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7

# Ion Association in Soil Solution as a Cause of Pb Mobility and Availability to Plants

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***Apstract:*** *A soils restoration important condition in different regions of the world is a soil solution correct management. Soil solution chemical equilibrium determines dynamics of its material composition, migration and accumulation of salts. 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* $CaHCO_3^+$, $MgHCO_3^+$, $NaCO_3^-$, $NaSO_4^-$, $CaOH^+$, $MgOH^+$.

*A method was proposed of real ion forms in the soil solution quantitative assessment taking into account the ions association. Depending on the concentration and composition of soil solution, in Kastanozem of the Southern Russia in the south-east part of Rostov region are presented the ionic pairs: 15–45%* $Ca^{2+}$; *16–49%* $Mg^{2+}$; *0.6–8.4%* $Na^+$; *2.2–17.6%* $HCO_3^-$ *16–51%* $SO_4^{2-}$ *and up to 88%* $CO_3^{2-}$.

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*The thermodynamics has been studied of Pb forms in soil solution of Chernozem in the standard conditions and after phosphogypsum application to a 20–40 cm soil layer at the doses of 0, 10, 20, and 40 t ha$^{-1}$. A soluble $Pb^{2+}$ form content in a water extract was calculated by the mathematical chemical-thermodynamic model of ion pairs association in soil solution using the algorithm and computer programs ION–2 and ION–3. A heavy metal (HMs) ions association in the soil solution coefficient $k_{as}$ was proposed for calculation of HMs equilibrium concentration. The model showed that the calculated $Pb^{2+}$ association coefficient is up to 25.0, and a $Pb^{2+}$ ion is presented in the soil solution mostly in a $PbOH^{+}$ and $Pb(OH)_2^0$ form.*

*A chemical soil engineering device for the intra-soil mechanical processing and intra-soil application of amendments and other substances was developed. Intra-soil milling provides a close contact between the soil fine particles and the fine particles of ameliorative substance into a treated soil layer ensuring the HMs passivation, high ameliorative effect, soil fertility and environmental safety.*

*Keywords: Soil Solution, Chemical Equilibrium, Ion Association, Mathematical Modelling, Programs ION–2, ION–3, Chemical Soil Engineering, Intra-soil Amendments and Pollutants Application Device*

## 7.1. Introducton

The soils face considerable vulnerability due to combined effects of climate change and human activities threatening regional ecological security and societal development (Duanyang Xu et al. 2024; Musasa et al. 2024). Improvement, conservation and management of a natural capital are important to achieve sustainable development goals (Brander et al. 2024; Kalinitchenko et al. 2024; Mao and Jiao 2024; Seidl et al. 2024), including a soil, humans and planet health (Kopittke et al. 2024). A soils restoration important condition in different regions of the world is a soil solution correct management (Smith et al. 2021).

Soil solution is most mobile, volatile and active part of the soil. The destruction and synthesis of organic substances, secondary minerals and organomineral compounds occur in the soil solution (Amakor et al. 2013; Hunenberger and Relf, 2011; Minkin and Endovitskii 1978; Opfergelt et al. 2014; Visconti and de Paz 2012; Garcia-Araez et al. 2010).

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

Plugatyr et al. 2011; Chialvo et al. 1995). This balance plays an important role in the genesis and evolution of soil. An important reason causing the soil solution composition and high probability of its excess saturation with CaCO3 are association of ions, formation of ionic complexes (Maiti and Rogers 2011; Lui et al. 2011; Luo et al. 2013; Minkin and Endovitskii 1978; Adams 1971; Debye and E. Hückel 1923; Davies 1962; Bjerrum 1958).

The electrically neutral ion pairs $CaCO_3^0$; $CaSO_4^0$, $MgCO_3^0$, $MgSO_4^0$ and charged ion pairs $CaHCO_3^+$, $MgHCO_3^+$, $NaCO_3^-$, $NaSO_4^-$, $CaOH^+$, $MgOH^+$ are formed in the soil solution. An interaction between associated ions is not as strong as in molecules but diverse (Hunenberger et al. 2011; Stoyanov et al. 2011; Raiteri et al. 2012; Dave and Dikshit 2011; Zhang et al. 2012; Mandzhieva et al. 2014; Tertre et al. 2012; Wright 2007; Davie 1962; Adams 1971; Nicholson and Quirke 2003). A soil carbonate system is not a completely open system. It is under an influence of the biological process, soil – atmosphere gas exchange, partial pressure and seasonal $CO_2$ cycles.

A heavy metals (HMs) increasing content in the ecosphere requires improved methods to recycle the containing HMs wastes as soil amendment. This will reduce their uncontrolled transfer, passivate into the soil, decrease a HMs excessive influence on the carbon stock, and trophic chains providing HMs correct use as plant nutrition microelements (Adriano 2001; Kalinitchenko 2016; Kalinitchenko et al. 2024; Minkina et al. 2012a; 2014; Sparks 2003; Xiong et al. 2014). This is the way to improve the living systems algorithms (Tsvetkov 2016), which will help to ease and overcome a biosphere and technology conflict (Glazko and Glazko 2015) and provide the soil health (Semenov and Sokolov 2016; Kopittke et al. 2024).

Pb is a soil pollutant of a first hazard class, especially in its dissolved form. A Pb total content in Russian soils is not too high, no more than 20 mg kg−1 soil DW. All over the world, a Pb soil content is approximately the same, and much variable. According to the different regulations, a Pb concentration limit depends on the soil and landscape use. The limit value is from 10 to 2000 mg $kg^{-1}$ and higher (Land contamination 2015; McGrath and Loveland 1992; McGahren et al. 2024). HMs are dangerous for landscape and soil in a result of a water mass-transfer over the earth's surface, through the soil, and in the vadose zone (Sposito 2013; Motuzova et al. 2014; Lisetskii et al. 2016, 2018). There are new data on a HMs selective chemical extraction from soil and lithosphere (Favas et al. 2011) causing further developments of the HMs passivation methods. The study of biological, geochemical and other natural barriers for a HMs spread is of a great importance. This will provide a possibility to apply properly the natural HMs spread barriers and form the artificial barriers.

It has been shown that the liming increases a soil pH and reduces a HMs content in plants significantly. In calcareous soils, a Pb2+ ion is weakly transferred to plants, even at a high soil total content (Alloway 1995).

This is a good practice to reduce the soil HM transfer to plants (Land contamination 2015; McGrath and Loveland 1992) and improve the soil remineralization (Tskhovrebov 2012) and compost composition (Belyuchenko and Antonenko 2015). A Pb input into plant depends on a soil carbonates content and a pH value. It is linked to a $Pb^{2+}$ free ions thermodynamic activity and a $Pb^{2+}$ ion bound into associates with other ions degree. It was shown for the soil solution of alkaline calcareous solonetzic soil that a $Pb^{2+}$ ion active concentration (activity) molar fraction does not exceed 0.13%, a $Pb^{2+}$ ion activity in the water extract is only 0.24% (Endovitsky et al. 2009a, 2014; Kalinitchenko et al. 2020, 2021; Okolelova et al. 2022).

Phosphogypsum is a byproduct of the water acid phosphorus fertilizer technology. Its amount is of 150–280 t year−1. Phosphogypsum contains more than 60 chemical elements including Pb (Goswami and Nand, 2015; Pérez-López et al. 2016; McGahren et al. 2024), and is one of ecosphere leading pollutants. A phosphogypsum utilization common practice is open stack. It causes different direct and delayed adverse pollution effects and is hazardous in terms of a further ingress of pollutants' content in the landscape, soil and water. The phosphogypsum stacks are the source of pollutants aeolian transfer and unfavorably affect vast adjacent areas abruptly deteriorating the area's image, habitation and recreation.

In the Russian Federation, the phosphogypsum is produced from the Kovdor deposit apatite. Its environmental quality is much higher than that of phosphogypsum from the Morocco, Florida and many other ores (Lapin and Lyagushkin 2014; Soil Liquid Phase Composition 2001). The Kovdor apatite radioactivity and HMs content are smallest over the world deposits and the fertilizer and phosphogypsum produced from this ore are safe for the soil (Gázquez et al. 2014). A phosphogypsum utilization is fulfilled in solonetz soils (Sukovatov 2009). However, the phosphogypsum utilization is possible in the chernozem too, despite a widely held opinion that the chernozem is the soil which has no morphological and physicochemical signs for the chemical reclamation. A HMs accumulation in the soil after application of phosphogypsum was noted by some authors (Tayibi et al. 2009), but no significant changes were observed compared to natural HMs contents (Mays and Mortvedt 1984; Nayak et al. 2011; Minkin et al. 1992; Endovitsky et al. 2009a). A degree of HMs passivation into the soil is linked to ion activity according ion association in soil solution (Endovitsky et al. 2014, 2017).

The aim of this review was to characterize quantitatively the soil solution thermodynamics in an example of Kastanozem and apply this knowledge in characterizing the dynamics of Pb2+ in a Chernozem Calcic soil solution before and after the phosphogypsum application and reveal the possibility and rate of the phosphogypsum environmentally safe recycling.

## 7.2. Materials and Methods

### 7.2.1. Study area

The study area was the South-West of Russian Federation, Rostov Region and Krasnodar Territory (Kuban). The parent rocks are Carbonate and Carbonate-sulfate loess-like loam and clay. The climate of Rostov Region is arid with annual precipitation of 300–350 mm. The climate of Krasnodar Territory is semiarid with annual precipitation of 450–500 mm. The studied area is situated in the southwest of the Russian Federation.

### 7.2.2. Objects of research

The objects of research were the dry steppe Kastanozem (Rostov Region) and steppe Chernozem (Krasnodar Territory). The parent rocks are Carbonate and Carbonate–sulfate loess-like loam and clay. The climate is continental semiarid.

### 7.2.3. Sampling and analysis of soil

The Kastanozem is moderate thick, medium solonized. Properties: 2.6% of humus, 47.7% of physical clay, 29.5% of clay, 0.15% of $CaCO_3$ (up to 3–10% at a depth of 0.8-1.5 m), pH=7.8, the exchangeable cations: $Ca^{2+}$ – 182 mmol/kg, $Mg^{2+}$ – 65 mmol/kg, $Na^{+}$ – 34 mmol/kg.

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

## 7.2.4. Soil analysis

### 7.2.4.1. Kastanozem

The Solonetz is a Kastanozem soil complex biologically unproductive component. The Solonetz soil cross-section 37 has been laid in an automorphic landscape. The soil was sampled from a cross-section wall down to a depth of 1 m, and deeper by the soil auger with a drill cup of diameter 5 cm. In the soil samples preparation procedure, the soil was crushed and sifted, sieve openings of 2 mm, then mixed with quartz sand in a 1:2 ratio (Mandzhieva et al. 2014; Zhang et al. 2012; Tertre et al. 2012; Soil Sampling and Methods of Analysis 2008). The mixture was charged into a glass tube with inner diameter of 3.4 cm and length of 100 cm. At a bottom of a tube was an outlet for the solution draining off. A direct allocation of soil solution from the soil column with ethyl alcohol was applied (Mandzhieva et al. 2014; Zhang et al. 2012; Tertre et al. 2012; Soil Sampling and Methods of Analysis, 2008). The extraction volume of emitted soil solution from single soil column was 20–60 ml.

The soil solution and soil water extracts properties were determined by the standard analytic methods as follows (Kar and Berenjian 2013; Mari et al. 2014; Opfergelt et al. 2014; Minkin and Endovitskii 1978; Visconti and de Paz 2012; Minkina et al. 2012b; Shtiza and Swennen 2011; Amakor et al. 2013; Garcia-Araez et al. 2010; Soil Sampling and Methods of Analysis 2008). Soil moisture was determined by a thermostat method at 105°C. The soil dry residual was determined by thermostat 105°C method. A pH was measured in thermostat (20±0.2°C) by pH-meter with a glass electrode. The carbonate and bicarbonate ions were titrated directly by 0.01 M hydrochloric acid detecting titration, endpoint on color change of indicators phenolphthalein and methyl orange. A chloride ion was determined by an argentometric method with potassium chromate. The $Ca^{2+}$ and $Mg^{2+}$ total content was determined with a complexometric titration. The $Ca^{2+}$ content was detected complexometrically in another aliquot. The $Mg^{2+}$ content was calculated from the difference between the two determinations described here above. The sulfate was analyzed by a $BaSO_4$ sedimentation method. $Na^{+}$ was analyzed by the flame photometric detection method.

### 7.2.4.2. Chernozem

In Krasnodar Territory, the soil was sampled from the 0–20 and 20–40 cm layers. The soil layer was appointed in a view of the highest need for reclamation of illuvial soil horizon. This methodological approach avoids a waste aeolian

distribution after its utilization in the upper soil layer and excludes an anthropogenic HM excess in this soil layer.

In a soil samples preparation procedure, the soil was crushed and sift through a 2 mm sieve. After sifting, the soil was mechanically mixed with water in ratio 1:5 for 5 min to provide a soluble salts water extraction. The water extraction was made on a paper filter. The extracted solution volume of 20-60 ml was analyzed by the standard methods presented above.

A Pb total soil content was determined by the 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 Pb concentration in soil solution was determined by atomic absorption spectrophotometry (AAS). An X-ray fluorescent method and AAS methods allowed deviation in the soil HMs determination is less than 10–15%.

The phosphogypsum contains many other HMs – Be, B, Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Ag, Cd, Sb, Cs, Ba, Tl, Th, U – which can cause the additional peculiarities in the waste recycling.

### 7.2.5. Model experiment

Phosphogypsum used in the Chernozem amendment experiment in the Krasnodar Territory is a byproduct of phosphorus fertilizer industry – the sulfuric acid technology of Kovdor apatite raw material at the Belorechensk chemical plant. The $Pb^{2+}$ total content in phosphogypsum is 55.98 mg $kg^{-1}$ soil DW. The $Pb^{2+}$ water-soluble form contents are 10.48 mg $kg^{-1}$ soil DW.

At the Belorechensk chemical plant, a typical end-of-pipe waste utilization water version technology is used. The production stages are as follows: a mechanical removal of phosphogypsum after a $P_2O_5$ extraction, a phosphogypsum acid residue neutralization with a lime milk, a pulp transportation to open sludge collectors. These collectors are a source of the surface runoff, soil and ground water environmentally dangerous pollution.

The phosphogypsum was applied to the soil in the doses of 0 (control), 10, 20, and 40 t $ha^{-1}$. The experiment was performed in triplicate. The phosphogypsum application doses were substantiated from the thermodynamic point of view.

The main salt components thermodynamic state in the soil system before and after addition of the neutralized to pH 5.0–5.3 phosphogypsum to the soil was studied in the model experiment and mathematical model.

An adequate synthesis of the model ion thermodynamic state in soil solution is based on the analytical quantity of main ions. In our calculations, the data on water extract were used. A free and associated ion molar fraction is a universal characteristic of the macro-ions and microelement thermodynamic state in soil solution.

A thermodynamic origin of the carbonate calcium equilibrium (CCE) is important in a chemical equilibrium of soil solution. CCE depends on, and, in its turn, influences a chemical composition, the pH, Eh and buffering properties of the soil liquid phase. The dissolution, migration and precipitation of carbonates in the soil profile and landscape, ion exchange processes at the interface of solid and liquid phases depend on the CCE. Relying on the CCE is crucial for a true modeling of HMs state and transfer in the soil (Anisimov et al. 2015; Endovitsky et al. 2009a, 2017).

The carbonate system of water solution is the main system altered by an ion association and a wide diversity of influencing processes. These are the biological process, soil-atmosphere gas exchange and $CO_2$ partial pressure and seasonal cycle.

## 7.3. Results

### 7.3.1. Kastanozem soil solution thermodynamic model

In a given paper, we have formulated a methodological basis of the main ions state in soil solution calculation taking into account the ideas of ions association in soil solution and its quantitative assessment.

An analytical composition of solution rather adequately characterizes a chemical system at a low concentration of main ions in diluted solution. In a real solution, a measure of real salts and separate ions participation in soil chemical reactions is their activity. The analytical composition of the studied Kastanozem soil solution is presented in Table 7.1.

Table 7.1. Composition of Kastanozem steppe solonetz soil solution, mmol-eq $l^{-1}$

*Таб. 7.1. Састав раствора земљишта солонца степског Кастанозема, mmol-eq $l^{-1}$*

| Layer, cm | Soil moisture, % | Solid residual, g $l^{-1}$ | 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 | - | 4.15 | 4.52 | 2.84 |
| 13–21 | 33.7 | 1.67 | 8.22 | 5.11 | 4.35 | 14.95 | - | 6.47 | 10.41 | 7.53 |
| 55–65 | 29.8 | 37.74 | 8.15 | 30.21 | 207.28 | 372.60 | - | 3.12 | 328.52 | 278.45 |
| 80–90 | 20.4 | 31.86 | 7.78 | 29.58 | 120.25 | 358.43 | - | 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 |

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

The concentration of free and associated ion forms was calculated according to the analytical ion concentration. The following methods were used: an iteration to solve the system of algebraic equations of the material balance of ions; a linear interpolation to calculate an equilibrium constant tabular form value.

The basis of calculations is the ionic pairs method (Adams 1971; Davies 1962; Endovoitsky et al. 2009b, 2017; Minkin and Endovitskii 1978; Minkina et al. 2016; Visconti and de Paz 2012; Opfergelt et al. 2014; Kalinichenko et al. 2020, 2024; Kar and Berenjian 2013; Mandzhieva et al. 2014). The ionic pairs method accounts the law of initial concentration preservation and the law of equilibrium system operating masses. The Eqs. (1)–(6) of a main ions material balance are as follows:

$$\sum Ca^{2+} = [Ca^{2+}] + [CaCO_3^0] + [CaHCO_3^+] + [CaSO_4^0]; \quad (1)$$

$$\sum Mg^{2+} = [Mg^{2+}] + [MgCO_3^0] + [MgHCO_3^+] + [MgSO_4^0]; \quad (2)$$

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

$$\sum CO_3^{2-} = [CO_3^{2-}] + [CaCO_3^0] + [MgCO_3^0] + [NaCO_3^-]; \quad (4)$$

$$\sum HCO_3^- = [HCO_3^-] + [CaHCO_3^+] + [MgHCO_3^+]; \quad (5)$$

$$\sum SO_4^{2-} = [SO_4^{2-}] + [CaSO_4^0] + [MgSO_4^0] + [NaSO_4^-]; \quad (6)$$

wherein $[Ca^{2+}]$, $[Mg^{2+}]$, and other is an equilibrium concentration of the ion free form, $[CaCO_3^0]$, $[MgCO_3^0]$, and other is an equilibrium concentration of the ion associated form (ion pair).

The next equations group are the ionic pair dissociation concentration constants according the operating masses law. Eqs. (7)–(9) are grouped by cations:

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

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

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

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

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

An equilibrium concentration of ionic pairs in Eqs. (1)–(6) were replaced with their values according to the relevant dissociation constants (7)–(9). The transformed ion material balance equations system is as follows, Eqs. (10)–(15):

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

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

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

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

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

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

Dissociation concentration constants in Eqs. (10)–(15) were recalculated according to the Davies equation for constants in Eq. (16) (Davies 1962):

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

wherein *K* – is an ionic pair concentration dissociation constant; $K^0$ – is a corresponding thermodynamic constant; A – is Debye-Huckel constant 0,5042 at

20°C; $\Delta z^2$ – is the algebraic sum of squares of a particle's charge in the dissociation constant Equation; I – is anionic strength of solution.

Thermodynamic dissociation constants values were as follows:

$pK^0_{CaCO_3}$=3.2; $pK^0_{CaHCO_3}$=1.26; $pK^0_{CaSO_4}$=2.31;

$pK^0_{MgCO_3}$=3.4; $pK^0_{MgHCO_3}$=1.16; $pK^0_{MgSO_4}$=2.36;

$pK^0_{NaCO_3}$=1.27; $pK^0_{NaSO_4}$=0.72.

The solution formal ionic strength was calculated using the analytical ion concentration data via Eq. (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 pK value rather adequately follows from the Eq. (16). At the ionic force of 0.1 mol $l^{-1}$, an error is less than 3%, and at 0.5 mol $l^{-1}$ – less than 8%.

The ion free form equilibrium concentrations were used as unknown values $X_{Ca}$, $X_{Mg}$, and other. The ion forms total value was used as the analytical concentration. The system was obtained of six equations with the six unknowns.

To find a free ion equilibrium concentration, the iteration procedure was used. An ion pair equilibrium concentration was determined via the Eqs. (7)–(9) for dissociation constants.

Taking into account an equilibrium concentration of all ion forms, the solution effective ionic force was calculated in Eq. (18):

$$I^{*}=0.5\left\{4\left[Ca^{2+}\right]+4\left[Mg^{2+}\right]+\left[Na^{+}\right]+4\left[CO_3^{2-}\right]+\left[HCO_3^{-}\right]+4\left[SO_4^{2-}\right]+ +\left[CaHCO_3^{+}\right]+\left[MgHCO_3^{+}\right]+\left[NaCO_3^{-}\right]+\left[NaSO_4^{-}\right]+\left[Cl^{-}\right)\right\}, \text{mol l}^{-} \quad (18)$$

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

Upon the soil solution ion forms calculation iterative procedure, the ion free form quantity was determined.

Ion association coefficient $\gamma_e$ was proposed as a ratio of ion free form to its analytical content, Eq. (19):

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

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

Software products ION–2 and ION–3 developed by the authors (Endovoitsky et al. 2009b; Minkina et al. 2016) were used to perform calculations (Afzal and Yasin 2002; Kalinichenko et al. 2019; 2020, 2021; Okolelova et al. 2022; Mandzhieva et al. 2014; Minkin and Endovitskii 1978; Visconti and de Paz 2012).

### 7.3.2. $Pb^{2+}$ thermodynamics in Chernozem methodology

Belorechensk chemical plant by-product – phosphogypsum – recycling has been fulfilled to a layer 20-40 cm of Chernozem 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 the soil solution. In the soil solution are formed associate and complex HMs ions. The model ION–3 has been applied to reveal a $Pb^{2=}$ ion thermodynamic state in the Chernozem of Krasnodar Territory. With the free anion and ion pair equilibrium concentrations [$CO_3^{2-}$], [$HCO_3^-$], [$SO_4^{2-}$], [$Cl^-$] and [$OH^-$], a $Pb^{2+}$ soluble form content in water extract was calculated from the mass balance Eq. (20) (Endovitsky et al. 2009b; Minkina et al. 2016):

$$Pb^{2+} = \left[Pb^{2+}\right]\left(1+\frac{\left[CO_3^{2-}\right]}{K_{PbCO_3}}+\frac{\left[CO_3^{2-}\right]^2}{K_{Pb(CO_3)_2}}+\frac{\left[HCO_3^-\right]}{K_{PbHCO_3}}+\frac{\left[SO_4^{2-}\right]}{K_{PbSO_4}}+\frac{\left[Cl^-\right]}{K_{PbCl}}+\frac{\left[OH^-\right]}{K_{PbOH}}+\frac{\left[OH^-\right]^2}{K_{Pb(OH)_2}}\right) \quad (20)$$

The Eq. 20 is written out of the main equation system (10)–(15) frame because the Pb soil content and Pb concentration in soil solution is much less compared to the macro-ions content. Consequently, the Pb contribution to the formal and effective soil solution ionic force value is insignificant. The less number of equations in the system provides the better possibilities for a successful iteration. The Eq (21) gave a possibility to calculate the mobile fraction of free and associated $Pb^{2+}$ forms in the studied water extracts from individual soils. This allows a higher level approximation of the HMs behavior in the soil in the local pedogenesis conditions.

A set of associates was selected considering for only the inorganic part of soil solution composition determined from the data on the water soil extracts. The $PbCO_3^0$, $PbCO_3^0$, $Pb(CO_3)_2^{2-}$ and $PbHCO_3^+$ associate thermodynamic stability constants were chosen according to Sposito (1989) $pK^0(PbCO_3)$=6.49, $pK^0(Pb(CO_3)_2)$=9.30, $pK^0(PbHCO_3)$=3.22, $pK^0(PbSO_4)$=2.62, $pK^0(PbCl)$=1.62, $pK^0(PbOH)$=7.52, $pK^0(Pb(OH)_2)$=10.54.

The unstable associates were not considered because their influence on the ion association process and thus on the calculation result is insignificant.

The selected associates set considers only a soil solution inorganic part. In soil solution, the soil organic matter forms the protonic complexes with the salt cations, but these complexes play a significant role only at a high soil organic matter content and under the special conditions. For soil considered in this paper, the organic matter and salt cations complexes are insignificant compared to phenomena in a soil solution mineral part. Should the presence of organic complexes in soil solution be considered in Eq. (20), a calculated concentration of the $Pb^{2+}$ associates and complexes would become higher, and therefore the environmentally safe dose of phosphogypsum can be higher too. It is an additional reasonable guarantee of a proposed model reliability margin.

In the soil, a potentially hazardous HM can be considered as a microelement, and its thermodynamic state in the soil solution and water extract can be characterized using an association coefficient of microelement $k_{as(ME)}$ (Endovitsky et al. 2009a, 2017; Minkina et al. 2016). Association coefficient indicates a degree of the potentially hazardous HM binding into associates and complexes with the main ions of soil solution. A quantity of microelement is less than macro-elements, thus there is no need to include the equation for microelement into the equation system for macro-elements.

Given the $k_{as(ME)}$, a HM model final version in Eq. (20) can be written as follows:

$$C_{ME} = \left(1 + k_{asME}\right)\left[C_{ME}\right], \tag{21}$$

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

The $Pb^{2+}$ association coefficient was calculated according to the Eq. (21) by transformation of the Eq. (20) to the Eq. (22) as follows:

$$k_{asPb} = \frac{\left[CO_3^{2-}\right]}{K_{PbCO_3}} + \frac{\left[CO_3^{2-}\right]^2}{K_{Pb(CO_3)_2}} + \frac{\left[HCO_3^{-}\right]}{K_{PbHCO_3}} + \frac{\left[SO_4^{2-}\right]}{K_{PbSO_4}} + \frac{\left[Cl^{-}\right]}{K_{PbCl}} + \frac{\left[OH^{-}\right]}{K_{PbOH}} + \frac{\left[OH^{-}\right]^2}{K_{Pb(OH)_2}} \tag{22}$$

The term “coefficient of association $k_{as}$” is a development of electrolyte and surface waters thermodynamic concepts on the *in vitro* and *in situ* experiments data basis. In the Eq. (22), the $k_{as(ME)}$ is a constant for a given soil solution. It depends on the equilibrium concentrations of major ions, pH value, and trace element concentration instability constant of associates and complexes with the major anions. It does not depend on the trace element total concentration. This is because the macro-ions prematurely determine the value of ionic strength of

soil solution, and the trace element relatively low concentration has no effect on the ionic strength value.

Using the ion association coefficients, a free and bound microelement (HM) ion molar fraction can be calculated via Eqs. 23 as follows:

$$v_{free} = 1/(1 + k_{asME})\cdot 100, \%,$$

$$v_{bound} = 100 - v_{free}. \quad (23)$$

The data on the macro-ions and Pb in water extraction content were used for calculation according the Eq. (22).

A calculation of a Pb equilibrium concentration in water extract from the Chernozems was made for the phosphogypsum doses of 0 (control), 10, 20, and 40 t/ha using Eq. (20) in a chemical equivalent form on the basis of Pb water soluble forms content (Table 1), considering the soil density and soil to water ratio. As the Eq. (20) left part, a $Pb^{2+}$ total concentration in water extract in the initial soil and after the phosphogypsum application was used. As the Eq. (20) right part, the equilibrium concentrations of macro-ions from Eq. (10)–(15), and thermodynamic stability constants of the Pb associates were used, which are given here above after the Eq. (20) essence discussion.

A main ion forms in the soil solution of Chernozem calculation (Table 7.2) shows that the cations are bound into associates to a significantly lower degree than in the Kastanozem calcareous solonetz soil (Batukaev et al. 2014). In the Chernozem, the molar fractions of calcium and magnesium associates are similar: 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 the Kastanozem calcareous solonetz soil.

The Chernozem aqueous extract is of a calcium hydro-chemical composition Ca > Mg > Na, and remains the same before and after the phosphogypsum application (Table 1). A soil solution composition of original soil is calcium chloride. After an addition of phosphogypsum, a soil solution composition becomes calcium sulfate. Based on an aqueous extract, it can be concluded that a composition of soil solution after application of phosphogypsum has become of sulfate class. After a neutralized phosphogypsum application to the soil, a water extract pH decreases by 0.23–0.26 units as a phosphogypsum application dose increase.

The soil solution thermodynamic properties depend on a main ions association. In a result of the ion association, the ion free forms concentration and solution ionic strength ($\mu$) significantly decreased. An activity coefficient of the single-charged ($y'$) and double-charged ($y''$) ions increases. As a result, a stability constant of associates and complexes in the soil solution also changes. An anions

association degree in Chernozem is significantly higher than the association degree of cations. In particular, an associated carbonate ion molar fraction is 27.7–57.7% (in Kastanozem solonetz 31.0–38.6%), and that of associated sulfate ion is 6.3–12.9% (in Kastanozem solonetz 5.6–7.9%). Thus, the Chernozem and Kastanozem solonetz are similar in terms of carbonate and sulfate associates.

Table 7.2. Pb total and water-soluble forms content in soil, mg $kg^{-1}$
*Таб. 7.2. Укупан садржај и садржај водорастворљивих форми Pb у земљишту, mg $kg^{-1}$*

| Experiment option | Pb total content | Pb water-soluble form content | Pb water-soluble to total weight fraction contents, % |
|---|---|---|---|
| Control (no phosphogypsum) | 20.0 | 0.8960 | 4.48 |
| After phosphogypsum application of 10 t $ha^{-1}$ | 20.2127 | 0.9356 | 4.63 |
| After phosphogypsum application of 20 t $ha^{-1}$ | 20.4254 | 0.9752 | 4.77 |
| After phosphogypsum application of 40 t $ha^{-1}$ | 20.8509 | 1.0544 | 5.06 |

A $Ca^{2+}$ and $Mg^{2+}$ associates molar fraction in the soil solution of Chernozem increased to 21.8–20.6% ($Ca^{2+}$) and 18.5–22.4% ($Mg^{2+}$) with increasing phosphogypsum dose. A carbonate associates fraction increased to 64.7–78.2%, and this of sulfate associates increased to 22.5–29.2%. Despite the main ions concentration in the water extract is not too high, it is enough to influence the soil solution thermodynamics and to alter the ionic strength of soil solution ($\mu$) causing the main ions association. For example, the $K(PbCO_3)$ values at the different phosphogypsum doses were: 0 t $ha^{-1}$ $4{,}7292 \cdot 10^{-7}$, 10 t $ha^{-1}$ $6{,}7929 \cdot 10^{-7}$, 20 t $ha^{-1}$ $7{,}5404 \cdot 10^{-7}$, 40 t $ha^{-1}$ $8{,}7857 \cdot 10^{-7}$ (Table 7.3).

Table 7.3. Equilibrium concentrations, cmol (+/–) $kg^{-1}$ (above), and molar fractions, %, (below), of the free forms of main ions in soil solutions

*Таб. 7.3. Равнотежне концентрације, cmol (+/–) $kg^{-1}$ (горе), и моларне фракције, % (доље), слободних форми главних јона у растворима земљишта*

| Experiment option | Effective ionic strength, $\mu^*$ | Coefficient of the ions activity $y'/y''$ | $[Ca^{2+}]$ $\cdot 10^{-1}$ | $[Mg^{2+}]$ $\cdot 10^{-1}$ | $[Na^{+}]$ $\cdot 10^{-1}$ | $[SO_4^{2-}]$ $\cdot 10^{-1}$ | $[Cl^{-}]$ $\cdot 10^{-1}$ | $[CO_3^{2-}]_A$, $\cdot 10^{-4}$ | $[HCO_3^{-}]_A$, $\cdot 10^{-2}$ | $[OH^{-}]$, $\cdot 10^{-5}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Control (no phosphogypsum) | 0.001814 | 0.9537 | 0.343 | 0.0986 | 0.01199 | 0.0806 | 0.30 | | | |
| | | 0.8272 | 98.00 | 98.60 | 99.92 | 93.72 | 100.00 | 72.32 | 99.39 | |
| After phosphogypsum application of 10 t $ha^{-1}$ | 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 phosphogypsum application of 20 t $ha^{-1}$ | 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 phosphogypsum application of 40 t $ha^{-1}$ | 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 | |

The free anion and ion pair equilibrium concentrations $[CO_3^{2-}]$, $[HCO_3^-]$, $[SO_4^{2-}]$, $[Cl^-]$ and $[OH^-]$, the $Pb^{2+}$ soluble form content in water extract calculated from the mass balance Eq. (21) (Endovitsky et al. 2009b; Minkina et al. 2016) data are presented below in Eqs. (24)–(27).

Water extract before phosphogypsum application:

$$8.648\cdot10^{-5}=[Pb^{2+}](1+10^7[CO_3^{2-}]/4.7292+10^{10}[CO_3^{2-}]^2/7.3247+10^4[HCO_3^-]/7.2848 +10^3[SO_4^{2-}]/3.5060+10^2[Cl^-]/2.9001+10^8[OH^-]/3.6509+10^{11}[OH^-]^2/3.8332), \quad (24)$$

After the application of 10 t/ha phosphogypsum:

$$9.034\cdot10^{-5}=[Pb^{2+}](1+10^7[CO_3^{2-}]/6.7929+10^{10}[CO_3^{2-}]^2/10.5211+10^4[HCO_3^-]/8.7308 +10^3[SO_4^{2-}]/5.0359+10^2[Cl^-]/3.4758+10^8[OH^-]/4.3755+10^{11}[OH^-]^2/5.0293), \quad (25)$$

After the application of 20 t/ha phosphogypsum:

$$9.420\cdot10^{-5}=[Pb^{2+}](1+10^7[CO_3^{2-}]/7.5404+10^{10}[CO_3^{2-}]^2/11.678+10^4[HCO_3^-]/9.1986 +10^3[SO_4^{2-}]/5.5900+10^2[Cl^-]/3.6620+10^8[OH^-]/4.6100+10^{11}[OH^-]^2/5.4387), \quad (26)$$

After the application of 40 t/ha phosphogypsum:

$$10.192\cdot10^{-5}=[Pb^{2+}](1+10^7[CO_3^{2-}]/8.7857+10^{10}[CO_3^{2-}]^2/13.6074$$

$$+10^4[HCO_3^-]/9.9291+10^3[SO_4^{2-}]/6.5132+10^2[Cl^-]/$$

$$/3.9529+10^8[OH^-]/4.9761+10^{11}[OH^-]^2/6.1003). \quad (27)$$

A free ion form concentration decreases compared to an ideal low concentrated water solution. Thus, the calculated activity coefficients of singly-charged (*y'*) and double-charged (*y"*) ions are less than 1.0. The calculated stability constants of associates and complexes in the soil solution have changed in its turn compared to their thermodynamic values. In an initial carbonate-free slightly alkaline chernozem soil solution a quantity of cations bounded into associated forms is not high compared to saline soil, and the $Ca^{2+}$ and $Mg^{2+}$ associates calculated molar fractions are less than 10%.

An associates molar fraction in the soil solution increases proportionally to a phosphogypsum dose value up to 25% for $Ca^{2+}$ and 20% for $Mg^{2+}$. An associated anion fraction content increases in the same way for carbonate up to 65%, and for sulfate up to 25%.

After application of phosphogypsum to the soil, a $Pb^{2+}$ total and water-soluble forms content increased according to a dose with a maximum value at a dose of 40 t $ha^{-1}$. An average $Pb^{2+}$ increase was from 4.2% to 4.9%.

The calculated $Pb^{2+}$association coefficient is up to 25.0. A bounded $Pb^{2+}$ ion major part is in a $PbOH^{+}$ and $Pb(OH)_2^{0}$ hydroxo complexes form. A $Pb^{2+}$ ion equilibrium concentration and molar fraction in soil solution calculation showed a high degree $Pb^{2+}$ binding into associates and hydroxo complexes in the original soils. Because of the ion association and under the effect of soil solution ionic strength, a $Pb^{2+}$ ion activity in the initial solution was lower than its equilibrium concentration by 17.7% in Chernozem.

A carbonate associates $PbCO_3^{0}$ and $Pb(CO_3)_2^{2-}$ and hydrocarbonate associate $PbHCO_3^{+}$ quantity is lower than a hydroxo complexes content by 10–15 times. A $Pb^{2+}$ ion activity in the initial soil solution is lower than its equilibrium concentration by 18.0%. At a phosphogypsum dose 40 t $ha^{-}$, a $Pb^{2+}$ ion association coefficient decreases approximately by 2.0 times comparing to the initial soil, and a $Pb^{2+}$ free ion activity increases by 60.0%. The hydroxide-complexes molar fraction decreases for 4.0%, carbonate associates molar fraction decrease for 5.0%, and sulfate associates molar fraction increase for 4.5%. The model shows a dangerous increase of $Pb^{2+}$ ion activity in the soil solution after a phosphogypsum apply up to 90.0% and more of its total concentration. Nevertheless, an added with phosphogypsum produced from high environment class low contaminated Kovdor apatite ore $Pb^{2+}$ soil content is much less compared to a strictest in the world Russian limit and is of no hazard for the soil ecosystem.

## 7.4. Discussion

### 7.4.1. Ion association thermodynamic model

Ion association in the Kastanosem soil solution was calculated in a procedure specified in equations (7–18) using the data of the Table 7.1.

Association coefficient $\gamma_e$ was calculated according to ion species as a ratio of calculated amount of ion in a free form to its analytical content in the Table 7.3 via Eq. (19). The calculation results are presented in the Table 7.4.

Ion association varies. The variability observed in individual soils and layers. Increasing soil solution salinity amplifies the association of ions (Batukaev et al. 2014).

A real equilibrium concentration of various ion forms in soil solution was calculated. Depending on the soil solution concentration and composition, in a form of ionic pairs are: 15–45% of $Ca^{2+}$; 16–49% of $Mg^{2+}$; 0.6–8.4% of $Na^{+}$; 2.2–17.6% of $HCO_3^{-}$, 16–51% of $SO_4^{2-}$. The $CO_3^{2-}$ ion is most associated. Its share in a carbonate associated ion form makes up to 88%.

Table 7.4a. Ions form in Kastanosem steppe solonetz soil solution, % of total ion content
*Таб. 7.4а. Форме јона у раствору земљишта солонца степског Кастанозема, % од укупног садржаја јона*

Cations/*катјони*

| Depth, cm | *I* | *pH* | Calcium | | | | Magnesium | | | | Sodium | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | $[Ca^{2+}]$ | $[CaCO_3^0]$ | $[CaHCO_3^+]$ | $[CaSO_4^0]$ | $[Mg^{2+}]$ | $[MgCO_3^0]$ | $[MgHCO_3^+]$ | $[MgSO_4^0]$ | $[Na^+]$ | $[NaCO_3^-]$ | $[NaSO_4^-]$ |
| 0–12 | 0.016 | 7.74 | 84.08 | - | 3.81 | 12.11 | 83.50 | - | 3.00 | 13.50 | 99.40 | - | 0.60 |
| 13–21 | 0.035 | 8.22 | 77.73 | - | 4.59 | 17.68 | 76.80 | - | 3.60 | 19.60 | 98.88 | - | 1,12 |
| 55–65 | 0.893 | 8.15 | 54.47 | - | 0.59 | 44.94 | 51.70 | - | 0.44 | 47.86 | 91.56 | - | 8.44 |
| 80–90 | 0.723 | 7.18 | 54.67 | - | 0.48 | 44.85 | 51.88 | - | 0.37 | 47.75 | 91.65 | - | 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 |

Table 7.4b. Ions form in Kastanosem steppe solonetz soil solution, % of total ion content

*Таб. 7.4б. Форме јона у раствору земљишта солонца степског Кастанозема, % од укупног садржаја јона*

Anions/*анјони*

| Depth, cm | *I* | *pH* | Sulphates | | | | Hydrocarbons | | | Carbonates | | | Chlorides |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | $[SO_4^{2-}]$ | $[CaSO_4^0]$ | $[MgSO_4^0]$ | $[NaSO_4^-]$ | $[HCO_3^-]$ | $[CaHCO_3^+]$ | $[MgHCO_3^+]$ | $[CO_3^{2-}]$ | $[CaCO_3^0]$ | $[MgCO_3^0]$ | $[NaCO_3^-]$ | $Cl^-$ |
| 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 | I.92 | 11.56 | 12.51 | 5.69 | 68.24 | 13.56 | 100 |

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

Following the fulfilled soil solution thermodynamics theoretical generalizations, it is possible to claim that accounting ions association and activity and calculated soil solution saturation degree with chemicals provides a new understanding of chemical compounds migration and accumulation in the soils and landscapes, especially concerning the $CaCO_3$ forms.

In recent years, the modern nonthermodynamic techniques are used for an ion pairs association in nanotubes modeling (Izgorodina 2011; Izgorodina et al. 2014; Luo et al. 2013; Zhang 2012; Nicholson and Quirke 2003). An ion pair association in supercritical water (Sushkova et al. 2013; Chialvo et al. 1995) and in other conditions (Saito 2013) are of a scientific interest. The computer models of ion pairs formation in electrolyte, ion pairs 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) are developed. The imporved methods of direct ion pair study are on an agenda (Westerlund et al. 2011; Besser-Rogac et al. 2011; Wang et al. 2014; Shatti et al. 2011). Of a great importance are the possibilities of carbon nanotubes as a factor of the soil minerals and soil solution interaction, cation exchange on montmorillonite, nutrition, soil colloids stability, biodiversity concern, and soil monitoring research (Brande et al. 2024; Duanyang Xu et al. 2024; Kalinitchenko et al. 2024; Kopittke et al. 2024; Minkina et al. 2012a; Musasa et al. 2024; Tertre et al. 2011; Zhang et al. 2012; Wiatrak 2014; Jiang et al. 2012; Saito 2013; Seidl et al. 2024; Smith et al. 2021; Sushkova et al. 2013).

Carbonate calcium equilibrium study is of a high importance providing a new glance on an ions association in water solution phenomenon and a modeling of heavy metals state and transfer in the soil (Kalinichenko 2012; Kalinichenko et al. 2019, 2020, 2024; Mandzhieva et al. 2014). The obtained data and models confirm the basic tenets of the ions association in solution theory and justify the thermodynamic model of the soil macro-processes. These are the soil solution transfer, solid soil phase saturation, metamofization and accumulation of salts in the soil (Minkin and Endovitskii 1978; Visconti and de Paz 2012; Adams 1971; Debye and Hückel 1923; Davies 1962; Bjerrum,1958).

There is an information on the soil moisture sensor systems drawbacks (El Marazky et al. 2011). This corresponds to a problem of a true soil solution content determination and shows the importance of modelling. Thus, there is a perspective of a different approachs to the study of the soil productive reciprocity (Visconti and de Paz 2012). Computer programs ION–2 and ION–3

are available for different soil and environment conditions to overcome a methodological drawback of soil direct sensing and speed up the process of ion association calculation (Minkin and Endovitskii 1978; Endovitsky et al. 2009b; Garcia-Araez et al. 2010; Minkina et al. 2016).

Using an idea of ions association in the soil solution in rather accurately outlined solution ionic strength range and ionic composition framework, there is an opportunity to obtain a new glance on the processes in soil solution, soil and landscape (Afzal and Yasin 2002; Visconti and de Paz 2012; Okolelova et al. 2022). This helps to consider quantitatively the options of equilibria models for the soil *in vivo*, undisturbed by procedures of physical modeling.

Obtained results show a calcium carbonate behavior in soil solution taking into account ion association and not accounting this phenomenon fundamental difference. The ions association reveals that a thermodynamic precondition of $CaCO_3$ sedimentation in saline soil occurs at a much higher concentration of ions $Ca^{2+}$ and $CO_3^{2-}$ in the soil solution than it has been considered previously. Therefore, an earlier underestimated probability of carbonates high mobility in the soil and landscape is significant.

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 modelling of soil solution system proposed is not high instrumentally based, but nevertherless 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 complitely corresponds to the real soil – soil slution 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 dimention profiles. The layers of section and individual sections are interacting. The key problem of future research is not only to discribe 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 permeats 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 permit to get new understanding of water-salt pransfer, geochemical bariers 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.

### 7.4.2. $Pb^{2+}$ thermodynamics in Chernozem

The $CaCO_3$ deposition or dissolution is caused by a $Ca^{2+}$, $HCO_3^-$ and $CO_3^{2-}$ receipt or removal from the solution. This is why a carbonate equilibrium varies and shifts. A shift is combined with the soil solution ionic composition peculiarities. The processes mentioned determine the various carbonate form type migration and accumulation throughout the soil profile, lateral salt transfer and soil material sink to the vadose zone.

Along with the main ions, the soils contain different microelements, including HMs, which are potentially hazardous for human health, and a mobility of HMs is important. For the studied soil, a $Pb^{2+}$ total background content (Clark) is 20 mg $kg^{-1}$ soil DW. A $Pb^{2+}$ total content in the soil under agriculture varies from 0.1 to 20 mg $kg^{-1}$. According available data, a higher $Pb^{2+}$ total content degree has been taken to calculations fulfilled on a proposed algorithm and program basis (Table 7.2). The results of calculation show that $Pb^{2+}$ readily reacts with the main ions of soil solutions ($CO_3^{2-}$, $SO_4^{2-}$, $OH^-$). The hardly soluble carbonates, sulfates, and hydroxides are forming even at the comparatively low ionic strength of water extract from the not saline soil.

The total and water-soluble forms content of $Pb^{2+}$ in the original soil have been taken into the calculations in an accord to reported data on the Chernozem properties in different geographical locations corresponding to the reported variation ranges limit. The calculations performed on this basis are both representational and environmentally valid for the phosphogypsum application doses from 10 to 40 t $ha^{-1}$.

Ion association in the soil solution of Chernozem reduces $Pb^{2+}$ activity compared to its analytical water soluble form content. From an environmental point of view, there is a good reason to apply phosphogypsum containing $Pb^{2+}$ to the soil. Reduced $Pb^{2+}$ chemical activity is a cause of its reduced bioavailability. However, an alarming reason is that at a high phosphogypsum dose a $Pb^{2+}$ ion association coefficient decreases, and its free ion activity increases. A danger of a $Pb^{2+}$ comparatively high mobility is to be concerned as a motive of a phosphogypsum dose applied to soil limitation. It is important to mention – the studied soil has a low initial Pb contamination, and phosphogypsum produced from high quality

Kovdor ore contains a relatively low quantity of Pb. Consequently, the concern on the phosphogypsum dose limit in this case is only theoretical. The Pb water soluble form content, moreover – the content of free $Pb^{2+}$, according our data is many times less than the US EPA hazard standard (Rules and Regulations 2001; McGahren et al. 2024).

However, if the soil and/or phosphogypsum contamination with Pb is high, a $Pb^{2+}$ higher activity in soil after phosphogypsum applying concern becomes real. It is a reason to re-evaluate the encouraging reports about high doses of phosphogypsum as fully secure for the environment (Mays and Mortvedt 1984; Sukovatov 2009).

Water extract data are considered as less representative compared to direct soil solution extraction data because the water extraction distorted the soil solution composition. However, in a case of dry soil the water extract is the only method to study a dry soil salt content because the soil solution extraction is impossible.

An insignificant soil pH decrease abruptly increases a lead carbonates and hydroxides solubility. At a pH 6.5, the $Pb^{2+}$ hydroxide solubility in pure water solutions is about 100 μg $l^{-1}$. Considering the effects of a $Pb^{2+}$ state in the soil solution, including the hydrolysis, complexation with organic matter, adsorption of suspended soil particles, and other processes, it can be stated that a $Pb^{2+}$ compounds solubility *in situ* can be higher than that identified in the proposed models. Consequently, the model can be further specified in order to improve its approximating capacity. For this purpose, we took into account a $Pb^{2+}$ solubility dependence on a soil pH value and neutralized phosphogypsum pH (5.0–5.3) to assess a considered model approximation ability. A comparatively high $Pb^{2+}$ water-soluble form weight fraction 4.48% of its total content in the Chernozem was taken into account in calculations.

One more scientific position for discussion is the soil salinity. The higher is the soil salinity, the more in the soil solution is a comparative quantity of associated ions of different kind (Endovitsky et al. 2017). In the high salinity soil, a probable $Pb^{2+}$ forms dynamics in the soil solution is in contrast to the not saline soil. A phosphogypsum approximate dose for the saline soil can be higher than that for the low salinity soil. This approach can be extended to the low saline soil at the low moisture. In this case, the soil solution ionic forth is comparable to the saline soil, consequently, the phosphogypsum approximate dose can be higher too.

A generalization of the soil solution properties has some special reservations. In particular, a solution extracted from the soil by a direct displacement or any other pressure method does not completely correspond a soil liquid phase composition. An extracted solution loses its specific interactions with an original

soil system during an extraction procedure, hence, bears only a partial information about the properties of a native soil solution. As far as both methods – the water extract and direct soil solution extract – have their internal special disadvantages, it is more correct to take into account a difference between water extract and direct soil solution displacement data not only in an analytical procedure framework, but also in the modelling. An appropriate from the point of view of an easy execution and in a focus of a further apply in modeling is believed a method of soil paste. Therefore, a combined analytical-computational soil liquid phase model, not completely empirical and mostly based on a solution equilibrium chemical thermodynamic concept fundamentals, is able to solve the soil science problems in a water – soil solid phase interaction field, which have no direct experimental solution.

The studied system is diluted because the soil is not saline and a water-soil ratio of 5:1 was used for water extract procedure. We used this kind model system on purpose because this approach shows the fact that even at a high degree of dilution a Pb passivation in soil is noticeable, an ion association origin is manifested, and a biogeochemical barrier for HMs is high enough. At a higher soil solution ionic force, an ion association and ion complexes formation rate, especially taking into account the microelements and HMs, rapidly increases. It is important for a proper understanding of mixing the soil with a substance applied to soil and a soil water regime as the drivers of soil pollution. Dispersing the soil as well as dispersing the substance applied to the soil allow increased volume and internal interface of a mixed system, improve a HMs passivation in a 20-40 cm soil layer and a soil capacity to accept and environmentally safely process and transform a waste material (Kalinichenko 2015). This will help stabilize the climate owing an improved plant development (Kalinitchenko et al. 2024). An agronomy effect is most prolonged if a soil amendment is applied to a deeper 30-50 cm soil layer (Klymenko 2015).

A high soil moisture is a cause of dangerously high rate HMs delivery to the plant tissue (Kwasniewska 2014). The soil deep layer mechanical processing improves soil aggregation (Shein et al. 2016, 2017) and provides higher rate soil hydraulic conductivity (Shein et al. 2015). In a result, the soil water content is relative decreased ensuring a possibility to reduce a HMs mobility and therefore their bioavailability reduces in its turn (Anisimov et al. 2015; Kalinitchenko et al. 2020). At the same HMs total content and rather low high soil moisture, a biogeochemical barrier “soil–plant” is reliable, and a HMs quantity in plants is low (Minkina et al. 2012a). A HMs passivation into the soil can be radically increased in a framework of a new world water strategy (Kalinitchenko and Rykhlik 2019; Kalinitchenko et al. 2023), which provides a relatively low soil moisture content enhancing the ion association biogeochemical role (Batukaev et al. 2016) and reducing the HMs

solubility, mobility and bioavailability. The processes disclosed are important for a proper understanding of the matter dynamics in the ecosphere – the lateral transfer of substances from soil to vadose zone, landscapes and watersheds. A developed ion association approach as a driver of migration, metamorphism and accumulation of salts has a broad perspective to use not only at a level of the soil profile. The environmentally safe waste recycling becomes possible.

### 7.4.3. Substances transfer in soil and landscape given the association of ions in soil solution

HMs ions association and complexation reduce HMs activity and mobility in the soil, and their bioavailability to plants becomes low. The soil solution composition dynamics is related to the soil moisture. Not only continuous mass transfer fluxes, but also the origin and function of solution in discreet micro-basins in a rather dry soil continuum is to be revealed. This driving force of a Pb and other HMs transfer in the soil and landscape is to be taken into account because a soil solution concentration into discreet soil micro-basins is rather low compared to the soil in general. Ion association in a discreet soil micro-basin determines high level HMs mobility preconditions at a next soil humidification stage (Batukaev et al. 2016; Kalinitchenko et al. 2020). This process needs for additional future developments to reduce the influence of pollutant on plants.

Phosphogypsum recycling in the 20–40 cm soil layer allows: a pollutant utilizing, a soil fertility improving, a landscape environmental stability ensuring. $Pb^{2+}$ added to the soil in a form of phosphogypsum produced from high environment class low contaminated Kovdor apatite ore in doses up to 40 t $ha^{-1}$ is of no hazard to the soil and environment. Doses higher than 40 t $ha^{-1}$ can be environmentally sound being applied to Chernosem located on a plain watershed. In other cases, phosphogypsum doses should be applied considering the soil and recycling material properties, soil processing technology, watershed form and local hydrological regime.

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

Soil solution composition dynamics is related to a soil and aeration zone moisture. According to the simulations fulfilled above, a mass transfer in the soil

and vadose zone is noticeable at a low soil moisture content. Thus, a substance transfer in a dispersed system should be considered not only as an unbroken mass transfer flux, but also taking into account a soil solution micro-basins formation (Batukaev et al. 2016; Kalinitchenko et al. 2020). As the soil humidity reduces, an actual water and dissolved substances transfer zone becomes fragmented.

Soil solution flux discontinuity driving forces are a different water thermodynamic potential in individual capillaries and on internal soil interfaces, and a water surface curvature variation. At a subsequent soil wetting, a transfer agent does not pass to a dissolution stage, but quickly enters into a geochemical transfer process with a first portion of additional water. Micro-basin formation, on the one hand, is useful as a source of plant nutrients, but, on the other hand, it is dangerous in terms of useful substances easy loss from the soil and vice versa – an undesirable substances receipt.

Most soils in the world are under the influence of anthropogenic evolution – agriculture and environmental impact. A new danger in relation to the soil and aeration zone calcium-carbonate system is a high rate mass transfer as a result of a carbonate-calcium balance in soil solution and aeration zone distortion. This determines a need for the new findings in a soil and aeration zone management focused on a mobility of matter reducing, especially for the technological tools that will overcome a dangerous extracting of useful substances from the soil, as well as the receipt and accumulation of unfavorable substances. This is important for the agriculture and irrigation.

### 7.4.4. Heuristic soil mechanical processing and amendment application methodology

Heuristic synthesis of a new device for soil mechanical processing and simultaneous application of soil amendment and waste was focused on a higher level chemical soil engineering (Meshalkin et al. 2021). By the term “heuristic synthesis” we mean a nonstandard and new knowledge based approach to a technological development. We presumed that a soil processing system is not to be imitative but transcendental to some extent providing a new quality of technology compared to a natural or anthropogenic approach known at the moment.

The new soil mechanical processing methods and equipment are needed for soil structure loosening and soil macroaggregates and microaggregates mixing with

applied material to enrich and stabilize biogeochemical turnover (Bünemann et al. 2018; Mishchenko et al. 2009; Neuman 2017; Røder et al. 2019; Totsche et al. 2018). For this, a creation of multilevel heterogeneous soil architecture synthesis (Kharitonova et al. 2018; Lin 2012) and preferable long-term conditions for polymicrobial biofilms, humic substances and soil organic matter synthesis and function is important. (Bunkin et al. 2020; Kamjunke et al. 2019; Nardi et al. 2022; Swidsinski 2019; Sarker et al. 2018; Swidsinski and Loening-Baucke 2020; Swidsinski et al. 2020; Yadav et al. 2023).

Conditions to techno-soil heuristic synthesis were: a 0–25 cm upper horizon remains intact after the soil mechanical processing; a 25–50 cm horizon is crushed in soil mechanical processing to a particle size of 1–3 mm (up to 40% of the soil mass); the processed soil mass is well mixed; the water and phosphogupsum and other waste mixture (the pulp form is acceptable) is supplied to a 25–50 cm soil horizon and is mixed with the soil mass during the mechanical processing. A soil layer depth corresponds to a depth of different plants rhizosphere.

A soil processing depth selection is based on the soil properties. For heuristic synthesis, the BGT* methodology of soil processing devices synthesis, laboratory research, soil processing equipment tests in soil channel, and long-term field intra-soil processing trials and experiments, and own patents were used. (Kalinichenko 2010; Kalinichenko et al. 2012; Kalinichenko et al. 2013; Kalinitchenko 2016; Kalinitchenko et al. 2021).

A chemical soil engineering device (Figures 7.1 and 7.2) is mounted on a frame 1. The device is longitudinally symmetric and comprises the two vertical rotational chisels 2. A rotational chisel 2 comprises a ring cutter 6 with outer cutting teeth mounted on a disk 5. The ring cutter 6 via internal gear meshes a pinion 7 rotating a shaft 4 with milling cutters 3. The disk 5 is equipped with a channel 8 for feeding the pulp to a channel 10 in a ramp 9. The ramp 9 has forward-oriented fingers 11 for soil loosening and channels 12 for pulp distribution into the soil (Kalinichenko 2010).

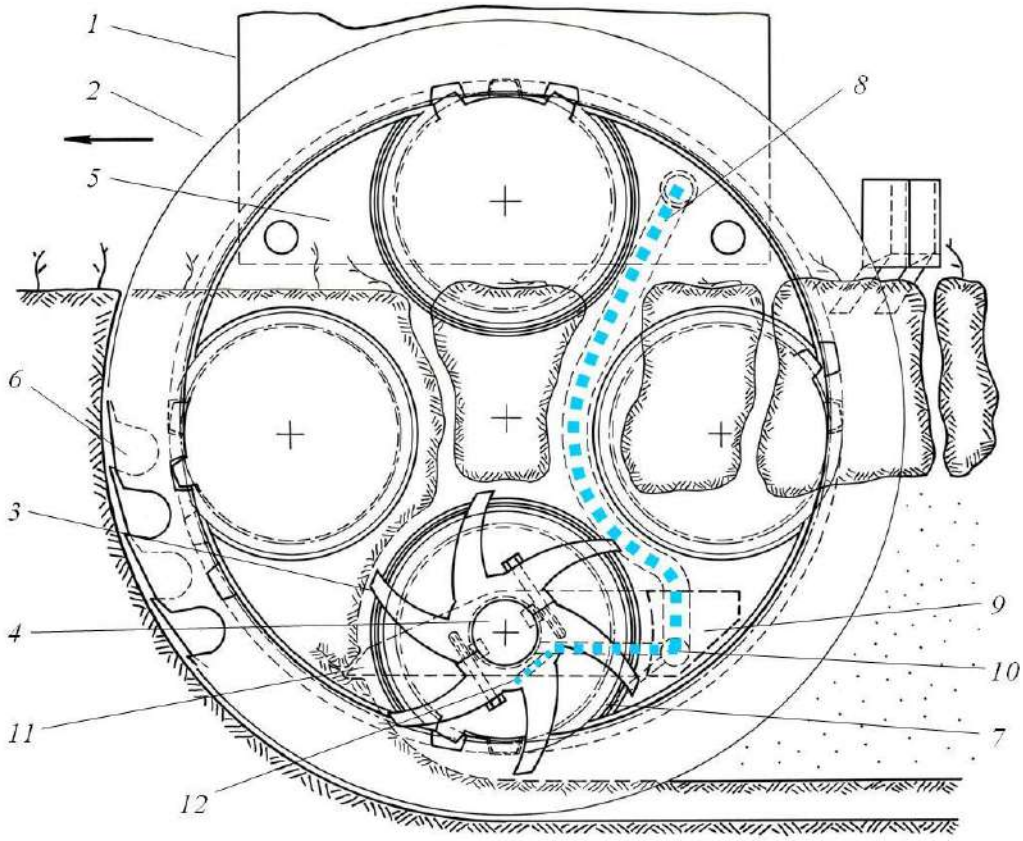


Fig. 7.1. Device for intra-soil milling and simultaneous intra-soil application of substances, side view. 1 – frame; 2 – vertical rotational chisel; 3 – milling cutters; 4 – shaft; 5 – disk; 6 – ring cutter; 7 – pinion; 8 – channel; 9 – ramp; 10 – channel; 11 – soil loosening finger; and 12 – channel

*Сл. 7.1. Уређај за мљевење унутар тла и истовремену примјену супстанци у земљишту, бочни поглед. 1 – оквир; 2 – вертикално ротирајуће длијето; 3 – млинске ножице; 4 – осовина; 5 – диск; 6 – прстенаста ножица; 7 – зупчаник; 8 – канал; 9 – рампа; 10 – канал; 11 – прст за разбијање земљишта и 12 – канал*

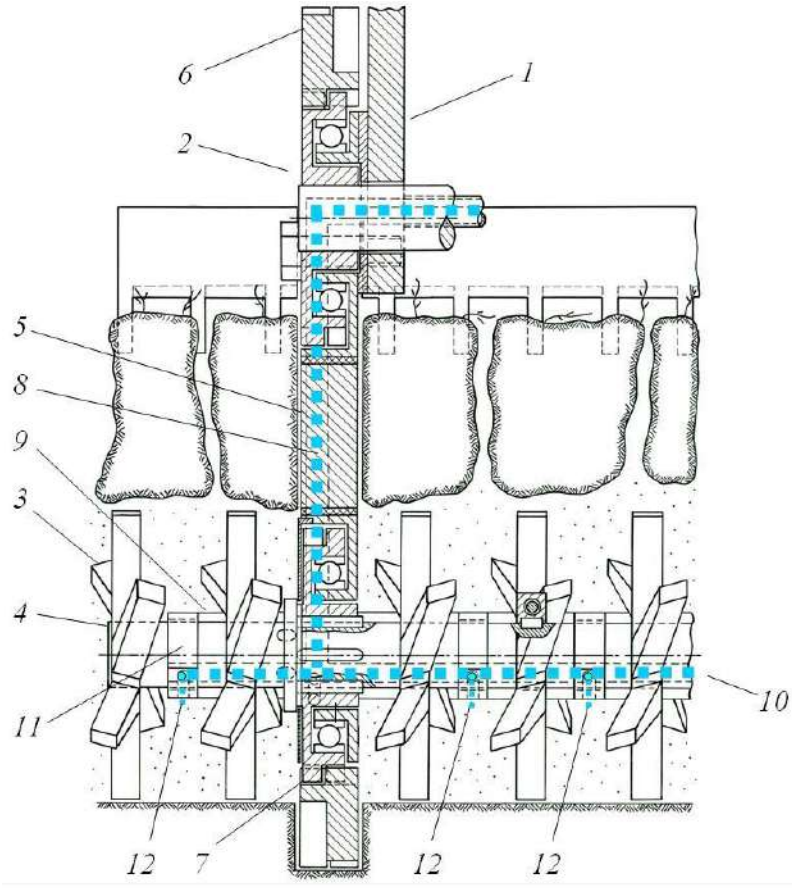


Fig. 7.2. Device for intra-soil milling and simultaneous intra-soil application of substances, front view; designations, see Figure 7.1.

*Сл. 7.2. Уређај за мљевење унутар тла и истовремену примјену супстанци у земљишту, предњи поглед; ознаке, видјети Сл. 7.1.*

During operation, the device is immersed into a 20–45 (or 30–70 cm) target soil layer. The ring cutter 6 cuts a slit in the soil while a device forward movement reducing a passive traction resistance for rotational chisels 2. The milling cutters 3 provide a soil fine-aggregate structure. A pulp is fed through channels 9, 11, and 12 into the milling zone and is mixed with the soil aggregates. The device provides a new chemical soil engineering technology ensuring a high life quality standard (Duanyang et al. 2024; Hentati et al. 2015; Kalinitchenko et al. 2020, 2023, 2024; Mao and Jiao 2024; USEPA 2020).

## 7.5. Conclusion

Ions association in the soil solution determines a soil solution chemical equilibrium and a pattern of salt migration and accumulation in the soil and vadose zone.

This is important for the salted soils modern evolution understanding and soil management in the Kastanozem and Chernozem standard regional rainfed agriculture, irrigation, plant nutrition management and the soil pollution with HMs control.

A $Pb^{2+}$ ion equilibrium concentration and molar fraction in Chernozem soil solution calculation showed a $Pb^{2+}$ high degree binding into the associates and hydroxo complexes revealing a possibility of a HMs contained in phosphogypsum recycling in the soil intra-soil passivation.

Intra-soil milling provides an amendment, waste and nutrition substances subsoil dispersed application ensuring a high level contact of substances with illuvial soil layer and high ameliorative effect, HMs passivation, soil fertility and environmental safety.

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## Literature

Duanyang Xu, Yuanqing Wang, Junfang Wang (2024) A review of social-ecological system vulnerability in desertified regions: Assessment, simulation, and sustainable management. Sci. Total Environ. 931:172604. doi:10.1016/j.scitotenv.2024.172604

Musasa T, Dube T, Marambanyika Th (2024) Landsat satellite programme potential for soil erosion assessment and monitoring in arid environments: A review of applications and challenges. Int. Soil Water Conserv. Res. 12(2):267–278. doi:10.1016/j.iswcr.2023.10.003.

Brander LM de Groot R, Schägner JP, Guisado-Goñi V, van 't Hoff V, Solomonides S, McVittie A, Eppink F, Sposato M, Do L, Ghermandi A, Sinclair M, Thomas R. (2024) Economic values for ecosystem services: A global synthesis and way forward. Ecosyst. Serv. 66:101606. doi:10.1016/j.ecoser.2024.101606.

Kalinitchenko VP, Swidsinski AV, Glinushkin AP, Overcash MR, Meshalkin VP, Minkina TM, Rajput VD, Chernenko VV, Mandzhieva SS, Sushkova SN, Rykhlik AE, Larin GS, Gudkov SV, Baryshev MG, Sevostyanov MA, Makarenkov DA (2024) New approach to soil fertility management: Biogeosystem Technique methodology (critical review). Land Degrad. Dev. 35(7):2367–2381.doi:10.1002/ldr.5065

Mao W, Jiao L (2024) Land-use intensification dominates China's land provisioning services: From the perspective of land system science. J. Environ. Manag. 356:120541. doi:10.1016/j.jenvman.2024.120541.

Seidl A, Cumming T, Arlaud M, Crossett C, van den Heuvel O (2024) Investing in the wealth of nature through biodiversity and ecosystem service finance solutions. Ecosyst. Serv. 66:101601. doi:10.1016/j.ecoser.2024.101601.

Kopittke PM, Minasny B, Pendall E, Rumpel C, McKenna BA (2024) Healthy soil for healthy humans and a healthy planet. Crit. Rev. Environ. Sci. Technol. 54(3):210–221. doi:10.1080/10643389.2023.2228651

Smith P, Keesstra SD, Silver WL, Adhya TK, De Deyn GB, Carvalheiro LG, Giltrap DL, Renforth P, Cheng K, Sarkar B, Saco PM, Scow K, Smith J, Morel J-Cl, Thiele-Bruhn S, Lal R, McElwee P. (2021) Soil-derived Nature's Contributions to People and their contribution to the UN Sustainable Development Goals. Phil. Trans. R. Soc. B 3762020018520200185. doi:10.1098/rstb.2020.0185

Amakor XN, Jacobson AR, Cardon GE (2013) Improving estimates of soil salinity from saturation paste extracts in calcareous soils. Soil Sci. Soc. Am. J. 3:792–799. doi:10.2136/sssaj2012.0235.

Hunenberger P, Relf M (2011) Single-Ion Solvation. Experimental and Theoretical Approachs to Elusive Thermodynamic Quantities. Editor – Jonathan Hirst. Royal Society of Chemistry. Thomas Graham House, Science Park, Milton Road. UK. Cambrige CB4 0WF. ISBN: 978-1-84755-187-0, pp. 690. www.rsc.org/shop/books/2011/9781847551870.asp

Minkin MB, Endovitskii AP (1978) Use of a graphical method for calculation of ion equilibrium in soil solutions. Soil Sci. 3:124–131. http://agris.fao.org/aos/records/US201302461626.

Opfergelt S, Burton KW, Georg RB, West AJ, Guicharnaud RA, Sigfusson B, Siebert C, Gislason SR, Halliday AN (2014) Magnesium retention on the soil exchange complex controlling Mg isotope variations in soils, soil solutions and vegetation in volcanic soils, Iceland. Geochim. Cosmochim. Acta. 125:110–130. doi:10.1016/j.gca.2013.09.036.

Visconti F, de Paz JM (2012) Prediction of the soil saturated paste extract salinity from extractable ions, cation exchange capacity and anion exclusion. Soil Res. 50:536–550. doi:10.1071/SR12197.

Garcia-Araez N, Climent V, Rodriguez P, Feliu JM (2010) Thermodynamic evidence for K+–SO42− ion pair formation on Pt (III). New insight into cation specific adsorption. Phys. Chem. Chem. Phys. 12(38):12146–12152. doi:10.1039/C0CP00247J.

Kar SZ, Berenjian A (2013) Soil formation by ecological factors: critical review. Am. J. Agri. Biol. Sci. 8(2):114–116. doi:10.3844/ajabssp.2013.114.116.

Mari IA, Ji C, Chandio FA, Arslan C, Tagar AA, Ahmad F (2014) Rheological properties of paddy soil under various pressure, water content and tool shapes. Am. J. Agri. Biol. Sci. 9(1):25–32. doi:10.3844/ajabssp.2014.25.32.

Plugatyr A, Carvajal-Ortiz RA, Svishchev IM (2011) Ion-Pair Association Constant for LiOH in Supercritical Water. J. Chem. Eng. Data 56(9):3637–3642. doi:10.1021/je2004808.

Maiti A, Rogers RD (2011) A correlation-based predictor for pair-association in ionic liquids. Phys. Chem. Chem. Phys. 13:12138–12145. doi:10.1039/C1CP21018A.

Lui MY, Crowhurst L, Hallett JP, Hunt PA, Niedermeyer H, Welton T (2011) Salts dissolved in salts: ionic liquid mixtures. Chem. Sci. 2:1491–1496. doi:10.1039/C1SC00227A.

Luo Y, Jiang W, Yu H, MacKerell AD, Roux B (2013) Simulation study of ion pairing in concentrated aqueous salt solutions with a polarizable force field. Faraday Discuss. 160:135–149. doi:10.1039/C2FD20068F.

Adams F (1971) Ionic concentrations and activities in soil solutions. Soil Sci. Soc. Am. J. 35:421–426. doi:10.2136/sssaj1971.03615995003500030028x.

Debye P, Hückel E (1923) The theory of electrolytes. I. Lowering of freezing point and related phenomena. Phys. Z. 24:185–206. http://archive.wikiwix.com/cache/?url=http://electrochem.cwru.edu/estir/hist/hist-12-Debye-1.pdf&title=lire%20en%20ligne

Davies CW (1962) Ion Association. Butterworths: Washington. pp. 190. www.sciencemag.org/content/143/3601/37.1.citation

Bjerrum J, Schwarzenbach G, Sillen LG (1958) Stability constants of metal-ion complexes with solubility products of inorganic substances. Part II. Inorganic ligands. London: The Chemical Society. http://link.springer.com/search?query=Bjerrum%2C+J.%2C+G.+Schwarzenbach+and+L.G.+Sillen%2C+1958.+Stability+constants+of+metal-

ion+complexes+with+solubility+products+of+inorganic+substances.+Part+II.+Inorganic+ligands.+London%3A+The+Chemical+Society. (accessed on 22 july 2012)

Stoyanov ES, Stoyanova IV, Reed CA (2011) The unique nature of H+ in water. Chem. Sci. 2:462–472. doi:10.1039/C0SC00415D.

Raiteri P, Demichelis R, Gale JD, Kellermeier M, Gebauer D, Quigley D, Wright LB, Walsh TR (2012) Exploring the influence of organic species on pre- and post-nucleation calcium carbonate. Faraday Discuss. 159:61–85. doi:10.1039/C2FD20052J.

Dave D, Dikshit AK (2011) Effect of different exogeneous compounds on biosorption of endosulfan. Am. J. Environ. Sci. 7:224–236. doi:10.3844/ajessp.2011.224.236.

Zhang L, Petersen JE, Zhang W, Chen Y, Cabrera M, Huang Q (2012) Interactions of 14C-labeled multi-walled carbon nanotubes with soil minerals in water. Environ. Pollut. 166:75–81. doi:10.1016/j.envpol.2012.03.008.

Mandzhieva SS, Minkina TM, Sushkova SN, Motuzova GV, Bauer TV, Chapligin VA (2014). The group composition of metal compounds in soil as an index of soil ecological state. Am. J. Agri. Biol. Sci. 9(1):19–24. doi:10.3844/ajabssp.2014.19.24.

Tertre E, Pret D, Ferrage E (2011) Influence of the ionic strength and solid/solution ratio on Ca(II)-for-Na+ exchange on montmorillonite. Part 1: Chemical measurements, thermodynamic modeling and potential implications for trace elements geochemistry. J. Colloid Interface Sci. 353:248–256. doi:10.1016/j.jcis.2010.09.039.

Wright MR (2007) An Introduction to Aqueous Electrolyte Solutions. Chichester, England, John Wiley. 602 p. www.amazon.com/An-Introduction-Aqueous-Electrolyte-Solutions/dp/0470842946

Nicholson D, Quirke N (2003) Ion Pairing in Confined Electrolytes. Preliminary Communication. Mol. Simul. 29(4):287–290. www.ingentaconnect.com/content/tandf/gmos/2003/00000029/00000004/art00006?crawler=true

Adriano DC (2001) Trace Elements in Terrestrial Environments: Biogeochemistry, Bioavailability, and Risks of Metals. Springer-Verlag, New York, Berlin, Heidelberg.

Kalinitchenko VP (2016) Technologies and technical means for matter recycling into the soil (Review). Int. J. Environ. Probl. 3(1):58–85. doi:10.13187/bgt.2015.4.104

Minkina TM, Motusova GV, Mandzhieva SS, Nazarenko OG (2012a) Ecological resistance of the soil-plant system to contamination by heavy metals. J. Geochem. Explor. 123:33–40.

Motuzova GV, Minkina TM, Karpova EA, Barsova NU, Mandzhieva SS (2014) Soil contamination with heavy metals as a potential and real risk to the environment. J. Geochem. Explor. 144:241–246. doi:10.1016/j.gexplo.2014.01.026

Sparks D (Ed.) 2003. Environmental soil chemistry. Academic Press, San Diego C.A.

Xiong T, Leveque Th, Shahid M, Foucault Ya, Mombo S, Dumat C (2014) Lead and cadmium phytoavailability and human bioaccessibility for vegetables exposed to soil or atmospheric pollution by process ultrafine particles. J. Environ. Qual. 43(5):1593–1600. doi:10.2134/jeq2013.11.0469

Tsvetkov VY (2016) Structural Analysis Based on Living Systems Algorithms. Biogeosyst. Tech. 7(1): 87–95. doi:10.13187/bgt.2016.7.87

Glazko VI, Galzko TT (2015) Conflicts of biosphere and agroecosystems. Int. J. Environ. Probl. 1(1): 4–16. doi: 10.13187/ijep.2015.1.4

Semenov A, Sokolov MS (2016) The concept of soil health: fundamental and applied aspects of the evaluation criteria. Agrochemistry 1:3–16.

Land contamination: soil guideline values (SGVs) (2015) www.gov.uk/government/publications/land-contamination-soil-guideline-values-sgvs (accessed on 29 July 2020)

McGrath SP, Loveland PJ (1992) The Soil Geochemical Atlas of England and Wales. Blackie Academic and Professional, Glasgow.

McGahren J, Feingold SR, Dupraz EJ (2024) New EPA guidance cuts prior residential soil lead levels in half. www.morganlewis.com/pubs/2024/01/new-epa-guidance-cuts-prior-residential-soil-lead-levels-in-half (accessed on 07/24/2024)

Sposito G (2013) Green water and global food security. Vadose Zone J. 12. doi:10.2136/vzj2013.02.0041.

Lisetskii FN, Stolba VF, Goleusov PV (2016) Modeling of the evolution of steppe chernozems and development of the method of pedogenetic chronology. Eurasian Soil Sci. 49:846–858. doi:10.1134/s1064229316080056

Lisetskii F, Zelenskaya E, Rodionova M (2018) Geochemical features of fallow land in ancient plots in the chora of Chersonesos. Geosciences 8:410. doi:10.3390/geosciences8110410

Favas P, Pratas J, Gomes MH, Cala V (2011) Selective chemical extraction of heavy metals in tailings and soils contaminated by mining activity: environmental implication. J. Geochem. Explor. 111(3):160–171. doi:10.1016/j.gexplo.2011.04.009

Alloway BJ (1995) Heavy metals in Soils. Springer Science & Business Media. Nature. 368 pages.

Tskhovrebov VS (2012) Changing the content of microelements under winter wheat due to remineralization of chernozem leached. Sci. J. KubGAU. 77(03).

Belyuchenko IS, Antonenko DA (2015) Influence of complex compost on aggregate composition and water-air properties of ordinary chernozem. Soil Sci. 7:858. doi: 10.1134/S1064229315070030

Endovitskii AP, Kalinichenko VP, Il'in VB, Ivanenko AA (2009a) Coefficients of association and activity of cadmium and lead ions in soil solutions. Eurasian Soil Sci. 42(2):201–208. doi:10.1134/S1064229309020112

Kalinitchenko VP, Glinushkin AP, Minkina TM, Mandzhieva SS, Sushkova SN, Sukovatov VA, Il'ina LP, Makarenkov DA (2020) Chemical soil-biological engineering theoretical foundations, technical means, and technology for safe intra-soil waste recycling and long-term higher soil productivity. ACS Omega 5(28):17553–17564. doi:10.1021/acsomega.0c02014

Kalinitchenko VP, Glinushkin AP, Swidsinski AV, Minkina TM, Andreev AG, Mandzhieva SS, Sushkova SN, Makarenkov DA, Ilyina LP, Chernenko VV, Zamulina IV, Larin GS, Zavalin AA, Gudkov SV (2021). Thermodynamic mathematical model of the Kastanozem complex and new principles of

sustainable semiarid protective silviculture management. Environ. Res. 194:110605. doi:10.1016/j.envres.2020.110605

Okolelova AA, Glinushkin AP, Sviridova LL, Podkovyrov IY, Nefedieva EE, Egorova GS, Kalinitchenko VP, Minkina TM Sushkova SN, Mandzhieva SS, Rajput VD (2022) Biogeosystem Technique (BGT*) Methodology Will Provide Semiarid Landscape Sustainability (A Case of the South Russia Volgograd Region Soil Resources). Agronomy 12:2765. doi:10.3390/agronomy12112765

Goswami M, Nand S (2015) Management of Phosphogypsum in India. Proc. of The IFA Global Safety Summit, Vancouver, Canada. www.fertilizer.org/En/Knowledge_Resources/Library/Technical_Publications.aspx?New_ContentCollectionOrganizerCommon=2 (accessed on 24 July 2021)

Pérez-López R, Macías F, Cánovas CR, Sarmiento AM, Pérez-Moreno SM (2016) Pollutant flows from a phosphogypsum disposal area to an estuarine environment: An insight from geochemical signatures. Sci. Total Environ. 553(15): 42–51. doi:10.1016/j.scitotenv.2016.02.070

Lapin AV, Lyagushkin AP (2014) The Kovdor apatite-francolite deposit as a prospective source of phosphate ore. Geology of Ore Deposits 56(1): 61–80.

Soil Liquid Phase Composition (2001) Eds: Snakin VV, Prisyazhnaya AA, Kovács-Láng E. Elsevier Science BV

Gázquez MJ, Mantero J, Mosqueda F, Bolívar JP, García-Tenorio R (2014) Radioactive characterization of leachates and efflorescences in the neighbouring areas of a phosphogypsum disposal site as a preliminary step before its restoration. J. Environ. Radioact. 137:79–87. doi:10.1016/j.jenvrad.2014.06.025

Sukovatov VA (2009) The duration of solonetzic complex chestnut soils reclamation. The thesis for the degree of Candidate of Agricultural Sciences / Don State Agrarian University. Persianovsky, 140 p. http://elibrary.ru/item.asp?id=19212993

Tayibi H, Choura M, López FA, Alguacil FJ, López-Delgado A. (2009) Environmental impact and management of phosphogypsum. J. Environ. Manage. 90(8):2377–86. doi:10.1016/j.jenvman.2009.03.007

Mays DA, Mortvedt JJ (1984) Crop Response to Soil Applications of Phosphogypsum. J. Environ. Qual. 15(1):78–81. doi:10.2134/jeq1986.00472425001500010018x

Nayak S, Mishra CSK, Guru BC, Rath M (2011) Effect of phosphogypsum amendment on soil physico-chemical properties, microbial load and enzyme activities. J Environ Biol. 32(5):613–617.

Minkin MB, Kalinichenko VP, Kornienko VI, Skuratov NS, Sypko ME (1992) Patent SU No 1704070. Method for the doze of phosphogypsum determining required for reclamation of alkaline soil. Application No 4683723. 04.25.89. Bul. No 1. 7.1.92.

Endovitsky AP, Kalinichenko VP, Minkina TM (2014) State of lead and cadmium in chernozem after making phosphogypsum. Soil Sci. 3:340–350.

Endovitsky AP, Batukaev AA, Minkina TM, Kalinitchenko VP, Mandzhieva SS, Sushkova SN, Mischenko NA, Bakoyev SYu, Zarmaev AA, Jusupov VU (2017) Ions association in soil solution as the cause of lead mobility and availability

after application of phosphogypsum to chernozem. J. Geochem. Explor. 182(B):185–192. doi:10.1016/j.gexplo.2016.08.018

Soil Sampling and Methods of Analysis (2008) Second Edition. Edited by Carter MR, Gregorich EG. Canadian Society of Soil Science. Taylor & Francis Group, LLC. www.planta.cn/forum/files_planta/methods_of_analysis_212.pdf

Minkina TM, Endovitskii AP, Kalinichenko VP, Fedorov YA (2012b) Calcium Carbonate Equilibrium in The System Water – Soil. Southern Federal University, Rostov-on-Don

Shtiza A, Swennen R (2011) Appropriate sampling strategy and analytical methodology to address contamination by industry. Part 2: Geochemistry and speciation analysis. Open Geosci. 3(1):53–70. doi:10.2478/v10085-010-0033-4

Afzal M, Yasin M (2002) Effect of soil to water ratios on chemical properties of saline-sodic and normal soil. Pakistan J. Agric. Res. 4(17):379–386. www.cabi.org/gara/FullTextPDF/2009/20093346417.pdf

Anisimov VS, Anisimova LN, Frigidova LM, Dikarev DV, Frigidov RA, Kochetkov IV, Sanzharova NI (2015) Evaluation of migration ability of Zn in the soil-plant system. Biogeosyst. Tech. 4(2):153–163.

Endovitsky AP, Kalinichenko VP, Bakoyev SY, Ivanenko AA, Sukovatov VA, Radevich EV (2009b) Certificate of the state registration of computer program. No 2009612162 ION–2. Patentee Don State Agrarian University.

Minkina TM, Kalinichenko VP, Bakoev SYu, Mandzhieva SS, Sushkova SN, Bauer TV, Zamulina IV, Voronov MB, Burachevskaya MV. (2016) ION–3. Certificate of registration of the computer program RU 2016616075, 06.06.2016. Application No. 2016613589 04.14.2016.

Kalinichenko VP, Glinushkin AP, Sokolov MS, Zinchenko VE, Minkina TM, Mandzhieva SS, Sushkova SN, Makarenkov DA, Bakoyev SY, Il'ina LP (2019) Impact of soil organic matter on calcium carbonate equilibrium and forms of Pb in water extracts from Kastanozem complex. J. Soils Sediments. 19:2717–2728. doi:10.1007/s11368-018-2123-z

Batukaev AA, Endovitsky AP, Minkina TM, Kalinichenko VP, Dikaev ZS, Sushkova SN (2014) Chemical equilibrium of soil solution in steppe zone soil. Am. J. Agri. Biol. Sci. 9 (3):420–429. doi:10.3844/ajabssp.2014.

Izgorodina EI (2011) Towards large-scale, fully ab initio calculations of ionic liquids. Phys. Chem. Chem. Phys. 13:4189–4207. doi:10.1039/C0CP02315A.

Izgorodina EI, Golze D, Maganti R, Armel V, Taige M, Schubert TJS, MacFarlane DR (2014) Importance of dispersion forces for prediction of thermodynamic and transport properties of some common ionic liquids. Phys. Chem. Chem. Phys. 16. doi:10.1039/C3CP53035C.

Sushkova SN, Minkina TM, Mandzhieva SS, Tjurina IG (2013) Elaboration and approbation of methods for benzo[a]pyrene extraction from soils for monitoring of the ecological state in technogenic landscapes. World Appl. Sci. J. 25(10):1432–1437. doi:10.5829/idosi.wasj.2013.25.10.11237

Chialvo AA, Cummings PT, Cochran HD, Simonson JM, Mesmer RE (1995) Na+–Cl− ion pair association in supercritical water. J. Chem. Phys. 103(21):9125–9516. doi:10.1063/1.470707.

Saito CH (2013) Environmental education and biodiversity concern: beyond the ecological literacy. Am. J. Agri. Biol. Sci. 8(1):12–27. doi:10.3844/ajabssp.2013.12.27.

Farnum BH, Gardner JM, Marton A, Narducci-Sarjeant AA, Meyer GJ (2011) Influence of ion pairing on the oxidation of iodide by MLCT excited states. Dalton Trans. 40:3830-3838. doi:10.1039/C0DT01447H.

Kielpinski D (2013) Viewpoint: Ion Pair Simulates Hybrid Excitations. Physics 6:112. doi:10.1103/Physics.6.112

Westerlund F, Elm J, Lykkebo J, Carlsson N, Thyrhaug E, Åkerman B, Sorensen TJ, Mikkelsen KV, Laursen BW (2011) Direct probing of ion pair formation using a symmetric triangulenium dye. Photochem. Photobiol. Sci. 10:1963–1973. doi:10.1039/C1PP05253E.

Besser-Rogac M, Stoppa A, Hunger J, Hefter G. Buchner R (2011) Association of ionic liquids in solution: a combined dielectric and conductivity study of [bmim][Cl] in water and in acetonitrile. Phys. Chem. Chem. Phys. 13:17588–1759. doi:10.1039/C1CP21371G.

Wang T, Liu J, Sun H, Chen L, Dong J, Sun L, Bi Y (2014) Exploring the mechanism of ion-pair recognition by new calix[4]pyrrole bis-phosphonate receptors: insights from quantum mechanics study. RSC Adv. 4:1864–1873. doi:10.1039/C3RA44380A.

Shatti LAA, Marafie HM, Shoukry AF (2011) Plastic membrane electrodes of coated wire type for micro determination of quininium cation in pharmaceutical tablets. Am. J. Applied Sci. 8:116–123. doi:10.3844/ajassp.2011.116.123.

Wiatrak P (2014) Evaluation of nitrogen application methods and rates with nutrisphere-n on soil nitrate-nitrogen in southeastern coastal plains. Am. J. Agri. Biol. Sci. 9(1):64–71. doi:10.3844/ajabssp.2014.64.71.

Jiang C-L, Sequaris J-M, Vereecken H, Klumpp E (2012) Effects of inorganic and organic anions on the stability of illite and quartz soil colloids in Na-, Ca- and mixed Na–Ca systems. Colloids and Surfaces A: Physicochem. Eng. Aspects 415:134–141. doi:10.1016/j.colsurfa.2012.10.007.

Kalinichenko VP, Sharshak VK, Zinchenko VE, Zarmaev AA, Ladan EP, Chernenko VV, Il'ina LP (2012) Long-term Impact of Rotary Method of Soil Mechanical Treatment on Soil Properties. Eur. Res. 31(10–1):1649–1656. www.erjournal.ru/journals_n/1351429721.pdf

El Marazky MSA, Mohammad FS, Al-Ghobari HM (2011) Evaluation of soil moisture sensors under intelligent irrigation systems for economical crops in arid regions. Am. J. Agri. Biol. Sci. 6:287–300. doi:10.3844/ajabssp.2011.287.300.

Rules and Regulations (2001) US Environmental protection agency. Federal Register 66(4):1211. www.epa.gov/lead/hazard-standards-lead-paint-dust-and-soil-tsca-section-403.

Kalinichenko VP (2015) Biogeosystem technique as a paradigm of non-waste technology in the biosphere. Biogeosyst. Tech. 3(1):4–28. doi:10.13187/bgt.2015.3.4

Klymenko O (2015) Impact of chemical melioration on soil properties and productivity of peach trees. Bull. Dnipropetrovsk State Agrar. Univ. Econ. 2(36):31–35.

Kwasniewska J (2014) Molecular cytogenetics serves environmental monitoring. Proc. of 3rd ScienceOne International Conference on Environmental Sciences. p. 25.

Shein EV, Kharitonova GV, Milanovsky EYu (2016) Aggregation of natural disperse formations: Value of organic matter, soluble salts and diatoms. Biogeosyst. Tech. 7(1):77-86. doi:10.13187/bgt.2016.7.77

Shein EV, Kharitonova GV, Amgalan B, Sambuu G, Krutikova VO, Kharitonov EV (2017) Salt neoformations in soils of Central Mongolia. Biogeosyst. Tech. 4(1):66–81. doi:10.13187/bgt.2017.1.66

Shein EV, Mady AY, Mohamed HA (2015) Soil saturated hydraulic conductivity assessment by direct and pedotransfer functions methods. Biogeosyst. Tech. 6(4):396–400. doi:10.13187/bgt.2015.6.396

Kalinitchenko VP, Rykhlik AE (2019) Biogeosystem Technique New World Water Paradigm for the Water Scarcity Overcoming. ACS Fall 2019 National Meeting & Exposition, Chemistry & Water, August 25–29, 2019. San Diego, CA. https://plan.core-apps.com/acs_sd2019/abstract/6dc4fdd9-0f1c-41b3-a54e-ac4e18736726

Kalinitchenko VP, Swidsinski AV, Glinushkin AP, Meshalkin VP, Gudkov SV, Minkina TM, Chernenko VV, Rajput VD, Mandzhieva SS, Sushkova SN, Okolelova AA, Shestakova AA (2023) New approach to soil management focusing on soil health and air quality: one earth one life (critical review). Environ. Geochem. Health 45(12):8967–8987. doi:10.1007/s10653-023-01550-7. PMID: 37138143

Batukaev AA, Endovitsky AP, Andreev AG, Kalinichenko VP, Minkina TM, Dikaev ZS, Mandzhieva SS, Sushkova SN (2016) Ion association in water solution of soil and vadose zone of chestnut saline solonetz as a driver of terrestrial carbon sink. Solid Earth 7(2):415–423. doi:10.5194/se-7-415-2016

Meshalkin VP, Dovì VG, Bobkov VI, Belyakov AV, Butusov OB, Garabadzhiu AV, Burukhina TF, Khodchenko SM (2021) State of the art and research development prospects of energy and resource-efficient environmentally safe chemical process systems engineering. Mendeleev Commun. 31(5):593–604. doi:10.1016/j.mencom.2021.09.003.

Bünemann EK, Bongiorno G, Bai Z, Creamer RE, De Deyn G, de Goede R, Fleskens L, Geissen V, Kuyper TW, Mäder P, Pulleman M, Sukke lW, van Groenigen JW, Brussaard L (2018) Soil quality – A critical review. Soil Biol. Biochem. 120:105–125. doi:10.1016/j.soilbio.2018.01.030

Mishchenko NA, Gromyko EV, Kalinichenko VP, Chernenko VV, Larin SV (2009) Ecological and recreational phosphogypsum recycling in chernozem on example of the Krasnodar Territory. Fertility 6:25–26.

Neuman J (2017) Soil Organic Matter Maintenance in No-Till and Crop Rotation Management Systems. Soil Organic Matter. Reference Module in Earth Systems and Environmental Sciences; Elsevier.

Røder HL, Olsen NMC, Whiteley M, Burmølle M (2019) Unravelling interspecies interactions across heterogeneities in complex biofilm communities. Environ. Microbiol. 22(1):5–16. doi:10.1111/1462-2920.14834.

Totsche KU, Amelung W, Gerzabek MH, Guggenberger G, Klumpp E Knief C Lehndorff E, Mikutta R, Peth S, Prechtel A, Ray N, Kögel-Knabner I (2018) Microaggregates in soils. J. Plant Nutr. Soil Sci. 181:104–136. doi:10.1002/jpln.201600451

Kharitonova GV, Shein EV, Krutikova VO, Ostrouhov AV (2018) Calcium Carbonate Formations in Edaphic Components of Ecosystems. Biogeosyst. Tech. 5(2):197–212. doi:10.13187/bgt.2018.2.197

Lin H (2012) Understanding Soil Architecture and Its Functional Manifestation across Scales. Part I: Overviews and Fundamentals. Hydropedology; Academic Press. Chapter 2. pp 41–74.

Bunkin NF, Glinushkin AP, Shkirin AV, Ignatenko DN, Chirikov SN, Savchenko IV, Meshalkin VP, Samarin GN, Maleki A, Kalinitchenko VP (2020) Identification of Organic Matter Dispersions Based on Light Scattering Matrices Focusing on Soil Organic Matter Management. ACS Omega 5(51):33214–33224. doi:10.1021/acsomega.0c04906

Kamjunke N, Hertkorn N, Harir M, Schmitt-Kopplin P, Griebler C, Brauns M, von Tümpling W, Weitere M, Herzsprung P. (2019) Molecular change of dissolved organic matter and patterns of bacterial activity in a stream along a land-use gradient. Water Res. 164:114919. doi:10.1016/j.watres.2019.114919

Nardi S, Schiavon M, Muscolo A, Pizzeghello D, Ertani A, Canellas LP, Garcia-Mina JM (2022) Editorial: Molecular Characterization of Humic Substances and Regulatory Processes Activated in Plants. Front. Plant Sci. 13:851451. doi:10.3389/fpls.2022.851451

Swidsinski A (2019) The colonic bioreactor – a forerunner model for future biotechnology (function, role, products & management). Fifth International Conference of CIS IHSS on Humic Innovative Technologies “Humic substances and living systems”, October 19–23, 2019.

Sarker JR, Singh BP, Dougherty WJ, Fang Yu, Badgery W, Hoyle FC, Dalal RC, Cowie AL (2018) Impact of agricultural management practices on the nutrient supply potential of soil organic matter under long-term farming systems. Soil and Tillage Res. 175:71–81, doi:10.1016/j.still.2017.08.005

Swidsinski A, Loening-Baucke V (2020) Spatial organization of intestinal microbiota in health and disease. www.uptodate.com/contents/spatial-organization-of-intestinal-microbiota-in-health-and-disease/print (accessed 11 March 2020)

Swidsinski A, Kalinitchenko V, Glinushkin A, Mukovoz P, Minkina T, Sushkova S, Mandzhieva S, Grishina H (2020) Soil biochemical process correction basing on the Biogeosystem Technique methodology for expanded polymicrobial

biofilms action in the soil. ACS Fall Meeting, San Francisco, Abstract ID: 3429460 doi:10.1021/scimeetings.0c07088

Yadav MR, Kumar S, Lal MK, Kumar D, Kumar R, Yadav RK, Kumar S, Nanda G, Singh J, Udawat P, Meena NK, Jha PK, Minkina T, Glinushkin, AP, Kalinitchenko VP, Rajput VD (2023) Mechanistic Understanding of Leakage and Consequences and Recent Technological Advances in Improving Nitrogen Use Efficiency in Cereals. Agronomy 13:527. doi:10.3390/agronomy13020527

Kalinichenko VP Patent RU No 2387115 C2. Device for entering a substance at intra-soil rotary hoeing. Application number 2008124500/12 (029710) 16.06.2008. Published on April 27, 2010. Bull. No 12. 7 p. : 2 fig.

Kalinichenko VP, Il'in VB, Endovitsky AP, Chernenko VV (2013) Patent RU No 2476055 C2. Method of substance synthesis inside a fine dispersed system. Published on February 27, 2013. Bull No 6. 7 p. : 2 fig.

Kalinichenko VP, Kodzoev MM, Tochiev AM, Mamilov BB, Bazgiev MA (2012). Soil ecosystem management in birdlime utilization. Eur. Res. 25(7):1042–1049. www.erjournal.ru/journals_n/1342466228.pdf

US Environmental Protection Agency. Risk-Based Screening Table—Generic Tables. www2.epa.gov/risk/risk-based-screening-table-generic-tables (date of access Jan 30, 2020).

Hentati O, Abrantes N, Caetano AL, Bouguerra S, Gonçalves F, Römbke J, Pereira R (2015) Phosphogypsum as a soil fertilizer: Ecotoxicity of amended soil and elutriates to bacteria, invertebrates, algae and plants. J. Hazard. Mater. 294:80–89. doi:10.1016/j.jhazmat.2015.03.034

# Асоцијација јона у раствору земљишта као узрок мобилности и доступности Pb за биљке

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## Сажетак

*Управљање раствором земљишта је важан услов за обнову земљишта у различитим регионима свијета. Хемијска равнотежа раствора земљишта одређује динамику његовог материјалног састава, миграцију и акумулацију соли. У раствору земљишта формирају се електрично неутрални јонски парови $CaCO_3^0$, $CaSO_4^0$, $MgCO_3^0$, $MgSO_4^0$, као и наелектрисани јонски парови $CaHCO_3^+$, $MgHCO_3^+$, $NaCO_3^-$, $NaSO_4^-$, $CaOH^+$, $MgOH^+$. Предложен је метод за квантитативну процјену стварних јонских форми у раствору земљишта узимајући у обзир асоцијацију јона. У зависности од концентрације и састава раствора земљишта, у Кастанозему јужне Русије, у југоисточном дијелу Ростовске области, представљени су јонски парови: 15–45% $Ca^{2+}$; 16–49% $Mg^{2+}$; 0,6–8,4% $Na^+$; 2,2–17,6% $HCO_3^-$; 16–51% $SO_4^{2-}$ и до 88% $CO_3^{2-}$.*

*Испитивана је термодинамика Pb форми у раствору земљишта чернозема у стандардним условима и након примјене фосфогипса у слој земљишта 20–40 cm у дозама од 0, 10, 20 и 40 t $ha^{-1}$. Садржај растворљиве форме $Pb^{2+}$ у воденом екстракту израчунат је помоћу математичког хемијско-термодинамичког модела асоцијације јонских парова у раствору земљишта, користећи алгоритам и компјутерске програме ION–2 и ION–3. Предложен је коефицијент асоцијације јона тешких метала (HMs) у раствору земљишта, $k_{as}$, за израчунавање равнотежне концентрације HMs. Модел је показао да је израчунати коефицијент асоцијације $Pb^{2+}$ до 25,0, и да је $Pb^{2+}$ јон у раствору земљишта углавном присутан у формама $PbOH^+$ и $Pb(OH)_2^0$.*

*Развијен је уређај за хемијско инжењерство земљишта за механичку обраду унутар земљишта и примјену измјене и других супстанци унутар земљишта. Измјене унутар земљишта обезбјеђује блиски контакт између ситних честица земљишта и ситних честица мелиоративне супстанце у третираном слоју земљишта, осигуравајући пасивацију токсичних метала, висок мелиоративни ефекат, плодност земљишта и еколошку сигурност.*

*Кључне ријечи*: раствор земљишта, хемијска равнотежа, јонска асоцијација, математичко моделовање, програми ION–2, ION–3, хемијско инжењерство земљишта, уређај за измјене унутар земљишта и примјену других супстанци