



## Intra-soil waste recycling provides safety of environment

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**Abstract** Amelioration and remediation technology was developed for phosphogypsum utilization in Haplic Chernozem of South-European facies (Rostov Region). The technology comprises phosphogypsum dispersed application into the soil layer of 20–45 cm during intra-soil milling. In the model experiment, the phosphogypsum doses 0 (control), 10, 20, and 40 t ha<sup>-1</sup> were studied. The Cd thermodynamic forms in soil solution were calculated via the developed mathematical chemical-thermodynamic model and

program ION-3. The form of ion in soil solution (or water extract) was considered accounting the calcium-carbonate equilibrium (CCE) and association of ion pairs  $\text{CaCO}_3^0$ ,  $\text{CaSO}_4^0$ ,  $\text{MgCO}_3^0$ ,  $\text{MgSO}_4^0$ ,  $\text{CaHCO}_3^+$ ,  $\text{MgHCO}_3^+$ ,  $\text{NaCO}_3^-$ ,  $\text{NaSO}_4^-$ ,  $\text{CaOH}^+$ ,  $\text{MgOH}^+$ . For calculation of the equilibrium of microelements concentration in soil solution ion including heavy metals (HMs), the coefficient of microelement association  $k_{\text{as}}$  was proposed. According to calculations, Cd<sup>2+</sup> ion in soil solution was mostly bounded to associates  $\text{CdOH}^+$ , partly to associates  $\text{CdCO}_3^0$  and  $\text{CdHCO}_3^+$ . The calculated  $k_{\text{as}}$  of Cd was 1.24 units in the control option of

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experiment and decreased to 0.95 units at phosphogypsum dose  $40 \text{ t ha}^{-1}$ . The ratio of “active  $[\text{Cd}^{2+}]$  to total Cd” reduced from 33.5% in control option to 28.0% in the option of phosphogypsum dose  $40 \text{ t ha}^{-1}$ . The biogeochemical barrier for penetration of HMs from soil to plant roots was high after application of phosphogypsum. According to calculation by ION-3, the standard soil environmental limitations overestimate the toxicity of Cd in soil solution. New decision for intra-soil milling and simultaneous application of phosphogypsum was developed to provide the environmentally safe waste recycling.

**Keywords** Heavy metals · Soil solution · Ion association · Calcium-carbonate equilibrium · Biogeosystem Technique · Environmentally safe phosphogypsum intra-soil recycling

## Introduction

Application of pesticides, nutrients, and amendment to the soil is a source of heavy metals (HMs) in the environment and biological production from contaminated soil (Enamorado et al., 2014; Nisti et al. 2015)

The current technology increases the level, uncertainty and danger of Cd for the biosphere (Moreno-Jiménez et al., 2014). The dangerous pollutant Cd is spreading in the ecosphere via eolian and water transfer, deteriorating soil health (Motuzova et al., 2014; Pardo et al., 2014; Zrelli et al., 2019).

Bioavailability of HMs relates to their activity in soil solution. Ion activity depends on the soil solution ionic strength, ion association, and complexation of ions (Endovitsky et al., 2015). The wet phosphorus fertilizer technology by-product is phosphogypsum. Standard phosphogypsum waste utilization technology increases the content of contaminants in soil (Saadaoui et al., 2017). This requires new waste recycling methods combined with soil mechanical processing and amendment application. The intra-soil passivation of dangerous substances reduces uncontrolled eolian and hydrological spread of contaminants in the environment (Kalinichenko et al., 2020a; Zrelli et al., 2019). Cd and many other contaminants are not only spreading, but also supplied with fertilizers and technogenic contaminants. It should be noted that the contaminants are simultaneously the microelements

and macroelements helpful for the plant nutrition and amendments for the enhancement of soil physical, chemical, and physicochemical properties. (Bech et al., 2014; Kalinichenko, 2016, 2017a; Xiong et al., 2014). But not all contaminants are the safe microelements and macroelements for plant nutrition. Cd is an extremely dangerous contaminant for plant and trophic chains (Dastyar et al., 2019). This circumstance presumes a special care of application to the soil the substance containing Cd.

The soil total and water-soluble Cd form content depend on geographical location, ionic composition of soil solution, and soil genesis. The mean total Cd content in soils of the South Russia is about  $1 \text{ mg kg}^{-1}$  SDW (Bezuglova et al., 2016). This value is approximately the same for the soils over the world. Cd content in soil is circa  $0.1\text{--}2.39 \text{ mg kg}^{-1}$  (Environment Agency, 2009). The soil limit concentration of Cd in different regulations makes up from  $1.8 \text{ mg kg}^{-1}$  DW in Great Britain according to Soil Guideline Values (SGV) (Environment Agency, 2009) and  $2 \text{ mg kg}^{-1}$  DW in Russia according to indicative permissible concentrations (IPC) (Maximum permissible concentrations, 2006) to  $12 \text{ mg kg}^{-1}$  (Dutch Target and Intervention Values, 2000; Guidelines for the Safe Application of Biosolids to Land in New Zealand, 2003; Envirolink, 2006 73p).

The limit depends on the soil and landscape properties and use (US Environmental Protection, 2020–01–30). The data on selective chemical extraction of HMs from soil and lithosphere encourage new developments in the field of HMs passivation (Hilton, 2015; Kalinichenko et al., 2013). Soil biogeochemical barrier prevents HMs penetration to the plants. This phenomenon supports an attempt to reinforce the barriers for HMs transfer throughout the ecosphere. For this purpose, new technologies of soil and landscape reclamation and remediation are to be synthesized.

The mobility of Cd in the soil solution as well as its penetration into the plants depends on the content of carbonates and pH of the soil. The remineralization, liming and composting of the soil are capable to reduce the HMs transfer and penetration to plants (Hideo & Crusciol, 2016). Cd mobility in soil is linked to the thermodynamic activity of the free  $\text{Cd}^{2+}$  ion and to the rate of  $\text{Cd}^{2+}$  binding to ion associates and complexes. Thermodynamic activity of  $\text{Cd}^{2+}$  ion depends on the calcium-carbonate equilibrium

(CCE) in the soil solution. Accounting on the CCE as an important phenomenon influencing the soil solution properties, the molar fraction of active Cd<sup>2+</sup> in soil solution is lower than the total content of Cd in soil (Endovitsky et al., 2015).

Phosphogypsum contains Cd<sup>2+</sup>. The phosphogypsum production in the world is from 150 to 280 t year<sup>-1</sup>. Phosphogypsum contains more than 60 chemical elements (Goswami & Nand, 2015; Saadaoui et al., 2017; Tayibi et al., 2009). USEPA has classified the PG as a “Technologically Enhanced Naturally Occurring Radioactive Material” (TENORM).<sup>19</sup> (Tayibi et al., 2009). Any use of phosphogypsum is banned in most countries. Phosphogypsum utilized is the open stack tailing or in ponds. The result is direct and delayed hazardous eolian and hydrological pollution (Hentati et al., 2015; Kalinichenko et al., 2020a).

Cd content in phosphogypsum depends on the Cd concentration in phosphate rocks (Cadmium in fertilizers, 2000). Cd content differs in the world deposits as follows: Phalaborwa (South Africa) 4 mg kg<sup>-1</sup>, Bou Craa (Morocco) 38 mg kg<sup>-1</sup>, North Carolina (USA) 47 mg kg<sup>-1</sup>, Nauru 100 mg kg<sup>-1</sup> (Contaminants and the Soil Environment 1996). The Kovdor apatite (Russia) ore is of high environmental quality. Concentration of Cd in this ore is low, about 0.2 mg kg<sup>-1</sup> (Lapin & Lyagushkin, 2014). The activity of the Morocco K deposit is 10 560 Bq kg<sup>-1</sup>; Florida deposit (USA) 1000 Bq kg<sup>-1</sup> (Casacubertaa et al., 2009; Hilton, 2010). The activity of the Kovdor apatite (Russia) ore is as low as 20 Bq kg<sup>-1</sup>. In consequence, the environmental quality for soil amelioration of phosphogypsum produced from the Kovdor apatite ore is high (Gázquez et al., 2014).

The Haplic Chernozem previously believed the soil has no morphological and physicochemical prerequisites for reclamation with phosphogypsum. According to new findings, this world famous soil acquired obvious features of degradation in recent decades (Bezuglova, 2019). Inappropriate land use has converted the Haplic Chernozem to the reservoir for phosphogypsum utilization. Many research noted the HMs accumulation in the soil after application of phosphogypsum (Tayibi et al., 2009, 2012). But the change of HMs content in soil after phosphogypsum application was not highly significant compared to the natural HMs content in soil (Nayak et al., 2011). However, an additional peculiarities of the phosphogypsum recycling in soil is not only a Cd content, but

the content of many other HMs—Pb, Be, B, Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Ag, Cd, Sb, Cs, Ba, Tl, Th, U (Amari et al., 2017; Enamorado et al., 2014).

There are few options for phosphogypsum application to the soil. In the no-till soil management system framework, the phosphogypsum is applied to the soil surface without mixing with soil (Crusciol et al., 2016). Phosphogypsum can be applied to the soil surface and then mixed with the top soil mechanically. Agricultural, construction and road machinery with passive working bodies are used to fulfill the operation of phosphogypsum application to the soil (Akanova, 2013). Soil processing of this kind causes poor soil crumbling and mixing. The soil blocks have too big transverse dimension about 50–100 mm. In result, the particles of phosphogypsum stay on the soil surface and thus are freely involving into the uncontrolled eolian transfer. Another part of phosphogypsum particles pour into the soil between the soil blocks while soil mechanical processing. Being not mixed with soil, these particles become involved into the uncontrolled hydrological process. Only a small part of the soil aggregate system is enriched with phosphogypsum as amelioration agent. In such circumstances, the concentration of HMs on the surface of soil aggregate is higher compared with mean target concentration in the soil layer to which phosphogypsum has been applied. At the same time, the plant roots prematurely occupy dispersed fine aggregated soil material between large soil blocks. HMs located in this zone of plant priority nutrition cause transfer of pollutants to plant and subsequent contamination of the biological product in consequence of the standard soil amelioration and remediation technology.

The pollutant toxicity, mobility and bioavailability in the soil are to be minimized (Bech et al., 2014; Hentati et al., 2015). The goal is declared to improve the phosphogypsum utilization methods and to develop the future chemical engineering (Hilton, 2015).

Most models of HMs bioavailability prediction consider the free ion form. However, the trace metals spread in the environment not only as free ions, but in the form of associated ions and complexes of HMs with organic and inorganic soil matter. Ion association and complexation decrease Cd mobility in soil. Thus, the Cd availability to enter the plant root system reduces. We have substantiated this circumstance on

the basis of theoretical thermodynamics of electrolytes and in the field experiments (Endovitsky et al., 2015; Sukovatov, 2009).

For understanding the origin of soil remediation, the pattern of carbonate-calcium equilibrium in the soil solution is important. The variability of the chemical composition of soil solution causes the destruction and synthesis of organic substances, secondary minerals, organomineral compounds. An important chemical equilibrium in soil solutions is calcium carbonate equilibrium (CCE) (Minkina et al., 2012). The CCE depends on and influences the chemical composition, pH, Eh, buffering properties of liquid phase, dissolution, migration, precipitation of carbonates in the soil profile and landscape. The ion exchange at the interface of solid and liquid phases is linked to the CCE. The CCE helps to calculate the  $\text{CaCO}_3$  solubility. The change of the ionic strength of solution determines the transformation of ion into the form of ion associate. The rate of  $\text{Cd}^{2+}$  transfer to the plant depends on the content of carbonates in soil as well as on the soil pH value. The thermodynamic activity of  $\text{Cd}^{2+}$  free ions can be decreased because  $\text{Cd}^{2+}$  ion bounds into associates with other ions (Minkina et al., 2012).

Based on our research, we have developed the chemical soil engineering technology to decide simultaneously the tasks of soil contamination decrease, soil amelioration and soil remediation (Kalinichenko et al., 2020a). The technology based on the Bio-geosystem Technique (BGT\*) methodology provides environmentally safe phosphogypsum application to the soil and helps to re-evaluate the current TENORM and other environmental limitations. The BGT\* methodology basis is a transcendental nature-similarity approach to the management of ecosphere health and productivity. The approach is focused not on the direct imitation of natural phenomena, but on triggering the process which nature does not bring to a finish. This new indirect transcendental nature-similarity approach provides formation of the new niche of developing capabilities to improve significantly the soil amelioration and remediation theory addressing environmental safety concerns of ecosphere management for better soil health (Kalinichenko, 2017b; Pardo et al., 2014).

The aims of research include: modelling the  $\text{Cd}^{2+}$  thermodynamic status in the soil solution of the Haplic Chernozem in the Rostov Region; substantiation of the

intra-soil ameliorative mechanical processing for environmentally safe phosphogypsum recycling in the Haplic Chernozem in the Rostov Region providing the remediation and stable evolution of fertile soil; heuristic synthesis of the new intra-soil device for the simultaneous soil reclamation, remediation, passivation of pollutants, and soil health improving.

## Materials and methods

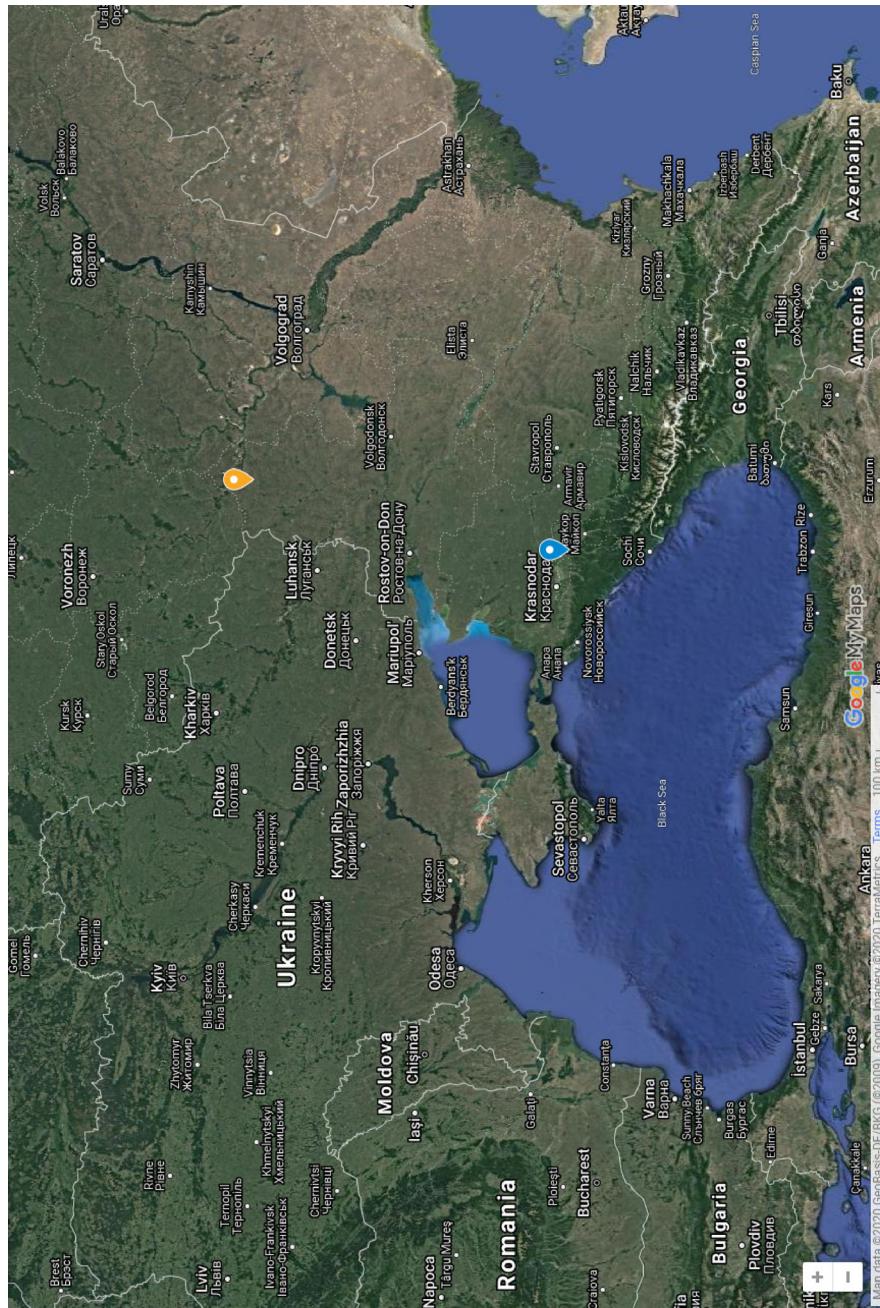
### Research object

The study object was Haplic Chernozem of the northern part of the Rostov Region (Fig. 1, blue mark). Terrain is a plains-type watershed for the river Don. The Haplic Chernozem area is located in the southwest of the Russian Federation. The soil belongs to the Eurasian steppe chernozem belt. According to the IUSS Working Group WRB (2015) classification, the soil full name is the “steppe non-saline low freezing Haplic Chernozem of South-European facies”.

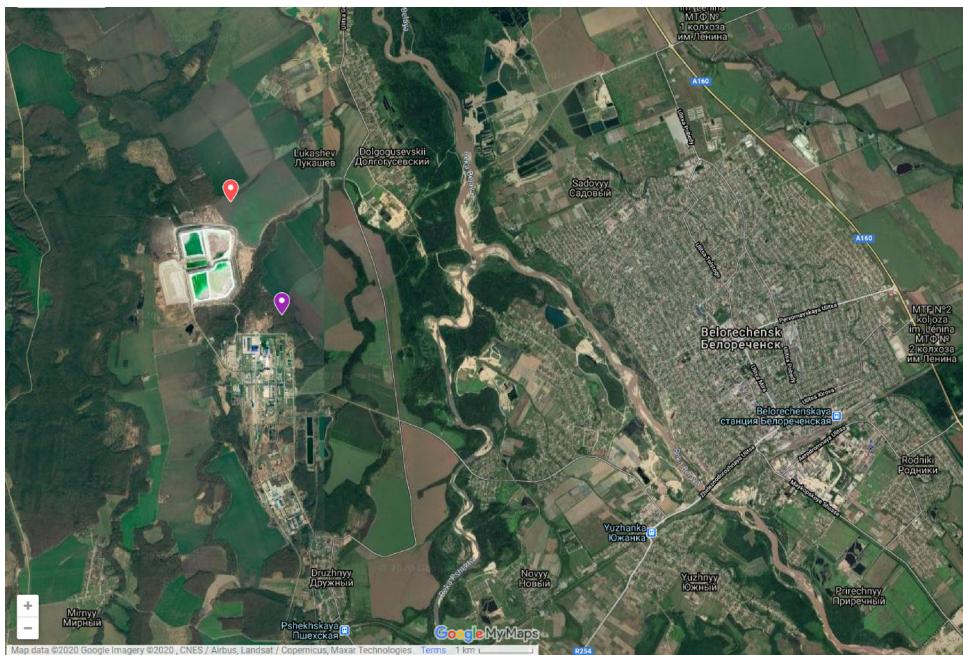
Soil environment in the Chernozem zone is closely associated with climate. The climate of the northern part of the Rostov Region is continental, semiarid. Annual precipitation is about 400–500 mm (Panov et al., 2006). The parent rocks are carbonate and carbonate-sulfate loess-like loam and clay. The landscape is automorphic. The Haplic Chernozem is moderately thick, horizon A of 52 cm, low solonized, humus 3.6%, physical clay 47.7%, clay 29.5%,  $\text{CaCO}_3$  0.15% (up to 3–10% at the depth of 0.8–1.5 m),  $\text{pH} = 7.8$ , exchangeable cations:  $\text{Ca}^{2+}$ —282  $\text{mmol kg}^{-1}$ ,  $\text{Mg}^{2+}$ —55  $\text{mmol kg}^{-1}$ ,  $\text{Na}^+$ —14  $\text{mmol kg}^{-1}$  (Bezuglova, 2019). The total background content of Cd (Clark) is about 1  $\text{mg kg}^{-1}$  SDW (Bezuglova et al., 2016).

### Phosphogypsum

Phosphogypsum used for research originated in the Belorechensk chemical plant (Fig. 2, red mark) from the Kovdor apatite ore as a by-product of the end-of-pipe sulfuric acid technology of the phosphorus fertilizer production. The phosphogypsum technological stages on the Belorechensk chemical plant include: mechanical removal of phosphogypsum after  $\text{P}_2\text{O}_5$  extraction; neutralization of the phosphogypsum



**Fig. 1** South Russia territory (Satellite map). \*Blue mark—Belorechensk chemical plant; yellow mark—North Rostov Region Haplic Chernozem



**Fig. 2** Belorechensk — the source of air, soil, water and landscape contamination with phosphogypsum (Satellite map). \*Violet mark—Belorechensk chemical plant; red mark—phosphogypsum ponds of the Belorechensk chemical plant

sludge acid residue to pH 5.0–5.3 using the lime milk; transportation of the pulp to the open sludge ponds. The open sludge ponds are the source of pollution of the soil, surface runoff, ground water, and the rivers Ganzha, Pshekha, and Belaya (Fig. 2). The total content of  $Pb^{2+}$  in phosphogypsum is  $55.98 \text{ mg kg}^{-1}$  SDW; the water-soluble form  $Pb^{2+}$  content is  $10.48 \text{ mg kg}^{-1}$  SDW. The total content of  $Cd^{2+}$  in the phosphogypsum is  $2.76 \text{ mg kg}^{-1}$ , and the content of  $Cd^{2+}$  water-soluble form is  $0.33 \text{ mg kg}^{-1}$  (Batu-kaev 2016). The total content of F is about 0.12% (Belyuchenko, 2014).

### Model experiment

In model experiment, the application of phosphogypsum in the 20–45 cm soil layer of Haplic Chernozem was simulated. The doses of phosphogypsum were 0 (control), 10, 20, and  $40 \text{ t ha}^{-1}$ .

For model experiment, the soil samples were taken from the illuvial horizon of Haplic Chernozem. This soil layer is inclined to the natural and technogenic compaction because of the heavy granulometric composition of soil. It has bad soil structure and adverse architecture of the soil porous media. The

properties of the illuvial horizon of Haplic Chernozem reflect a need for the soil chemical reclamation. We developed a methodological approach of direct amendment application to the target soil layer, improving properties of illuvial horizon and reducing HMs anthropogenic excess in the upper layer of Haplic Chernozem. Soil samples were grounded and sieved through a screen with 2-mm wire mesh. The sifted soil was mechanically mixed with phosphogypsum in the doses 0 (control), 10, 20, and  $40 \text{ t ha}^{-1}$ .

A prepared soil and phosphogypsum mix was humidified to 25–30% SDW. Then, the mix was placed in the hermetic container for a week. This period is sufficient for reaching the soil and phosphogypsum physicochemical equilibrium, providing reliability of further analyses (Endovitsky et al., 2017).

The scheme of the model experiment involved three repetitions.

### Sampling and analysis

Soil samples were analyzed by the conventional widely accepted standard analytical methods (Carter & Gregorich, 2007; Minkina et al., 2012; Shtiza & Swennen, 2011). The water extraction of soluble salts

was fulfilled under water-to-soil ratio 5:1, followed by shaking of the mixture for 5 min. Mixture was placed in a chemical funnel on a paper filter, and the soil solution was extracted. The water extract dry residue content was determined by oven drying at 105° C. The pH was measured in thermostat ( $20 \pm 0.2^\circ\text{C}$ ) using an ion meter with a glass electrode ITAN (TomAnalit Ltd, Russia). The carbonate and bicarbonate anions were titrated directly by 0.01 M hydrochloric acid with the endpoint determined by the color change of standard indicators. The  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ , and  $\text{Na}^+$  contents were measured by standard chemical methods: Chloride ion was analyzed by the argentometric method with potassium chromate;  $\text{Ca}^{2+}$  +  $\text{Mg}^{2+}$  total content was detected by complexometric titration, and  $\text{Ca}^{2+}$  was detected in another aliquot complexometrically; content of  $\text{Mg}^{2+}$  was calculated as a difference of  $\text{Ca}^{2+}$  +  $\text{Mg}^{2+}$  and  $\text{Mg}^{2+}$ ; sulfates were analyzed by  $\text{BaSO}_4$  sedimentation;  $\text{Na}^+$  content was analyzed by flame photometric detection using a flame photometer PFP7 (JENWAY, UK).

The soil total content of Cd was determined by X-ray fluorescence (XRF) method on the X-ray fluorescent scanning spectrometer “SPECTROSCAN MAX-GV” (NPO Spectron, St. Petersburg, Russia). This method is listed by producer for HMs determination in soil and is included in the register of methods approved for the state and industrial environmental monitoring of the Russian Federation (PND F 16.1.42–04, 2004). Analytical quality of the XRF measurements was controlled by analyzing reference standard soil sample “Chernozem” No. 29107. Duplicates and reagent blanks were also used to control the quality of analysis. The concentration of water soluble Cd in soil solution was determined by atomic absorption spectrophotometry (AAS) (KVANT 2-AT, Kortec Ltd, Russia). The allowed deviation of X-ray fluorescent methods and AAS methods was less than 10–15% for HM determination in soil.

#### Thermodynamic model of the soil solution

The thermodynamic approach was applied to study the soil solution origin and function and substantiate the phosphogypsum doses for application to the soil. The thermodynamic state of soil solution chemical equilibrium is influenced by CCE, which determines a proportion of molar fractions of free and associated

macro-ion as well as microelement ion in solution. In its turn, the CCE is altered by ion's association and depends on soil liquid phase chemical composition, pH, Eh. The buffering properties, dissolution, migration, and precipitation of carbonates in the soil profile and landscape influence the CCE much. The CCE is an important driver of the origin and function of ion exchange processes at the soil solid, liquid and gaseous phase interfaces (Endovitsky et al., 2015; Grassian, 2018; Tenno et al., 2016). The CCE influences the gas exchange in “soil—atmosphere” system, partial pressure and seasonal cycles of soil  $\text{CO}_2$ . In result of different equilibria, the ion pairs exist in the soil solution in the form of  $\text{CaCO}_3^0$ ;  $\text{CaSO}_4^0$ ,  $\text{MgCO}_3^0$ ,  $\text{MgSO}_4^0$  (neutral), and the  $\text{CaHCO}_3^+$ ,  $\text{MgHCO}_3^+$ ,  $\text{NaCO}_3^-$ ,  $\text{NaSO}_4^-$ ,  $\text{CaOH}^+$ ,  $\text{MgOH}^+$  (charged) ion pairs.

We developed a mathematical model ION-3 to reveal the soil solution thermodynamics (for details, see Supplementary Information). The model considers the fundamental laws of electrolyte theory (Endovitsky et al., 2015; Sposito, 1989, 2013). We applied to the model the chemical thermodynamics phenomena as follows.

The higher is the ionic strength of the solution, the more is the number of ions which pass to the formation of associated ions. The CCE system of soil solution involves the dynamic equilibria: adsorption-hydration; solution balance between the gas phase and bioorganic phase; carbonic acid dissociation stages; calcium carbonate equilibrium between soil solution, soil absorbing complex,  $\text{CaCO}_3$  and solid phase sedimentation; water ions equilibrium. Soil solution ionic strength, ions equilibrium constants, and free and bounded macro-ion forms interactions are accounted depending on the macro-ion origin.

The free anions and macro-ion pair equilibrium concentrations  $[\text{CO}_3^{2-}]$ ,  $[\text{HCO}_3^-]$ ,  $[\text{SO}_4^{2-}]$ ,  $[\text{Cl}^-]$ ,  $[\text{OH}^-]$  influence the  $\text{Cd}^{2+}$  soluble form content in water extract. In the given soil solution, the Cd content can be presented as a proportion of free and bounded macro-ion forms calculated using the thermodynamic stability constants of the  $\text{Cd}^{2+}$  forms.

A potentially hazardous HM in soil can be considered as microelement (Batukaev et al., 2016). To characterize the thermodynamic state of microelement in soil solution, we proposed the microelement association coefficient  $k_{\text{as(ME)}}$ . This coefficient indicates a level of potentially hazardous HMs binding

into associates and complexes with main ions of soil solution. The meaning of the term “coefficient of ion association  $k_{as}$ ” is consistent with the electrolyte thermodynamics theory and corresponds to different empirical data of experiments in vitro and in situ (Endovitsky et al., 2017).

The chemical thermodynamics equations for the HMs association in soil solution used in the model are presented below.

The equation for the microelement is as follows (Eq. (1)):

$$C_{ME} = (1 + k_{asME})[C_{ME}] \quad (1)$$

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

The association coefficient for the  $\text{Cd}^{2+}$  ion is as follows (Eq. (2)):

$$\begin{aligned} k_{asCd} = & [\text{CO}_3^{2-}] (K(\text{CdCO}_3))^{-1} \\ & + [\text{HCO}_3^-] (K(\text{CdHCO}_3))^{-1} \\ & + [\text{SO}_4^{2-}] (K(\text{CdSO}_4))^{-1} \\ & + [\text{Cl}^-] (K(\text{CdCl}))^{-1} + [\text{OH}^-] (K(\text{CdOH}))^{-1} \end{aligned} \quad (2)$$

where  $[\text{CO}_3^{2-}]$  and other are the equilibrium concentrations of macro-element ions;  $K(\text{CdCO}_3)$  and other are the equilibrium constants.

The free and bound microelement (HM) ion molar fractions were taken into account. Coefficient of ion association is as follows (Eq. (3)):

$$\nu_{\text{free}} = 1/(1 + k_{asME})100, \% ; \nu_{\text{bound}} = 100 - \nu_{\text{free}} \quad (3)$$

Equation (2) rewritten for the  $\text{Cd}^{2+}$  content is as follows (Eq. (6)):

$$\begin{aligned} \text{Cd}^{2+} = & [\text{Cd}^{2+}] [1 + [\text{CO}_3^{2-}] (K(\text{CdCO}_3))^{-1} \\ & + [\text{HCO}_3^-] (K(\text{CdHCO}_3))^{-1} \\ & + [\text{SO}_4^{2-}] (K(\text{CdSO}_4))^{-1} + [\text{Cl}^-] (K(\text{CdCl}))^{-1} \\ & + [\text{OH}^-] (K(\text{CdOH}))^{-1}] \end{aligned} \quad (4)$$

where  $[\text{Cd}^{2+}]$  is the equilibrium content of Cd.

As a rule, the Cd concentration in soil solution is much less than macro-ions concentration. This is why the Cd content has a little effect on the value of formal soil solution ionic strength as well as on effective soil solution ionic strength value. This was the reason to exclude Eq. (4) from the equation system for macro-ions. A separate equation for trace element simplifies the calculation procedure. The simplification increases the reproducibility and reliability of the mathematical model. The unstable associates of  $\text{Cd}^{2+}$  were considered in the model as insignificant. The thermodynamic contribution of unstable forms of  $\text{Cd}^{2+}$  associates to the resulting content of  $\text{Cd}^{2+}$  in soil solution is small and does not influence resulting equilibrium. The calculation procedure is more effective and reliable according to the less is an equation's number of the equation system for the content of  $\text{Cd}^{2+}$  in soil solution. The value of the associates of  $\text{Cd}^{2+}$  thermodynamic stability constants was borrowed from Sposito (1989)  $\text{CdCO}_3^0$ ,  $\text{CdHCO}_3^+$ , and Lurie (1975)  $\text{CdSO}_4^0$ ,  $\text{CdCl}^+$ ,  $\text{CdOH}^+$ .

The CCE thermodynamic mathematical model, algorithm, and program ION-3 are presented in more detail in our former publications (Batukaev et al., 2016, 2017; Endovitsky et al., 2015; Kalinichenko et al., 2018, 2020a; Minkina et al., 2016).

#### Heuristic synthesis of the device for intra-soil mechanical processing and intra-soil application of matter

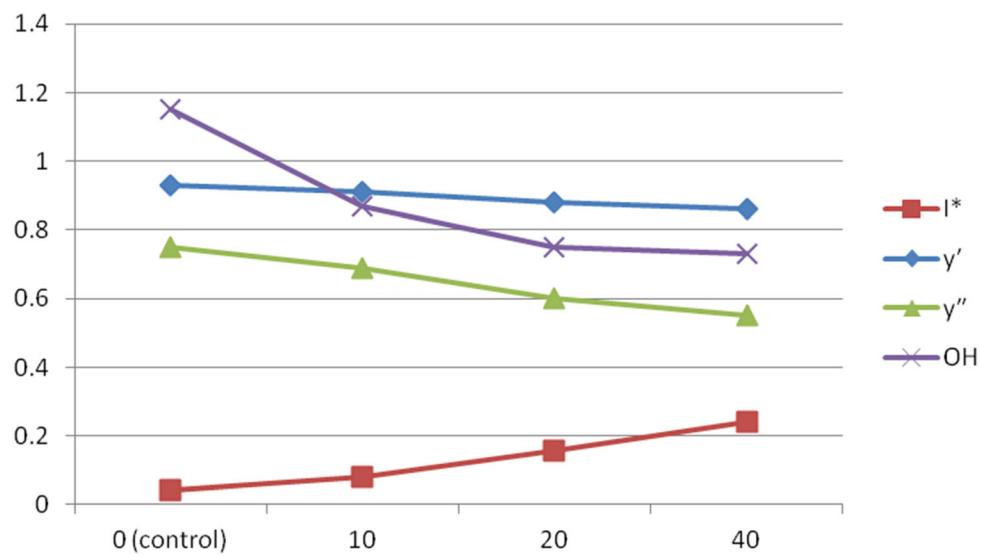
Heuristic synthesis of the new device for application of the soil amendment and waste at the same time with intra-soil mechanical processing has been made avoiding commonly used imitative biotechnical approach. Our approach can be qualified as an educated guess heuristic—when a decision responds the relevant multifaceted information relating to the problem, and carries the signs of brainstorming. We based the heuristic approach on the qualified intuition, which is capable to give a transcendental decisions (differed from previous knowledge having no direct analogy with natural processes and standard practice) to overcome the long-term systemic disadvantages of the known before approach. The transcendental transformation of intra-soil aggregate system and dispersed placement of amendment and waste in the newly

synthesized soil aggregate system provide new technology high quality compared to the approach known before.

We have taken into account a potential capability of the intra-soil mechanical processing to provide the soil structure loosening and the soil macroaggregates and microaggregates mixing with applied material. The new soil aggregate system stabilizes a biogeochemical barrier “soil—plant”, reducing penetration of pollutants into the plant. At the same time this ensures enriched biogeochemical turnover of the useful substances for plant nutrition applied intra-soil (Mishchenko et al., 2009; Peries & Gill, 2015; Totsche et al., 2018). The synthesized multilevel heterogeneous soil architecture provides polymicrobial biofilms and soil organic matter priority origination and function (Kamjunke et al., 2019; Lin, 2012; Swidsinski, 2019).

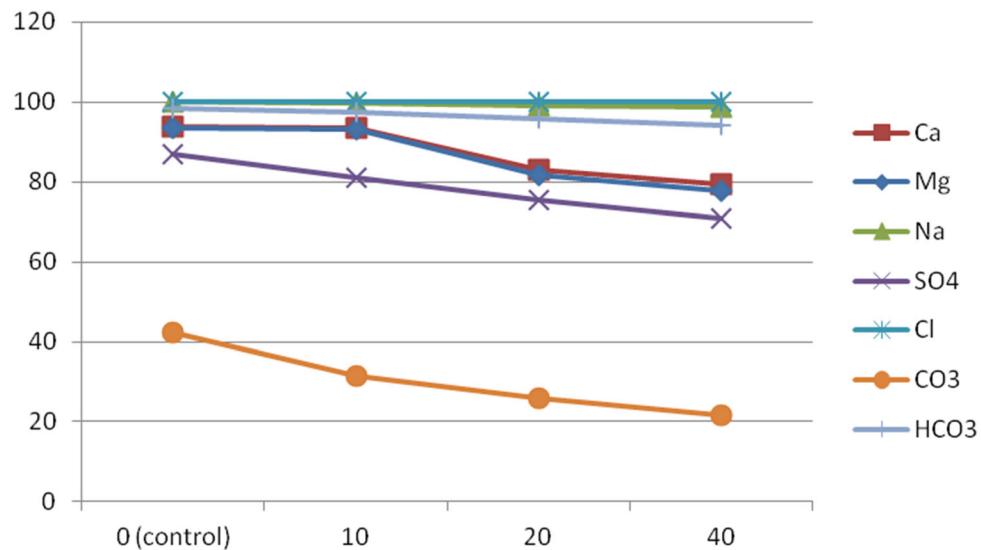
The heuristic preconditions of the techno-soil synthesis were as follows: A top soil horizon of 0–25 (or 0–30) cm after the soil mechanical processing remains intact; a horizon of 25–50 (or 30–70) cm was crushed via intra-soil mechanical processing to a particle size of 1–3 mm. The goal is to provide the portion of these particles in the soil mass about 40% (2–3 times higher than in initial compacted soil illuvial horizon); the processed soil mass is well mixed in the course of processing; the mixture of water and phosphogypsum and/or other waste (the pulp or granular form is acceptable) is supplied to the soil horizon of 25–50 cm (or 30–70 cm according to the soil and technological preconditions) and is mixed with soil mass simultaneously with its mechanical processing. Different soil layers 25–50 cm or 30–70 cm for intra-soil mechanical processing are chosen focusing on the rhizosphere potential depth of different plants. For the tree rhizosphere, the intra-soil mechanical processing of the 30–70 cm soil layers we assess is preferable (Kalinichenko et al., 2021). For the annual plants, the intra-soil mechanical processing of the 20–50 cm soil layers was tested (Kalinichenko et al., 2014). The reduced loss of mineral and organic nutritional matter from the soil was accounted. The choice of the soil horizon is for processing links to the regional soil properties. Heuristic synthesis of the device for intra-soil mechanical processing and simultaneous phosphogypsum dispersed application to the discussed layer is based on the BGT\* methodology. The BGT\* methodological approach to the synthesis of the soil processing devices has been tested in the

Dose of phosphogypsum, t ha <sup>-1</sup>	pH	Total alkalinity (Alk <sub>Σ</sub> ), mol L <sup>-1</sup>	Ca <sup>2+</sup> × 10 <sup>-3</sup>	Mg <sup>2+</sup> × 10 <sup>-3</sup>	Na <sup>+</sup> × 10 <sup>-3</sup>	SO <sub>4</sub> <sup>2-</sup> × 10 <sup>-3</sup>	Cl <sup>-</sup> × 10 <sup>-3</sup>	(CO <sub>3</sub> <sup>2-</sup> ) <sub>A</sub> × 10 <sup>-6</sup>	(HCO <sub>3</sub> <sup>-</sup> ) <sub>A</sub> × 10 <sup>-4</sup>
0 (control)	8.03	0.44	0.75	0.55	0.201	0.58	1.20	2.549	4.085
10	7.90	0.44	1.45	1.05	0.261	0.81	3.00	2.025	4.095
20	7.82	0.36	3.65	1.50	0.290	3.60	3.00	1.523	3.354
40	7.80	0.40	6.05	2.30	0.302	5.96	4.40	1.742	3.725



**Fig. 3** Activity of the macro-ions and  $\text{OH}^-$  in soil solution after application of phosphogypsum (calculated by ION-3). \*Horizontal scale: dose of phosphogypsum,  $\text{t ha}^{-1}$  vertical

scale: effective ionic strength  $I^*$ ,  $\text{mol L}^{-1} \times 10^{-3}$ ; coefficient of ion activity  $y'$ ; coefficient of ion activity  $y''$ ; activity of the hydroxyl ion  $\text{OH}^-$



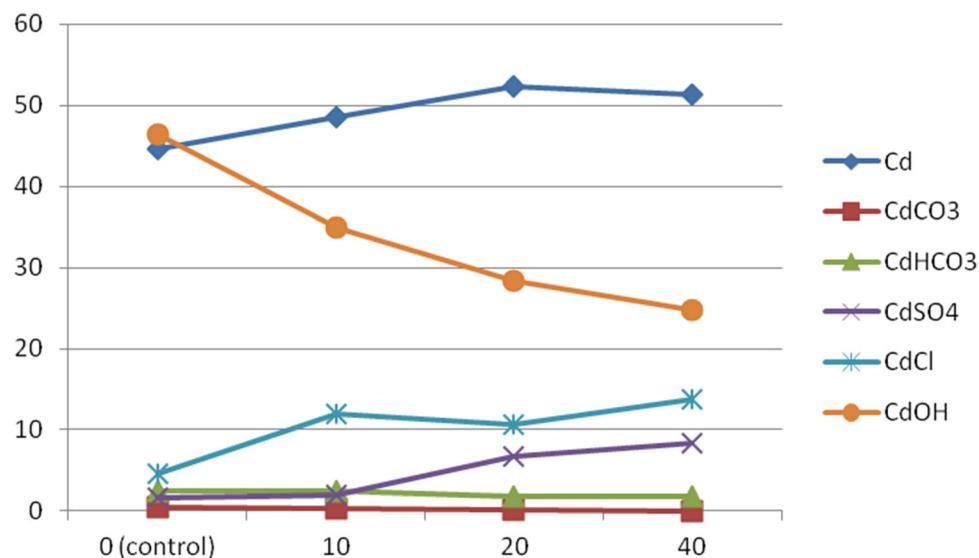
**Fig. 4** Equilibrium concentration of the soil solution macro-ion free form after application of phosphogypsum (calculated by ION-3). \*Horizontal scale: dose of phosphogypsum,  $\text{t}$

$\text{ha}^{-1}$ . Vertical scale: macro-ion free form percentage in soil solution,  $[\text{Ca}^{2+}]$ ,  $[\text{Mg}^{2+}]$ ,  $[\text{Na}^+]$ ,  $[\text{SO}_4^{2-}]$ ,  $[\text{Cl}^-]$ ,  $[\text{CO}_3^{2-}]_A$ ,  $[\text{HCO}_3^-]_A$

laboratory research, trials of equipment in the soil channel. The intra-soil processing has been applied and studied in the long-term field experiments. There are own patents on the theme of intra-soil processing and simultaneous application of matter (Kalinichenko, 2010, 2016; Kalinichenko et al., 2013, 2014, 2016, 2019).

#### Data statistical processing

The experiments were performed in triplicate. Calculations of the associated errors and statistical significance of the data were performed with Statistica v.10.0.1011, developed by StatSoft (USA). All data



**Fig. 5** Percentage of the mole fraction of water-soluble Cd in water extract from soil after phosphogypsum application (calculated by ION-3). \*Horizontal scale: dose of

presented in the tables and in the text are statistically significant at the level of  $p < 0.05$ .

## Results and discussion

### Analytical content of macro-ions

The analytical content of macro-ions in water extract from Haplic Chernozem after application of phosphogypsum in different doses was obtained in the model experiment (Table 1). The data on the macro-ion content are typical for the soil studied.

### Results of thermodynamic mathematical modeling of the Cd equilibrium concentration

Calculation of the Cd equilibrium concentration in water extract was carried out using the equation system of the soil solution macro-ion equilibrium forms by the thermodynamic mathematical model ION-3 (see the Supplementary Information, Endovitsky et al., 2015; Kalinichenko et al., 2018). The calculation was fulfilled according to the data of Table 1. The results of calculation by ION-3 of activity of the macro-ions and  $\text{OH}^-$  in soil solution after application of phosphogypsum are presented in Fig. 3. The equilibrium concentration of the soil

phosphogypsum,  $\text{t ha}^{-1}$ . Vertical scale: mole fraction of water-soluble Cd in water extract,  $[\text{Cd}^{2+}]$ ,  $[\text{CdCO}_3^0]$ ,  $[\text{CdHCO}_3^+]$ ,  $[\text{CdSO}_4^0]$ ,  $[\text{CdCl}^+]$ ,  $[\text{CdOH}^+]$

solution macro-ion-free form after application of phosphogypsum is presented in Fig. 4.

According to the data of Table 1, the macro-ion concentration in water extract was low. Nevertheless, according to Figs. 3, 4, the soil solution ionic strength influences significantly the thermodynamic process of macro-ions association. The stability constants of associated and complex ions were calculated via thermodynamic mathematical model ION-3 according to the soil solution ionic strength. Calculated values of stability constants differed from the corresponding thermodynamic values. In particular, the calculated values of ion activity coefficient reduced for both single-charged ( $y'$ ) and double-charged ( $y''$ ) ions. The  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{SO}_4^{2-}$  molar fraction in solution calculated according to the value of effective ionic strength  $I^*$  (see Supplementary Information), became a little bit less compared with the ionic strength value  $I$  calculated according to the data in Table 1. At a higher phosphogypsum dose, the calculated percentage of the  $\text{CO}_3^{2-}$  molar fraction is reduced by several times compared analytical value.

The typical Cd water soluble forms content in Haplic Chernozem about 13–14% was accounted in further calculations (Bezuglova et al., 2016; Minkina et al., 2012).

Left part of Eq. (4) was substituted with  $\text{Cd}^{2+}$  total concentration value in the water extract. This value

was equal to the initial soil water extract value for the control option of the model experiment. The left part of Eq. (4) is the sum of the Cd<sup>2+</sup> content in the water extract from initial soil and the corresponding Cd<sup>2+</sup> content in the given phosphogypsum dose option of the model experiment. Macro-ions equilibrium concentrations and thermodynamic stability constants of corresponding Cd associated ions, calculated via ION-3 (see Supplementary Information), are presented in the right part of Eq. (4). Equilibrium constants of ions were borrowed from G. Sposito (1989). These data were accounted in the calculation of thermodynamic stability constant.

The concentration of water-soluble Cd<sup>2+</sup> and the mole fraction form of Cd<sup>2+</sup> in the water extract from soil were calculated via the program ION-3. Equilibrium concentration of [Cd<sup>2+</sup>] was calculated using the Cd<sup>2+</sup> total concentration value and corresponding  $k_{as}$ . Active (free) concentration a[Cd<sup>2+</sup>] was calculated as a product of the [Cd<sup>2+</sup>] equilibrium concentration and corresponding Cd<sup>2+</sup> ion activity (mole fraction). Result of calculation is presented in Eqs. (5–6) and in Figs. 5–7.

The calculation of the soil solution equilibrium for the phosphogypsum doses of 0 (control) and 40 t ha<sup>-1</sup> via Eq. (4) is presented in the digital form by Eqs. (5–6):

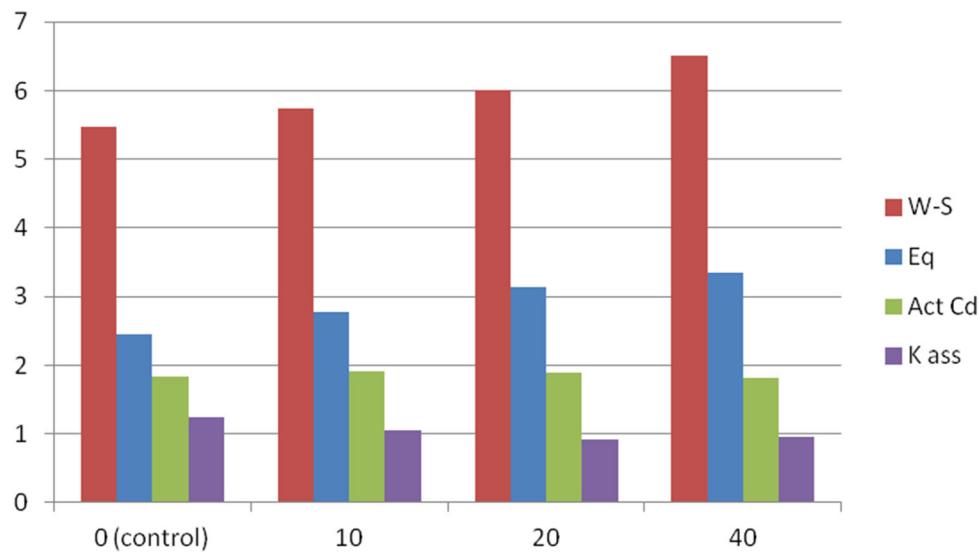
$$\begin{aligned} \text{Phosphogypsum } 0 \text{ t ha}^{-1} \\ 5.872 \times 10^{-8} = & [\text{Cd}^{2+}] (1 + 10^5 [\text{CO}_3^{2-}]) / 10.37 \\ & + 10^3 [\text{HCO}_3^-] / 7.30 \\ & + 10^3 [\text{SO}_4^{2-}] / 13.75 \\ & + 10^3 [\text{Cl}^-] / 11.86 \\ & + 10^7 [\text{OH}^-] / 11.07 \end{aligned} \quad (5)$$

$$\begin{aligned} \text{Phosphogypsum } 40 \text{ t ha}^{-1} \\ 6.91 \times 10^{-8} = & [\text{Cd}^{2+}] (1 + 10^5 [\text{CO}_3^{2-}]) / 19.73 \\ & + 10^3 [\text{HCO}_3^-] / 10.07 \\ & + 10^3 [\text{SO}_4^{2-}] / 26.15 \\ & + 10^3 [\text{Cl}^-] / 16.36 + 10^7 [\text{OH}^-] / 15.27. \end{aligned} \quad (6)$$

Cd<sup>2+</sup> ion is prematurely bound to hydroxo complex CdOH<sup>+</sup>. Contents of carbonates and bicarbonates CdCO<sub>3</sub><sup>0</sup> and CdHCO<sub>3</sub><sup>+</sup> forms of Cd<sup>2+</sup> were less than the content of the hydroxo complex form.

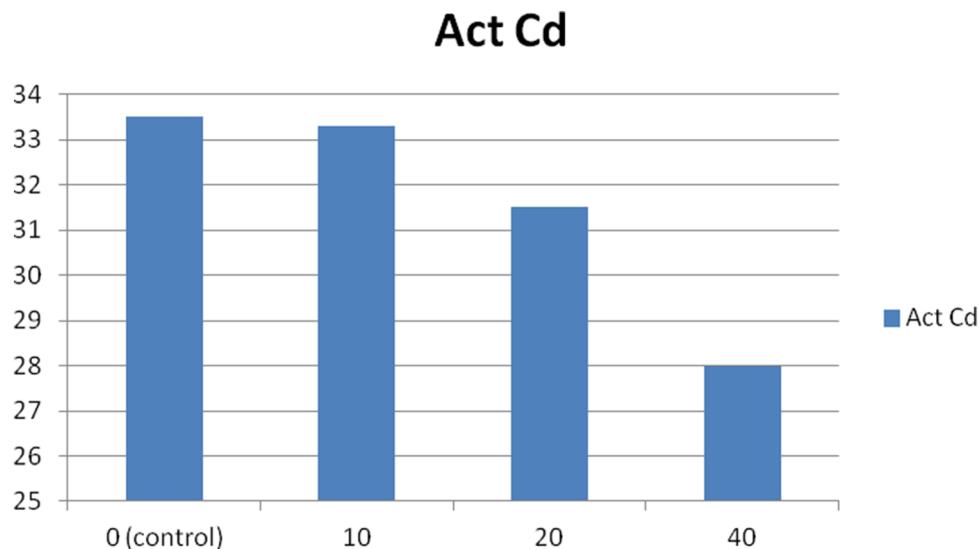
Calculation of the equilibrium forms of macro-ions showed that the large portion of ions Ca<sup>2+</sup>, Mg<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, and CO<sub>3</sub><sup>2-</sup> were presented in soil solution in the form of associates (Fig. 5). To assess the degree of ion binding to associate, we used a quantitative criterion—a difference of the total content of the ion (100%) and its free form percentage. According to the current state of equilibrium in the CCE system, the adsorption or the removal of Ca<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup>, and CO<sub>3</sub><sup>2-</sup> from the soil solution causes CaCO<sub>3</sub> deposition from the soil solution (or on the contrary—dissolution to the soil solution). This phenomenon of CCE determines the type of migration and accumulation of various carbonate forms and salts transfer throughout the soil profile and laterally between the soil complex components. This phenomenon determines a sink of carbonates to the vadose zone as well (Batukaev et al., 2016). When the phosphogypsum dose was higher, the calculated macro-ion activity reduced. Consequently, the assessment of the unfavorable mass transfer into the soil was less, as well as the prognosis of the uncontrolled mass transfer from soil to the vadose zone.

The content of Cd water-soluble form circa 0.031–0.037 mg kg<sup>-1</sup> was much less compared to the total content of Cd in soil about 0.22–0.29 mg kg<sup>-1</sup>. This circumstance is positive, concerning the probability of the HM penetration into the plant and after that to the trophic chains. The model ION-3 showed a change of activity of Cd<sup>2+</sup> in the soil solution after phosphogypsum application. Calculation by Eq. (2) showed that the  $k_{as}$  of Cd was 1.24 units in the control option of experiment and decreased with phosphogypsum dose increasing. At phosphogypsum dose 40 t ha<sup>-1</sup>  $k_{as}$  of Cd was 0.95 units. Calculated association coefficient  $k_{as}$  was 1.3 times less for the phosphogypsum dose of 40 t ha<sup>-1</sup> compared to the control option. We assess this decrease as not important circumstance, taking into account the fact that the value of ratio “active [Cd<sup>2+</sup>] to total Cd” reduced from 33.5% in control option to 28.0% in the option of phosphogypsum dose 40 t ha<sup>-1</sup>. A percentage of active concentration a[Cd<sup>2+</sup>] at phosphogypsum dose 40 t ha<sup>-1</sup> was lower by 1.2 times compared with the control option. The opposite tendencies substantiate a point of view that the biogeochemical barrier for penetration of HMs from soil to plant roots was sufficiently high after phosphogypsum application.



**Fig. 6** Concentration of the Cd forms in water extract from soil after phosphogypsum application (calculated by ION-3). \*Horizontal scale: dose of phosphogypsum,  $t \text{ ha}^{-1}$ . Vertical

scale: Water-soluble  $\text{Cd}^{2+}$ ,  $\text{mol L}^{-1} \times 10^{-7}$ ; equilibrium  $[\text{Cd}^{2+}]$ ,  $\text{mol L}^{-1} \times 10^{-7}$ ; Active  $[\text{Cd}^{2+}]$ ,  $\text{mol L}^{-1} \times 10^{-7}$ ;  $k_{\text{as}}$  of Cd



**Fig. 7** Percentage of the active Cd in soil solution (calculated via ION-3). Horizontal scale: dose of phosphogypsum,  $t \text{ ha}^{-1}$ . Vertical scale: percentage of active  $[\text{Cd}^{2+}]$  to total  $\text{Cd}^{2+}$  in soil solution

This point of view is confirmed empirically by our previous research (Sukovatov, 2009).

According to calculations (Fig. 5),  $\text{Cd}^{2+}$  content in the forms of  $\text{CdCO}_3^0$  and  $\text{CdHCO}_3^+$  associated ions is important for the reduction of  $\text{Cd}^{2+}$  activity. Association of  $\text{Cd}^{2+}$  ion in the form of hydroxo complex  $\text{CdOH}^+$  is a main cause of the biogeochemical passivation of  $\text{Cd}^{2+}$ . This is because the hydroxo

complex  $\text{CdOH}^+$  is a main form of  $\text{Cd}^{2+}$  content in the soil solution (Fig. 4). The phenomena reduce both the sink of  $\text{Cd}^{2+}$  from soil to vadose zone and activity of  $\text{Cd}^{2+}$  penetration to the tissue of plants. The basis for the last assessment is the calculated higher percentage of hydroxo complex bound forms in soil solution compared to that of the other ion complexes. Priority  $\text{Cd}^{2+}$  binding to the  $\text{CdOH}^+$  associated ions is inherent

to neutral or slightly alkaline soil pH. As the phosphogypsum is a product of acid technology, the soil pH value after phosphogypsum application was reduced. This fact corresponds to the results of calculation by program ION-3. Reduction of the soil pH value after phosphogypsum application could be taken into account as an obstacle of soil amelioration with phosphogypsum. But we developed new chemical soil engineering based on the BGT\* methodology which is capable of minimizing the last obstacle. This is because new chemical soil engineering provides improvement of the soil geophysical structure and architecture simultaneously with phosphogypsum application. Improved soil geophysical structure and architecture is an additional starter of the plant development. The priority biological process provides pH close to 7 in rhizosphere.

The low content of water soluble form of Cd<sup>2+</sup> in soil (Fig. 6), as well as the low content of Cd<sup>2+</sup> free form in soil solution (Fig. 7), indicates that in real soil a probability of Cd adverse influence on plant organogenesis and quality of production is small.

According to calculation by ION-3, Cd toxicity in soil solution is less dangerous for soil biota and plant than this is defined by the standard soil environmental limitations (Dutch Target and Intervention Values 2000; Guidelines for the Safe Application of Biosolids to Land in New Zealand, 2003; Envirolink, 2006 73p; Environment Agency, 2009; Maximum permissible concentrations, 2006). Our opinion is that the standard soil environmental assessment procedure overestimates the level of HMs toxicity for soil biota and plants. This opinion suits the results of our research and modelling. We propose to accept the official current limit of the soil water-soluble Cd as a too strict criterion.

#### Passivation of HMs in soil solution after phosphogypsum application

Now, the application to the soil of phosphogypsum produced from contaminated ores is prohibited. The motives are the TEMORM content and HMs danger, and thus, phosphogypsum is piled in the stacks and ponds in Florida and Morocco and throughout the world (Tayibi et al., 2009). Concentrated phosphogypsum storage is incorrect, accounting to environmental reasons. The data of the long-term field experiments worldwide showed a high environmental

quality of the biological production grown after phosphogypsum application to soil (Akanova, 2013; Crusciol et al., 2016; Enamorado et al., 2014; Endovitsky et al., 2017; Mays & Mortvedt, 1984; Sukovatov, 2009). This was shown even in example of the phosphogypsum from Florida ore which is highly radioactive and highly contaminated with HMs (Mays & Mortvedt, 1984). Optimistic results were obtained after application to the soil of phosphogypsum which was of low activity and low contaminated with HMs (Kalinichenko, 2017a; Sukovatov, 2009).

According to mathematical model, the CCE, ion association and other discussed phenomena ensure passivation of HMs in soil solution compared to the HMs water-soluble content (Figs. 5–7) (Endovitsky et al., 2017). This thermodynamic circumstance explains environmental safety of rather high phosphogypsum doses up to 112 t ha<sup>-1</sup>, which were successfully tested by D.A. Mays and J.J. Mortvedt (1984). Obviously, the phosphogypsum high radioactivity and high HMs content were passivated taking into account their behavior in soil solution according to the chemical phenomena presented in the ION-3 model. To a great extent, the HMs passivation can be increased in result of intra-soil mechanical mixing of phosphogypsum in the soil continuum. Generally, a question of the environmentally sound phosphogypsum dose value is to be considered accounting for the properties of soil, recycling material, soil processing technology, and the form of watershed. For lands of specially protected natural areas, the permissible content of phosphogypsum in the soil is ≤ 2.0%, for agricultural lands and settlements ≤ 6.8%, for lands of forest and water resources, industry and transport ≤ 9.6% (Yakovlev et al., 2013).

Usually, the content of water in the soil is high at the early stage of plant organogenesis. Therefore, the first biogeochemical barrier at “soil–roots” interface is weak and does not provide selective consumption of chemicals from soil. The risk of pollutant intake by plants is high. In the framework of the proposed technology, an amelioration and/or remediation substance is applied to the processed soil layer at a depth of about 20–45 cm. Thus, a hazardous effect of the amendment for the not fully developed and not deeply spread root system of young plant is excluded.

Developed technology provides improved soil carcass architecture. Soil becomes easily accessible for the vast root zone. New deep and well-aggregated

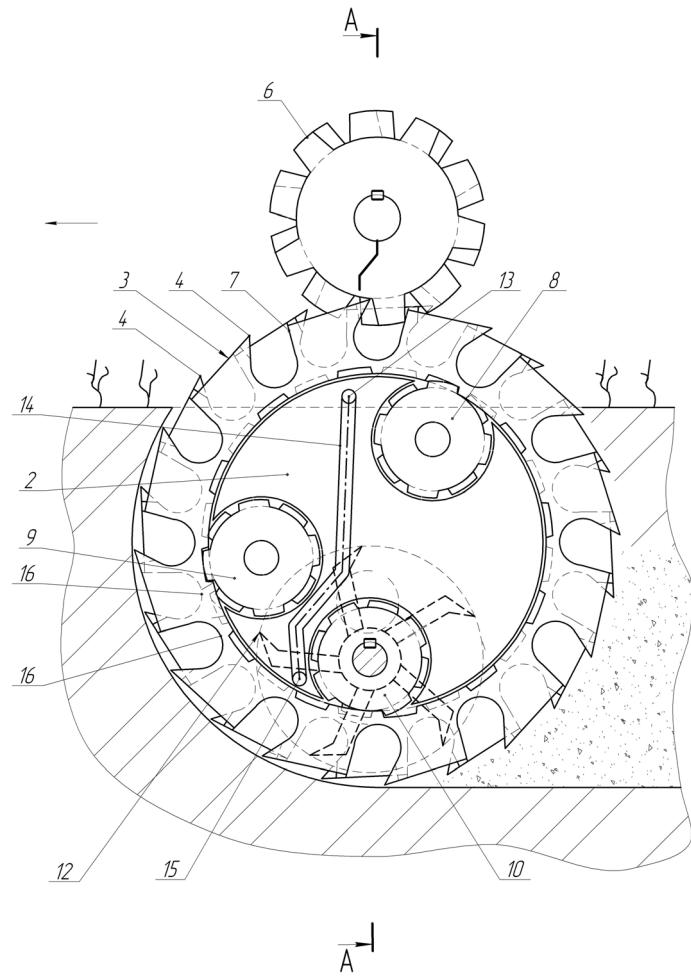
soil profile ensures relatively low soil moisture content at the same soil water volume compared to standard plowing technology. In consequence, a soil water matrix potential is relatively low. This increases the presence of the associated and complex ion form in the soil solution and decreases solubility and flux of pollutants to the root system (Kalinichenko et al., 2018). The role of ion association is perceptible in reliable, environmentally safe waste recycling.

Rhizosphere plant nutrition process can be assessed as a superposition of the root hair and soil–solution interactions in the discrete micro-basin of soil architecture carcass at the “micro-basin–soil structural particle” interface (Batukaev et al., 2016). The transfer of substances through the soil aggregate system is not an unbroken mass transfer flux. The transfer medium is a chain of discrete micro-basins of soil solution formed in the separated areas between

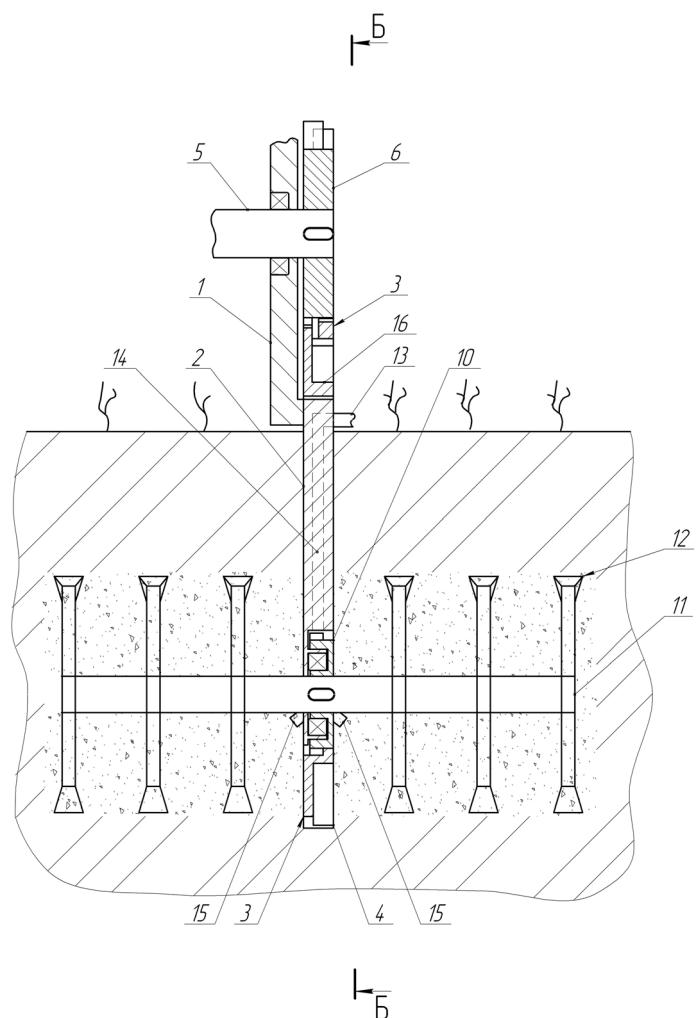
soil aggregates. The soil solution in micro-basins is prematurely insulated one from another during periods of low soil water content. A plant hair supplies carbon dioxide into a micro-basin and consumes a product of the carbonic acid exposure to the soil aggregate via this root hair. Some root hair can penetrate a micro-basin, which contains pollutants. “Finding” the initial portion of soil solution improper, the plant shuts consumption through this root hair. Well-developed soil solution micro-basin system provides selective prevention of contaminant penetration to the plant. Proposed technology provides reduced portion of pollutant in the plant biological product due to increased plant aboveground and underground biomass.

The HMs regime varies from plant high level pollution to HMs passivation according to soil water regime. The plant gets into unfavorable organogenesis

**Fig. 8** Device for intra-soil milling and simultaneous intra-soil apply of substances, side view \*1—frame; 2—disk; 3—ring; 4—complementary cutters; 5—shaft; 6—drive gear; 7—complementary gearing; 8—centering gear; 9—support gear; 10—driven gear; 11—shaft; 12—milling cutter; 13—inlet; 14—channel; 15—nozzle; 16—container



**Fig. 9** Device for intra-soil milling and simultaneous intra-soil apply of substances, front view; designations, see Fig. 8



conditions when soil moisture is high because the soil hazardous substances become highly soluble and mobile. Ionic strength of the diluted soil solution is low, and the ion association and ion complexation are reduced. In result, the ions are present in free form. The “root–soil” biogeochemical barrier is weak, and the dangerous HMs penetrate plant root freely (Kwasniewska, 2014). When the soil water content is extremely low, the HMs are totally passivated. But at the same time, the water supply of plant is insufficient. From the point of view of both priority association and complexation of HMs ions and preferable plant growth, the matrix potential in soil is to be from  $-0.2$  to  $-0.4$  MPa (Kalinitchenko et al., 2020b). This matrix potential value ensures higher soil solution ionic strength. Contemporaneously, the soil solution flux from rhizosphere to the

plant root system at this matrix potential is most preferable from the point of view of maximal nutrient flux, concerning rather high concentration of soil solution. To provide less contaminated healthy biological product from contaminated soil, the water regime of such soil is to be controlled more strictly than it is possible now at the current technological level (Kalinitchenko et al., 2020c). The new findings in the field of artificial water supply to the soil are urgent. Quite different devices are to be developed compared to the known standard irrigation equipment.

## Device for intra-soil milling and simultaneous intra-soil applying of ameliorative and remediation substances

Soil reclamation and remediation success depends on the possibility of the soil biological process expansion provided by chemical soil engineering technology (Kalinitchenko et al., 2020a). In standard technology, plowing does not ensure the multilevel structure and architecture for biogeochemical process, soil stability and fertility. The soil mixing with applied material does not provide a reliable contact of soil and amendment (Peries & Gill, 2015).

New BGT\*-based chemical soil engineering is capable to increase the area of internal surface of the 20–40 (30–70) cm soil layer (Kalinitchenko et al., 2020a). Technology improves soil aggregate system and provides high rate co-dispersing of soil and substance applied into the soil. The technology ensures HMs passivation into processed soil layer, allowing environmentally safe waste recycling, soil amelioration and agronomy effect (Kalinitchenko et al., 2020a, 2020b, 2020c).

New BGT\*-based chemical soil engineering technology decides the following tasks (Kalinitchenko, 2016; Kalinitchenko et al., 2020a): stable equilibrium, dynamics and turnover of macroaggregates and microaggregates for the full-fledged soil biogeochemical processes; soil living space for diverse organisms; synthesis of the soil heterogeneous architecture and enhanced conditions for soil evolution; controlled soil spatial-temporal multilevel pore space variability; developed soil interfaces in the complex soil system (Kalinitchenko et al., 2020a; Lin, 2012).

New device was developed in the framework of BGT\* chemical soil engineering methodology for intra-soil milling processing and simultaneous intra-soil application of amendments and/or other substances (Figs. 8, 9). The device contains vertical rotational chisel gear and intra-soil milling system mounted on the frame 1. Rotational chisel gear comprises the disk 2 and the ring 3 with outer complementary cutters 4. Torque is transmitted by the drive shaft 5 to the drive gear 6. The complementary gearing of the drive gear 6 transmits the torque to the ring 3 by outer complementary gearing elements 7. The ring 3 is installed by complementary gearing on the centering 8, support 9, and driven 10 gears, mounted on the disc 2. Via internal complementary

gear, the ring 3 meshes the driven gear 10, rotating the shaft 11. The shaft 11 equipped with milling cutters 12 comprises an intra-soil milling system. The disk 2 is equipped with the inlet 13, channel 14 and nozzles 15 for feeding and distribution the pulp, granular or liquid matter into the soil. Container 16 receives the soil from cutters 4, excluding bottom hole soil compaction and providing translational motion of device (Kalinitchenko, 2010, 2013; Kalinichenko et al., 2012, 2013, 2014, 2016, 2019).

Device operates as follows. The ring 3 cuts a slot in the soil. Rotary slit cutting reduces passive traction resistance of the translational movement of the rotational chisel gear along the slot. The shaft 11 with milling cutters 12 is immersed into the 20–45 (or 30–70 cm) target soil layer. The milling cutters 12 provide a fine aggregate structure of the initially compacted soil illuvial horizon. Pulp is fed through the inlet 13, channel 14 and nozzles 15 into the intra-soil milling zone, mixing with soil aggregates. Soil and plant remediation and health advantages of device for providing the new chemical soil engineering technology are as follows: Intra-soil milling provides development high level soil structuring and multilevel architecture of the soil aggregate system; application of amendments and nutrition substances into the soil during the intra-soil milling ensures reliable contact of applied matter with soil; intra-soil dispersed placement of matter provides the soil improvement, high level passivation of pollutants and remediation of environment; good soil and plant health, higher level of plant resistivity to pathogens, higher amount and better environmental quality of the biological production; high profitability of technology owing to low energy consumption and higher yield.

The soil porous system formed via standard technology is a rule dead-ended at the level of up to 99%. This does not provide the rhizosphere development (De Gryze et al., 2006; Shein et al., 2016). The soil porous system architecture is extremely important for the soil carcass stability, nutrition substance's transfer via rhizosphere, and plant high rate growth.

Based on the BGT\* methodology, intra-soil milling provides fine soil structure and multilevel soil micro- and small macroaggregate architecture of the illuvial horizon. This increases soil hydraulic conductivity and improves rhizosphere development. The soil transforms into the vast biochemical continuum for priority biological process (Kalinitchenko et al., 2019).

Phosphogypsum as a dispersed system improves the soil, dividing the soil fine structural elements mechanically. The initial structural system provides further soil improvement after intra-soil milling (Kalinichenko et al., 2014). High content of chemically activated Ca in phosphogypsum is an important agent for soil improvement because of the Ca priority adsorption to the SAC. Higher Ca portion in SAC provides reinforcement of the basic fine soil micro- and macroaggregates shell improving the soil multi-level architecture stability. The soil carcass became a superposition of the soil micro- and macro-elements which improved mechanical structure and provided high rate biological processes. The total amount of pollutant should be taken into account concerning a long-term effect of possible changes in the migration conditions of elements, stimulating the transition of HMs to highly mobile forms. The BGT\* methodology helps to control the consequences of phosphogypsum application to the soil. The intra-soil milling ensures better soil continuum structure providing high rate passivation of the pollutants by organic and mineral soil phases. On more possibility to prevent migration conditions of elements is a pulse intra-soil continuous-discrete watering system (Kalinichenko et al., 2020b). This system reduces matrix potential of the soil solution, provides fresh water saving, better plant growth conditions, and ensures pollutant passivation into the soil.

There are attempts to apply a facile approach to remediation technology which is focused on the primitive simulation of the natural phenomena of waste degradation (Jiang et al., 2015; Peries & Gill, 2015). It is a dangerous simplification because the soil ecosystem is complicated and does not respond linearly to the poor external indignation because soil evolution is multifaceted not completely clear phenomenon of the different intra-soil interfaces (Grassian, 2018). Dissolved organic matter fraction is leached from soil and degrades, especially when conditions of the soil organic matter reservation were broken by the simplified remediation technology.

New technology provides geophysical, chemical, physicochemical structural and architectural prerequisites for the stable soil evolution and expansion of the soil biogeochemical process, reducing HMs contamination of plant and soil biota (Coleman et al., 2018; Lisetskii et al., 2015, 2018; Totsche et al., 2018). We developed the intra-soil carbon containing waste

recycling system of gasification byproduct (Kalinichenko et al., 2019) which is promising compared to the standard environmentally dangerous incineration (Fang et al., 2020). New technology is a prerequisite of the soil organic matter stabilizing and enriched biological turnover (Withers et al., 2014). The phosphogypsum doses up to 9.6% SDW are permissible for the soil, and conditions for the soil biota development are appropriate (Yakovlev et al., 2013). The earthworm number even increases because a mills spacing along the milling shaft of 50 to 70 mm provides partial cutting of earthworms increasing their number (Akulova et al., 2010). Intra-soil system of mineral and organic waste recycling is capable as a basis of the new strategy of soil contamination mitigation, soil improvement and high soil health (Glazko & Glazko, 2015).

## Conclusion

The developed BGT\*-based transcendental remediation and reclamation chemical soil engineering technology ensures priority soil geophysical micro- and macroaggregate structure, multilevel soil architecture. The technology provides phosphogypsum intra-soil mixing and recycling, soil health and a long-term higher productivity and environmental quality of biological production of plants. The technology provides a higher rate consumption of atmosphere CO<sub>2</sub> to photosynthesis and higher rate aboveground and underground biomass production, which is promising for the C reversible biological sequestration. Higher rate environmentally safe biological production is a prerequisite for the stability of the climate system.

The environmental advantage of the new technology compared to known technological solutions is the selective plant nutrition from micro-basins which contain high-quality soil solution. This is due to discrete fine dispersed placement of ameliorative substance close to the structural fine elements of the soil aggregate interfaces. In result of the preferable rhizosphere development and priority plant growth, the soil reaction is biologically stabilized close to the value about pH 7. The pH value provides reduced Cd<sup>2+</sup> mobility and reliable “soil–root” biogeochemical barrier for this dangerous contaminant. The reinforced biogeochemical barrier simultaneously provides a higher rate control of eolian and

hydrological spread of pollution, environmental safety, including compliance with TENORM standards. Reduced Cd<sup>2+</sup> bioavailability ensures soil health and environment quality of the plant biological product.

The reversible biological carbon sequestration will become real due to higher soil biological productivity and increased soil-biological carbon turnover. BGT\* methodology provides transcendental stabilizing of the biosphere and the climate system.

**Author contributions** VPK contributed to conceptualization, formulation of a research problem, writing. APG contributed to data curation, writing—reviewing. TMM contributed to writing. SSM contributed to data processing, methodology, discussion. SNS contributed to analytical work, HPLC, data collection. VAS contributed to data processing. LPI conducted experiments. DAM contributed to visualization, statistical processing. AAZ contributed to methodology. TSD contributed to writing—review and editing. AIB conducted experiments, data collection. DVB conducted experiments, contributed to writing—reviewing.

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**Availability of data and material** The raw/processed data required to reproduce these findings cannot be shared at this time as the data also form part of an ongoing study.

## Declarations

**Conflict of interest** The authors declare there is no conflict of interest in this work.

**Ethical approval** It is not applicable since the manuscript has not been involved in the use of any animal or human data or tissue.

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