10.7) that provide the system operation. The system is indispensable for the Plasmolite H_2O_2, Selenium nanoparticles and activated potassium phosphate fertilizer and other nanomaterials because these preparations are to be supplied in micro-doses. Only intra-soil pulse sequential-discrete device is capable to apply these substances to the soil and provide plant physiology and soil-biological process synergy (Niu and Liao 2016).

Plasmolite H_2O_2, Selenium nanoparticles and activated potassium phosphate fertilizer effect on the plant physiology and soil-biological process is synergetic (Niu and Liao 2016). This direct and indirect potential is vital for the soil organic matter, humic substances (Canellas, Olivares 2014; Nardi et al. 2022) and soil polimicrobial biofilm starters (Swidsinski, 2019) functioning. Intra-soil liquid fertilizers and biological preparations injection provides agronomical advantages (Chaplygin et al. 2022; Kalinitchenko et al. 2023; Niemoeller et al. 2011; Swidsinski et al. 2020) in plant protection and soil watering because a rather low soil water potential and corresponding reduction of water and HMs consumption by plants. Energy and resource-efficient environmentally safe chemical engineering ensures soil and human health (Meshalkin 2021; Meshalkin et al. 2021; Swidsinski, 2019).

10.5. Conclusions

A soil solution material composition, migration and accumulation dynamics is determined by soil solution chemical equilibrium. Soil solution contains associated electrically neutral ion pairs $CaCO_3^0$; $CaSO_4^0$, $MgCO_3^0$, $MgSO_4^0$ and charged ion pairs $CaHCO_3^+$, $MgHCO_3^+$, $NaCO_3^-$, $NaSO_4^-$, $CaOH^+$, $MgOH^+$. To assess the real ion forms in soil solution of the Kastanozem soil complex and Haplic Chernozem, a soil solution chemical equilibrium quantitative calculation method is developed and programs Ion–2 and Ion–3 are created. An analytical saturation of soil solution with $CaCO_3$ in relation to the thermodynamic solubility product S^0 is up to 100 units, and taking into account the ion association and ion activity a calculated saturation decreases to the value ≈1.

In the soil solution of original soil, the Cd^{2+} calculated equilibrium concentration and molar fraction showed Cd^{2+} predominant binding into associates with hydroxocomplexes $CdOH^+$, a Cd^{2+} ion association coefficient is 0.919.

At the phosphogypsum dose of 40 t ha^{-1}, a Cd^{2+} molar fraction bounded into hydroxocomplexs ion associates $CdOH^+$ and $Cd(OH)_2^0$ decreased. The Cd^{2+} sulfate associates $CdSO_4^0$ fraction and free Cd^{2+} ions contents increased, a Cd^{2+} ion association coefficient was 0.533.

The application of phosphogypsum increases a Cd^{2+} free form soil content by 57.1%, but it makes no hazard in the case of phosphogypsum from Kovdor phosphate ore applied for soil reclamation because the Cd^{2+} content in ore and phosphogypsum is low, and the small additional quantity of Cd^{2+} is spread throughout the soil continuum while soil processing at concentration lower Clark. The phosphogypsum application to the initially uncontaminated with heavy metals non-saline Haplic Chernozem is environmentally permissible. The total content of Cd^{2+} in soils increases by 14.4% at the of 40 t ha^{-1} phosphogypsum, however, it does not reach the Cd MPC value of 2 mg kg^{-1} DW.

An intra-soil milling methodology was developed. For a methodology implementation, a device has been created that is capable in a phosphogypsum and other substances supply in dispersed, pulp or liquid form to a processing soil layer of 20–45 cm (up to 40–70 cm). This improves the soil architechture and physicochemical properties excluding an uncontrolled eolian spread and transfer of unsafe substances in the environment and providing appropriate rhizobacteria and organic matter synthesis, soil humeome functions and priority plant growth.

An intra-soil pulsed sequential-discrete humidification methodology is capable in a fresh water saving, a plants HMs consumption reducing and a soil additives and plant stimulants supplying.

The BGT* methodology was developed as a system of non-standard technical means and technologies for a long-term optimization of the soil geophysical, chemical, water, biological properties, plant phytopathogens protection and crop productivity. A soil equilibrium accounting provides an ecosphere and human health in a circular economy.

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Асоцијација јона у растворима сланог земљишта у пејзажу сланих земљишта

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Сажетак

Проучавање и управљање земљиштем су кључни за примјену кружне економије. Састав материјала у раствору земљишта, као и динамика миграције и акумулације одређени су хемијском равнотежом раствора земљишта. Раствор земљишта садржи асоциране електрично неутралне јонске парове $CaCO_3^0$; $CaSO_4^0$, $MgCO_3^0$, *као и наелектрисане јонске парове* $CaHCO_3^+$, $MgHCO_3^+$, $NaCO_3^-$, $NaSO_4^-$, $CaOH^+$ *и* $MgOH^+$. *Предложен је метод израчунавања хемијске равнотеже раствора земљишта за квантитативну процјену стварних јонских облика у раствору земљишта комплекса кастанозема и хапличног чернозема. Асоцијација јона варира у појединачним земљиштима и слојевима земљишта, повећавајући салинитет раствора земљишта и појачавајући асоцијацију јона. У облику јонских парова у раствору земљишта представљено је: 11,8–53,8%* Ca^{2+}; *9,4–57,3%* Mg^{2+}; *0,7–11,9%* Na^+; *2,2–22,3%* HCO_3^-, *11,8–62,7%* SO_4^{2-}. *У асоцираном облику* CO_3^{2-} *јон учествује до 92,7%. Предложен је коефицијент асоцијације јона као однос слободног облика јона према његовом аналитичком садржају* $\gamma_e = C_{ass} / C_{an}$.

Термодинамичко стање Cd у хапличном чернозему у условима рекултивације земљишта са фосфогипсом у дозама од 10, 20 и 40 t ha^{-1} *је процијењено у односу на хемијску равнотежу у раствору земљишта. На основу алгоритма карбонатно-калцијумске равнотеже (CCE), развијени су компјутерски програми ION–2 и ION–3 за израчунавање стварних равнотежних облика јона у раствору земљишта. Асоцијација јона је израчуната у итеративној процедури на основу података о аналитичкој концентрацији јона у воденом екстракту земљишта, узимајући у обзир материјални биланс јона, линеарну интерполацију константи равнотеже, методу јонских парова, закон очувања почетне концентрације, закон рада маса равнотежног система и константе дисоцијације јонских парова. За карактеризацију везивања јона* Cd^{2+} *у асоцијате у раствору земљишта* *предложен је коефицијент асоцијације јона тешких метала* k_{as}*. Примјена фосфогипса повећава садржај слободног облика* Cd^{2+} *у земљишту за 57,1%.*

Методологија BGT је развијена за примјену кружне економије као систем нестандардних техничких средстава и технологија за дугорочну оптимизацију геофизичких, хемијских, водних, биолошких својстава и продуктивности земљишта.*

Дугогодишњи теренски експеримент у зони кастанозема показао је да методологија мљевења унутар земљишта у слоју 20–45 cm омогућава равномјеран развој ризосфере у цијелом обрађеном профилу земљишта брзином од 2,2 коријена по cm^{-2} *у слоју 0–20 cm и 1,7 коријена по* cm^{-2} *у слоју 20–40 cm. Нови активни погонски дизајн машине за мљевење земљишта обезбјеђује пет пута мањи отпор вуче, 80% већу поузданост и преполовљене трошкове енергије.*

Базирана на BGT методологији, беспилотни систем за пулсно секвенцијално-дискретну земљишну обраду који функционише унутар земљишта обезбјеђује наводњавање земљишта и истовремену испоруку стимуланса и/или других супстанци у земљиште, као и контролу равнотеже раствора земљишта, синергију хумусних супстанци и полимикробних биофилмова, високу брзину биолошких процеса у земљишту, отпорност биљака на фитопатогене и продуктивност земљишта. Методологија система за пулсно секвенцијално-дискретну земљишну обраду може смањити апсорпцију тешких метала код биљака, обезбјеђујући висок ниво контроле уноса земљишних додатака и стимуланса биљака. BGT* методологија осигурава заштиту еко-сфере и људског здравља у оквиру кружне економије.*

Кључне ријечи: раствор земљишта, хемијска равнотежа, јонска асоцијација, програми ION–2 и ION–3, биогеосистемска техника