

Chemical Soil-Biological Engineering Theoretical Foundations, Technical Means, and Technology for Safe Intrasoil Waste Recycling and Long-Term Higher Soil Productivity

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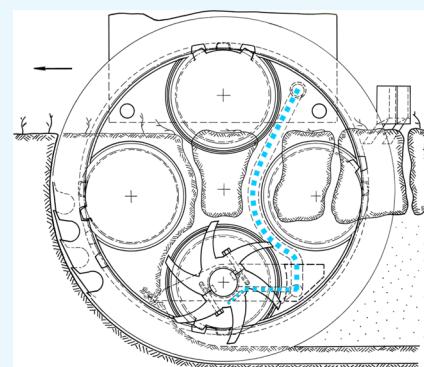
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ABSTRACT: The amelioration and remediation technology was developed on the basis of research of phosphogypsum and utilization in the Haplic Chernozem of South-European facies (Rostov Region). Phosphogypsum was utilized via dispersed application into a soil layer of 20–45 cm with intrasoil milling of this layer. The phosphogypsum utilization doses were 0, 10, 20, and 40 t ha⁻¹. The Pb analytical content in soil solution was studied in the model experiment. The soil solution Pb thermodynamic forms were calculated. The mathematical chemical-thermodynamic model ION-2 was developed to calculate the real soil solution (water extract) calcium-carbonate equilibrium (CCE) ion forms, considering the ion pair association. The associated ion pairs CaCO₃⁰, CaSO₄⁰, MgCO₃⁰, MgSO₄⁰, CaHCO₃⁺, MgHCO₃⁺, NaCO₃⁻, NaSO₄⁻, CaOH⁺, and MgOH⁺ were accounted for in soil solution equilibrium macroion form calculation. The procedure for the microelement ion [including heavy metals (HMs)] equilibrium concentration in the soil solution coefficient k_{as} calculation was proposed to account for the real soil solution CCE, macroions, and HM (including Pb) association. The Pb²⁺ ion in soil solution was mostly bound to associates PbOH⁺, Pb(OH)₂⁰, PbCO₃⁰, Pb(CO₃)₂²⁻, and PbHCO₃⁺. The calculation of CCE and ion association in soil solution revealed 14.5–21.5 times HM passivation compared to HM water-soluble values. The calculated HM activity in the soil solution in the example of the Pb²⁺ ion was less than 4% after phosphogypsum application in the target amelioration layer of 20–45 cm. The studied phosphogypsum doses were substantiated as environmentally safe. This was because the real soil solution CCE provided HM ion form association and consequent passivation. The dry steppe soil remediation after phosphogypsum application was justified as highly probable. The intrasoil milling chemical soil-biological engineering technology was developed for simultaneous soil amelioration and remediation on the basis of the biogeosystem technique (BGT*) transcendental methodology. The BGT*-based technology was tested in the long-term field experiments and is capable of ensuring the priority geophysical micro- and macroaggregate structure via intrasoil milling and mixing of soil illuvial and transitional horizons. This helps synthesize soil multilevel architecture, providing intrasoil-dispersed environmentally safe recycling of wastes of different origin. Addressing the environment safety concerns, a new decision of the intrasoil milling device was proposed for phosphogypsum and other substance application to soil.



1. INTRODUCTION

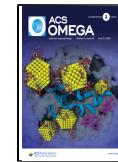
Soil contains macroions and microelements, including potentially hazardous heavy metals (HMs) of natural origin and/or HMs applied to soil with pesticides, nutrients, and amendments. HM mobility, accumulation, bioavailability, and degree of passivation into the soil are linked to ion activity. Ion activity in soil solution depends on ionic strength, ion association, and ion complexation.¹ Increased content of contaminants of natural and technogenic origin in the ecosphere at standard phosphogypsum waste utilization requires new waste recycling methods combined with soil mechanical processing and amendment application. The intrasoil passivation of dangerous substances is to be provided. This will reduce uncontrolled eolian and hydrological spread of contaminants. Conditions for environmentally safe and correctly dosed use of materials

containing contaminants will be improved. Contaminants simultaneously are the microelements and macroelements for plant nutrition trophic chain optimization and amendments for the soil physical, chemical, and physicochemical property enhancement.^{2–5} Some contaminants are extremely dangerous for plants. These kind substances are to be applied with special care. The high-level improved algorithms of biosphere strategic

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management in agronomy, irrigation, and environmental practices can be obtained using the basis of the safe soil application of contaminants.⁶ The high potential nature-based up-to-date chemical soil engineering technology development will be possible, focusing on physical, chemical, and complex biological living systems of the soil. Carbon and other chemical element loss from active biosphere to other bioinert geospheres, which is dangerous for the life prospect on the Earth, will be reduced.⁷ Conflict of the biosphere and technology will be eased.⁸ The strategy will be obtained for soil degradation reversing, biosphere-extended reproduction, and high soil health/quality at all scales.^{9,10}

The dangerous pollutant Pb is spreading in the ecosphere via eolian and water transfer.^{11–14} The Pb and many other contaminants are supplied to soil with fertilizers and waste. The mean total Pb content in soils of the Russian Federation is about 20 mg kg⁻¹ SDW.¹⁵ The value is approximately the same for the soils over the world. Soil Pb limiting concentration in different regulations ranges from 10 to 2000 mg kg⁻¹ depending on the soil and landscape properties and use.¹⁶ There are data on selective chemical extraction of HMs from soil and lithosphere, encouraging new developments for HM passivation.¹⁷ The origin of soil biogeochemical barriers for HM penetration into the plants provides a useful possibility to reinforce these barriers synthesizing new soil and landscape reclamation and remediation technologies.

Pb mobility into the soil solution and penetration into the plants depend on the soil carbonate content and pH. The liming, remineralization, and composts are used to reduce HM transfer to plants.¹⁸ Pb mobility in soil is linked to the free Pb²⁺ ion thermodynamic activity and to the rate of Pb²⁺ binding to ion associates and complexes. Calcium-carbonate equilibrium (CCE) in the soil solution is an important phenomena influencing Pb²⁺ ion thermodynamic activity. Accounting soil solution CCE, the molar fraction of active Pb²⁺ in soil solution does not exceed 0.13%, and the Pb²⁺ activity in the water extract is about 0.24% of the Pb total content.¹

Phosphogypsum is a byproduct of wet phosphorus fertilizer technology. Total phosphogypsum production in the world is about 150–280 t year⁻¹. Phosphogypsum contains more than 60 chemical elements, including Pb.^{19–21} USEPA has classified PG as a “Technologically Enhanced Naturally Occurring Radioactive Material” (TENORM).¹⁹ Phosphogypsum use has been banned in most countries. Standard phosphogypsum utilization practice is open-stack tailing or liquid fraction storage in ponds.²² This practice causes direct and delayed hazardous eolian and hydrological pollution of the vast terrains.^{22–24} Phosphogypsum stack view abruptly deteriorates the area appearance, worsening habitation conditions and recreational potential of the landscape all over the world (<https://en.wikipedia.org/wiki/Phosphogypsum#/media/File:GypStack.JPG>). There are attempts to use phosphogypsum in civil engineering, as a rare-earth element source, and soil amendment.^{25–27}

The Russian Kovdor apatite ore deposit is of high environmental quality compared to Morocco, Florida, and others ores.²⁸ Cd concentration of phosphate rocks is Kovdor (Russia) 0.2 mg kg⁻¹, Phalaborwa (South Africa) 4 mg kg⁻¹, Boucraa (Morocco) 38 mg kg⁻¹, North Carolina (USA) 47 mg kg⁻¹, Nauru 100 mg kg⁻¹.²⁹ Phosphogypsum rock activity concentrations is Kovdor (Russia) 20 Bq kg⁻¹, Morocco K-10 560 Bq kg⁻¹, Florida (USA) 1000 Bq kg⁻¹.³⁰ Consequently, the phosphogypsum from

Kovdor apatite ore can be assessed as environmentally safe for soil amelioration.³¹

The Haplic Chernozem is one of the reservoirs for phosphogypsum utilization. The soil has no obvious morphological and physicochemical prerequisites for chemical reclamation from the standard soil biology and soil reclamation point of view. This standard opinion is to be assessed as outdated according to new findings. Now, there are obvious signs of degradation of this world famous soil.³² Some research noted a potential accumulation of HMs in soil after phosphogypsum application.¹⁹ However, most literature sources show insignificant changes in the HM soil content after phosphogypsum application compared to natural soil HM contents.³³ However, 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, and U which cause additional peculiarities for waste recycling.^{34,35}

As a rule, the phosphogypsum is applied to the soil surface. Then, the phosphogypsum is mechanically mixed with soil by passive working bodies of agricultural, construction, and road machinery.³⁶ Phosphogypsum is applied only to the soil surface in some applications. This option is used in the no-till system.³⁷ Soil blocks after standard agricultural or ameliorative soil processing with passive working bodies have a transverse dimension up to 50–100 mm because of poor soil crumbling and mixing. A large part of phosphogypsum remains on the soil surface or is involved into the uncontrolled eolian and hydrological transfer. The phosphogypsum particles spread partly between the soil blocks while soil mechanical processing. The plant roots occupy prematurely the dispersed fine-aggregated soil material between large soil blocks. The relatively small part of soil fine-aggregated material is enriched with product entered into the soil with phosphogypsum, including HMs, and here, the HM concentration is higher compared with estimated mean concentration in the whole target soil layer. The relatively high local concentration of HMs in this zone of plant priority nutrition causes contamination of the plant biological product. This is an adverse consequence of standard soil amelioration and remediation technology.

The pollutant toxicity, mobility, and bioavailability are to be minimized in soil.^{2,24} The independent global phosphogypsum study declares the search for the new phosphogypsum utilization methods as a high reputation base of the nearest future chemical engineering.³⁸ There is a possibility to decide the integrated list of tasks of soil contamination decrease and to achieve the goals of soil amelioration and soil remediation simultaneously in a single high-level chemical soil engineering technological process based on our recent research.^{3,4} An opportunity to re-evaluate the TENORM limitations and to provide the environmentally safe phosphogypsum soil application is real.

High technical level chemical soil engineering management is crucial for the low contamination, productivity, health, and prospects of soil. For this, we have proposed the Biogeosystem Technique (BGT*) methodology. The BGT* methodology refines soil amelioration and remediation theory using the transcendental approach. The BGT* methodology of chemical soil engineering addresses environmental safety concerns of ecosphere management.^{3,39,40}

The aims of research

- physical and mathematical modeling of Pb²⁺ thermodynamics in Haplic Chernozems soil solution to justify new

Table 1. Analytical Macroion's Content of Water Extract, mol L⁻¹^a

doses of phosphogypsum apply t ha ⁻¹	pH	total alkalinity (Alk _Σ), mol L ⁻¹	×10 ⁻³						
			Ca ²⁺	Mg ²⁺	Na ⁺	SO ₄ ²⁻	Cl ⁻	(CO ₃ ²⁻) _A × 10 ⁻⁶	(HCO ₃ ⁻) _A × 10 ⁻⁴
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

^aThe calculation results are presented in Table 2.

Table 2. Calculation by the ION-2 Program Equilibrium Concentration and Molar Fraction of the Soil Solution Macroion Free Form after Different Phosphogypsum Doses Apply^a

doses of phosphogypsum apply, t ha ⁻¹	effective ionic strength, I*	ion activity coefficient y' (above) y'' (below)	×10 ⁻¹							
			[Ca ²⁺]	[Mg ²⁺]	[Na ⁺]	[SO ₄ ²⁻]	[Cl ⁻]	[CO ₃ ²⁻] _A × 10 ⁻⁴	[HCO ₃ ⁻] _A × 10 ⁻²	[OH ⁻] _A × 10 ⁻⁵
0 (control)	0.00435	0.9310	0.70	0.51	0.20	0.51	1.20	1.08	4.02	11.51
		0.7514	93.87	93.45	100.00	87.07	100.00	42.33	98.51	
10	0.00791	0.9104	1.36	0.98	0.26	0.66	3.00	0.64	3.99	8.72
		0.6872	93.59	93.05	99.77	80.86	100.00	31.46	97.41	
20	0.01575	0.8808	3.03	1.22	0.29	2.72	3.00	0.40	3.21	7.50
		0.6020	83.01	81.53	99.14	75.43	100.00	25.9	95.80	
40	0.02416	0.8591	4.80	1.79	0.30	4.22	4.40	0.38	3.51	7.34
		0.5448	79.40	77.65	98.81	70.80	100.00	21.76	94.20	

^aNote: equilibrium forms of ions—above cmol kg⁻¹, below—%.

possibilities of environmentally safe phosphogypsum recycling;

- heuristic synthesis of device and technology for intrasoil ameliorative mechanical processing, simultaneous remediation, and passivation of pollutants applied into the soil with ameliorant to provide a high-level chemical soil engineering for stable environmentally safe fertile soil evolution synthesis and efficient land use.

2. RESULTS AND DISCUSSION

2.1. Analytical Data and Thermodynamic Mathematical Modeling. Water extract macroion analytical content data in Haplic Chernozems (South Russia) after phosphogypsum apply were obtained in the model experiment (Table 1). The data were used for calculation of Pb equilibrium concentration in the water extract based on the thermodynamic mathematical model ION-2 of the soil solution macroion equilibrium form equation system.^{1,41–43}

The macroion concentration in the water extract was low. Nevertheless, according to Table 2, the influence of soil solution ionic strength was significant on the association of macroions. Associates and complex stability constants were calculated via thermodynamic mathematical model ION-2.⁴³ The calculated values differed from the corresponding thermodynamic values.⁴⁴ The single-charged (y') and double-charged (y'') ion activity coefficient values reduced, the molar fraction of Ca²⁺, Mg²⁺, and SO₄²⁻ values became a little bit less, and the CO₃²⁻ molar fraction percentage reduced by 2 times at a higher phosphogypsum dose.

The Pb water-soluble form content (Table 3) was used in further calculations.

Equilibrium concentration of Pb²⁺ was calculated using eq 6 (see the Experimental Section).

The left part of eq 6 was substituted with the Pb²⁺ total concentration value in the water extract. This value was equal to

Table 3. Pb Total and Water-Soluble Forms Content in Soil, mg kg⁻¹

doses of phosphogypsum apply, t ha ⁻¹	Pb total content	Pb water-soluble form content	Pb water-soluble form to total Pb content ratio, %
0 (control)	18.0000	0.7560	4.20
10	18.2463	0.8021	4.40
20	18.4926	0.8482	4.59
40	18.9852	0.9404	4.95

the initial soil water extract value for control option of the model experiment. The left part of eq 6 is the sum of the Pb²⁺ content in the water extract from initial soil and the corresponding Pb²⁺ content in the given phosphogypsum dose for another model experiment option. In the right part of eq 6 are presented the macroion equilibrium concentrations and calculated thermodynamic stability constants of corresponding Pb associated ions. The free-ion equilibrium constants were borrowed from G. Sposito (1989) and accounted in thermodynamic stability constant calculations.⁴⁴

The digital examples of calculation via eq 4 for the phosphogypsum doses of 0 (control) and 40 t ha⁻¹ are as follows: eqs 1 and 2

Phosphogypsum 0 t ha⁻¹

$$7.298 \times 10^{-7} = [\text{Pb}^{2+}] (1 + 10^7[\text{CO}_3^{2-}]/5.73 + 10^{10}[\text{CO}_3^{2-}]^2/8.88 + 10^4[\text{HCO}_3^-]/8.02 + 10^3[\text{SO}_4^{2-}]/4.25 + 10^2[\text{Cl}^-]/3.20 + 10^8[\text{OH}^-]/4.02 + 10^{11}[\text{OH}^-]^2/4.43) \quad (1)$$

Phosphogypsum 40 t ha⁻¹

$$\begin{aligned}
 9.078 \times 10^{-7} = & [\text{Pb}^{2+}] (1 + 10^7[\text{CO}_3^{2-}]/10.90 \\
 & + 10^{10}[\text{CO}_3^{2-}]^2/16.89 + 10^4[\text{HCO}_3^-] \\
 & /11.06 + 10^3[\text{SO}_4^{2-}]/8.08 \\
 & + 10^2[\text{Cl}^-]/4.40 + 10^8[\text{OH}^-]/5.54 \\
 & + 10^{11}[\text{OH}^-]^2/7.17) \quad (2)
 \end{aligned}$$

The calculation of Pb^{2+} water-soluble concentration and mole fraction in the water extract from soil was fulfilled via eq 6 in the form of eqs 1 and 2 (Table 4). Pb^{2+} ions were bound prematurely to hydroxo complexes PbOH^+ , $\text{Pb}(\text{OH})_2^0$. The carbonates and bicarbonates PbCO_3^0 , $\text{Pb}(\text{CO}_3)_2^{2-}$, and PbHCO_3^+ content were less compared with hydroxo complexes form. Association coefficient k_{as} calculated by eq 4 was by 2.1 times less for the phosphogypsum dose of 40 t ha^{-1} compared to the control option. $[\text{Pb}^{2+}]$ equilibrium concentration was calculated by eqs 3 and 5 using Pb^{2+} total concentration and corresponding k_{as} . Active concentration of a $[\text{Pb}^{2+}]$ was calculated as a product of the $[\text{Pb}^{2+}]$ equilibrium concentration and corresponding ion activity coefficient (Table 4). Active concentration of a $[\text{Pb}^{2+}]$ percentage at phosphogypsum dose 40 t ha^{-1} was higher by 1.6 times compared with the control option.

The macroion equilibrium form calculation (Table 2) showed that ions Ca^{2+} , Mg^{2+} , SO_4^{2-} , and CO_3^{2-} to a large extent were bound to associates. We used a quantitative criterion of ion binding to associate. It is a difference of ion total content (100%) and its free form percentage in Table 2. Adsorption or removal of Ca^{2+} , HCO_3^- , and CO_3^{2-} from the soil solution according to the current CCE system equilibrium causes the CaCO_3 deposition (or dissolution). CCE determines the type of migration and accumulation of various carbonate forms and salt transfer throughout the soil profile and laterally between the soil complex components, as well as the sink of carbonates to the vadose zone.⁷ The higher was the phosphogypsum dose, the less was the macroion activity. In consequence, the less was unfavorable mass transfer into the soil, as well as the mass transfer to the vadose zone.

The Pb water-soluble form content $0.75\text{--}0.94 \text{ mg kg}^{-1}$ was much less than Pb total content of $18.00\text{--}18.99 \text{ mg kg}^{-1}$ (Table 3).

The model ION-2 showed some increase of Pb^{2+} activity in the soil solution in result of the phosphogypsum application (Table 4). The “active $[\text{Pb}^{2+}]$ to total” value increased from 2.332% in control option to 3.663%. However, the increase was not a significant circumstance concerning the great reduction of Pb^{2+} activity compared to the total concentration of water-soluble Pb in the soil–water extract. The calculated association coefficient was high from 14.543 to 31.207 units (Table 4). Therefore, the soil geochemical barrier for HMs penetration into plant was high enough after phosphogypsum application.

The hydroxo complex-bound forms PbOH^+ , $\text{Pb}(\text{OH})_2^0$ are the most important agents of the Pb^{2+} activity reduction and the rate of Pb sink from soil. This is because the hydroxo complex-bound form percentage is higher than that of the other complexes (Table 4). The content of Pb^{2+} in the PbCO_3^0 , $\text{Pb}(\text{CO}_3)_2^{2-}$, and PbHCO_3^+ ions is important for reducing Pb^{2+} activity. Binding of Pb^{2+} to PbOH^+ and $\text{Pb}(\text{OH})_2^0$ is preferable at neutral or slightly alkaline soil pH. The phosphogypsum is a product of acid technology. Thus, the soil pH value was slightly reduced because of phosphogypsum application according to Table 1 and calculations by ION-2. A possibility to compensate the last

Table 4. Calculation by the ION-2 Program Concentration and Mole Fraction of Water-Soluble Pb in Water Extract from Soil after Different Phosphogypsum Dose Application

phosphogypsum doses, t ha^{-1}	mole fraction, %						association coefficient			
	water-soluble $[\text{Pb}^{2+}]$	equilibrium $[\text{Pb}^{2+}]$	active $[\text{Pb}^{2+}]$	active $[\text{Pb}^{2+}]$ to total $[\text{Pb}^{2+}] \%$	$[\text{PbCO}_3^0] + [\text{Pb}(\text{CO}_3)_2^{2-}]$	$[\text{PbHCO}_3^+]$	$[\text{PbSO}_4^0]$	$[\text{PbCl}^+]$	$[\text{PbOH}^+] + [\text{Pb}(\text{OH})_2^0]$	
0 (control)	7.298	0.2266	0.1702	2.332	3.105	5.850	1.558	0.369	0.117	89.001
10	7.743	0.3446	0.2367	3.057	4.450	4.140	2.024	0.574	0.408	88.404
20	8.188	0.4759	0.2862	3.496	5.812	5.571	1.866	2.384	0.438	86.930
40	9.078	0.5841	0.3325	3.663	6.434	2.238	2.041	3.359	0.643	85.285
										14.543
										31.207
										21.474
										16.206

obstacle of soil amelioration with phosphogypsum is the simultaneous improvement of the soil geophysical structure and architecture as the additional plant priority development starter.

The data on the Pb^{2+} water-soluble form content in soil, and the data on Pb^{2+} free-form contents in soil solution are low. This indicates small probability of Pb adverse influence on plant organogenesis and production quality in real soil. The Pb is less dangerous for soil biota and plants in focus of toxicity compared to the standard soil environmental assessments based on results of calculation by ION-2.⁴³ Standard soil environmental assessments cause an overestimation of the HM toxicity level for soil biota and plants according the research fulfilled. Current limiting soil water-soluble Pb value is to be assessed as a too high criterion.

2.2. High Environment Quality Biological Production Grown after Phosphogypsum Application. Now, phosphogypsum is concentrated in stacks and ponds in Florida, Morocco, and other territories of the world.¹⁹ Application to the soil of phosphogypsum produced from contaminated ores is prohibited by the motive of TEMORM and HM dangerous content. In our opinion, this reason is incorrect both based on the long-term field experiments worldwide and concerning the results presented in this paper, as well as our former publications.^{1,3,35,37,45,46} High environmental quality of the biological production grown after phosphogypsum application to soil was shown both for HM-contaminated and HM-low-contaminated phosphogypsum.^{4,45,47}

CCE and ion association in soil solution cause passivation of HMs for 14.5–21.5 times compared to HM water-soluble values (Table 4).⁴⁶ This thermodynamic circumstance of HM behavior in soil solution explains why even rather high phosphogypsum doses up to 112 t ha^{-1} were successfully tested as environmentally safe by Mays and Mortvedt (1984).⁴⁵

The soil water regime is a driver of dangerous soil pollution or, on the contrary, pollution passivation.

The plant gets into unfavorable organogenesis conditions under standard remediation technology and high soil moisture because of high solubility and mobility of hazardous substances. Diluted soil solution ionic strength is not high, and, according the ION-2 program, the ion association and ion complexation are weakened. The “root–soil” biogeochemical barrier becomes weak in turn, and the dangerous HMs penetrate the plant freely.⁴⁸

2.3. New Chemical Soil Engineering Based on BGT* Methodology. Soil reclamation and remediation success depends on soil biological process expansion in result of applied chemical soil engineering technology. It is not a facile task. The analysis of the current technical level of standard devices for soil mechanical processing and amendment application revealed a prevailing use of passive working bodies for operations with soil and amendment, including subsoil manuring.⁴⁹ The known soil mechanical processing methods give insufficient soil loosening and soil mixing for contact with the applied material.⁴ The known methods fail to ensure the multilevel structure and architecture for biogeochemical process, soil stability, and fertility.

New technology increased the 20–40 (30–70) cm layer soil internal surface area.⁵⁰ New technology ensured the soil aggregates and the substances applied into the soil high rate co-dispersing. HM passivation into this soil layer was improved to allow the environmentally safe waste recycling.⁴⁷ Agronomy and amelioration effects were improved.

The tasks of the new chemical soil engineering based on the BGT* methodology are as follows:³

- stable equilibrium, dynamics, and turnover of macroaggregates and microaggregates for the full-fledged soil biogeochemical processes;^{51–53}
- soil living space for diverse organisms;
- heterogeneous soil architecture synthesis and enhanced evolution;
- controlled soil spatial–temporal multilevel pore space variability;
- improved soil interfaces for the certainty of reaction fronts and matter flux pathways in the complex soil system.⁵⁴

A chemical soil engineering device for intrasoil mechanical processing and intrasoil application of amendments and other substances (Figures 1 and 2) is mounted on frame 1. The device

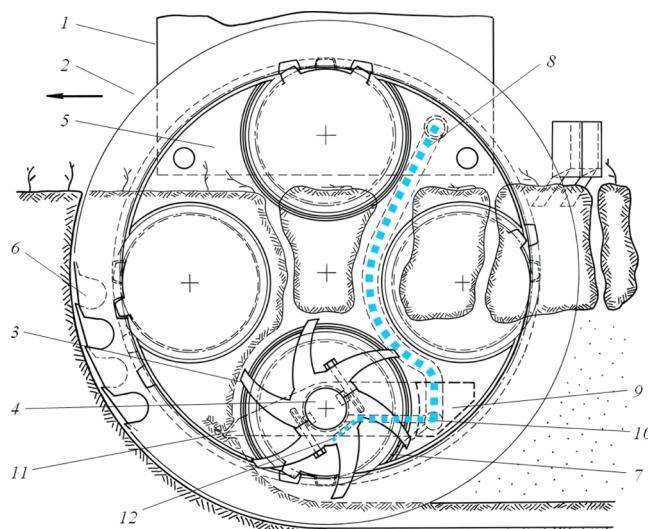


Figure 1. Device for intrasoil milling and simultaneous intrasoil application of substances, side view. 1—frame; 2—vertical rotational chisel; 3—milling cutters; 4—shaft; 5—disk; 6—ring cutter; 7—pinion; 8—channel; 9—ramp; 10—channel; 11—soil loosening finger; and 12—channel.

is longitudinally symmetric and comprises two vertical rotational chisels 2. Rotational chisel 2 comprises the ring cutter 6 with outer cutting teeth mounted on the disk 5. Ring cutter 6 via internal gear meshes the pinion 7 which rotates the shaft 4 equipped with milling cutters 3. The disk 5 is equipped with channel 8 for feeding the pulp to the channel 10 in the ramp 9. Ramp 9 has the forward-oriented fingers 11 for soil loosening and channels 12 for pulp distribution into the soil.⁵⁵

During the operation, the device is immersed into the 20–45 (or 30–70 cm) target soil layer. The ring cutter 6 performs a slit in the soil while the device is moving forward. This technical decision reduces passive traction resistance for the longitudinal movement of rotational chisel 2. The milling cutters 3 provide a fine-aggregate structure of initially compacted soil illuvial horizon. Pulp is fed through channels 9, 11, and 12 into the soil milling zone and is mixed with soil aggregates. The device provides a new chemical soil engineering technology:

- intrasoil milling processing during amendment and nutrition substance application into the soil ensures good contact of substances with soil;

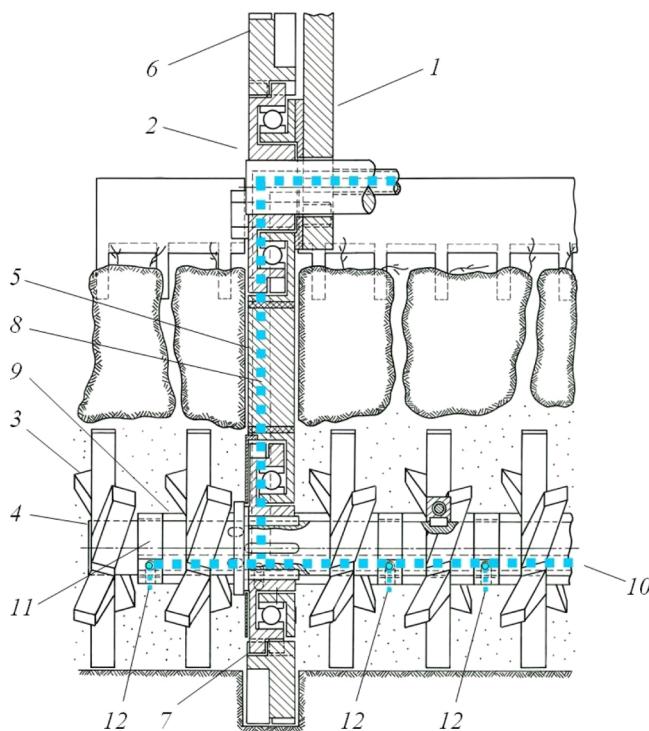


Figure 2. Device for intrasoil milling and simultaneous intrasoil application of substances, front view; designations, see Figure 1.

- preliminary soil cleaving by loosening finger improves intrasoil milling processing;
- rotating soil flux coming over the milling cutters and lengthwise soil flux coming along the loosening finger upper and lower surfaces confluence increase the illuvial horizon crumbling.

The natural as well as agrotechnical-formed soil porous system is dead-ended to the great extent.⁵⁶ The soil not acceptable for rhizosphere porous media dead-ended percentage is up to 99%.⁵⁷

The intrasoil milling processing BGT*-based methodology is an agent of the sought for soil structural micro- and macroaggregate units of 0.1–5 mm formation.⁵⁸ Intrasoil milling provides illuvial horizon fine soil structural aggregates and intrasoil multilevel architecture as a vast continuum for biochemical reactions.^{40,59,60} The soil hydraulic conductivity increases.⁵⁷

Ca of phosphogypsum improves the SAC ion content, reinforcing the basic soil structure elements. The soil micro- and macroaggregate shell is strengthening, and aggregates become more stable. Phosphogypsum helps to improve the soil mechanical structure itself, as it is a well-dispersed system dividing the soil structural element. The entire soil carcass architecture is a superposition of an improved soil micro- and macroelement mechanical structure and provides high rate biological processes.

Geophysical, chemical, physicochemical structural, and architectural prerequisites are synthesized for the soil stable evolution and soil biogeochemical process expansion.^{13,39,51–54,58,61,62} These prerequisites provide HM contamination reduction.⁶ New soil contamination mitigation strategies are becoming real.⁶³ Our intrasystem of the gasification byproduct recycling is more promising compared to environmentally dangerous phosphate recovering from sewage sludge incineration ash.⁶⁴

A facile approach-based remediation technology is dangerous for the complicated soil ecosystem.⁶⁵ Soil organic matter is a multifaceted intricate phenomenon. This is important from the chemical point of view concerning the origin and functions of different intrasoil interfaces.^{66–68} Soil organic matter insures plant nutrition, transformation of soil minerals into nutrients, and is the agent of soil structuring. Soil organic matter turnover is influenced by agrarian technology. Land-use gradient cause molecular change of dissolved organic matter and bacterial activity patterns.⁶⁹ Soil organic matter loss is a consequence of natural and anthropogenic soil dynamics. The most mobile fraction of soil organic matter is dissolved organic matter. The dissolved organic matter is not intrinsically recalcitrant but instead persists in soil as a result of simultaneous formation, consumption, and transformation. Its molecular composition and properties continuously change during the soil passage.⁷⁰ A fraction is leached from soil and degraded, especially when conditions of the soil organic matter reservation were broken.⁷¹

New technology is a prerequisite of soil organic matter stabilizing and enriched biological turnover. This is a step to phosphorus management rethinking.⁷² The technology will provide the intra-aggregate particulate organic matter (POM) decomposition by microorganisms into finer POM, priority rhizosphere expansion, formation and stabilization of soil aggregates, and a higher soil biological productivity.⁵³ Higher biological production of the biosphere is a buffer of climate system functioning stability.

3. CONCLUSIONS

The developed BGT*-based remediation and reclamation chemical soil engineering technology ensures priority geo-physical micro- and macroaggregate structure, multilevel architecture synthesis, waste intrasoil mixing and recycling. The soil structure is not erased by intrasoil milling. On the contrary, the intrasoil milling ensures soil structure and architecture synthesis. Technology is supported by the 30-year old field experiments. Intrasoil milling and intrasoil phosphogypsum application provided a long-term soil higher productivity compared to standard technology.^{47,50,59} Conditions for the soil biota development are appropriate. The worm number increased. The mill spacing along the milling shaft of 70 mm provided partial worm cutting increasing their number.⁷³ Biological production was higher than with standard technology. This caused higher rate CO₂ consumption to photosynthesis and a biologically reversible CO₂ sequestration in the form of aboveground and underground biomass.

The technology provides environmental advantages compared to known technological solutions. The technology ensures selective plant nutrition from microbasins containing high-quality soil solution because of the discrete fine-dispersed placement of ameliorative substances close to the soil structural fine-element surface. The soil pH 7 values will become biologically stabilized in result of provided preferable rhizosphere development and priority plant growth; reliable “soil–root” biogeochemical barrier will be formed; Pb²⁺ mobility and bioavailability will be reduced; and environmentally safe biological product of plants will be obtained.

The eolian and hydrological uncontrolled pollution transfer risk will be reduced, addressing environmental safety concerns and TENORM limitations. The dispersed waste utilization intrasoil is promising in different cases of pollution. It will prevent biotoxicity of biochars.^{74,75} The priority conditions for soil amelioration and remediation, high quality environment,

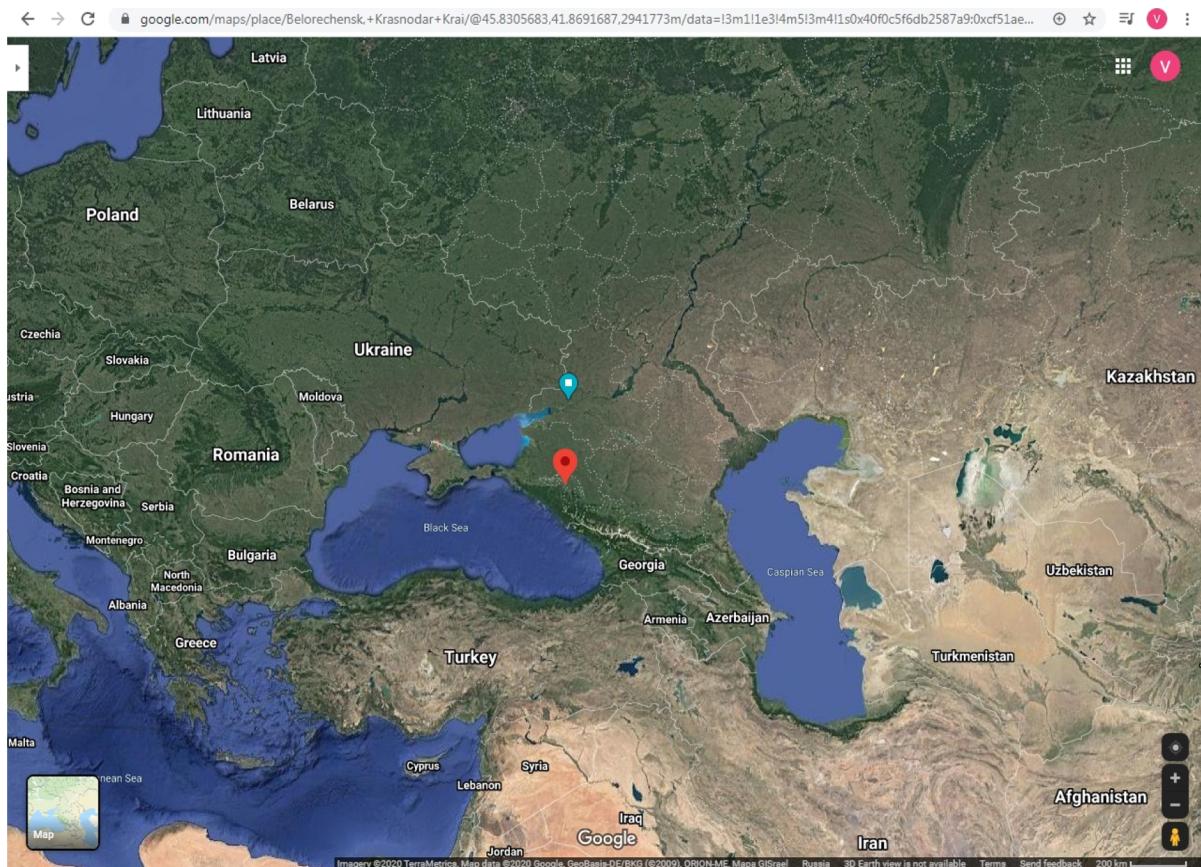


Figure 3. South Russia territory. Satellite Maps. 2020. Blue mark—Rostov Region Haplic Chernozem area; Red mark—Belorechensk chemical plant.

high-rate biogeochemical processes and yield, and economic benefit gaining will be provided in different applications.^{40,64,76,77} The reversible biological carbon sequestration will become real because of higher soil biological productivity and increased soil-biological carbon turnover.^{3,78}

BGT* chemical soil-biological engineering methodology gives a new transcendental prospect to stabilize the biosphere and the climate system of the Earth.³⁹

4. EXPERIMENTAL SECTION

4.1. Object. The study object was Haplic Chernozem. This soil type is spread in the southwest of the Russian Federation, including the Rostov Region (Figure 3, blue mark).

The area of research is the steppe of southern Russia, and in particular, the steppe nonsaline slightly frozen Haplic Chernozem of South-European facies [IUSS Working Group WRB (2015)].

The climate of the Rostov Region is continental, arid, with an annual precipitation of 350–450 mm. The parent rocks are carbonate and carbonate-sulfate loess-like loam and clay. The landscape is automorphic, and in some areas, semi-hydro-morphic. The Haplic Chernozem is moderately thick, horizon A of 52 cm, low solonized, humus 3.6%, physical clay 47.7%, clay 29.5%, CaCO_3 0.15% (up to 3–10% at the depth of 0.8–1.5 m), $\text{pH} = 7.8$, exchangeable cations: Ca^{2+} —282 mmol kg⁻¹, Mg^{2+} —55 mmol kg⁻¹, Na^+ —14 mmol kg⁻¹.³²

The background Pb total content (Clark) is 20 mg kg⁻¹ SDW.¹⁵

4.1.1. Phosphogypsum. Phosphogypsum used for research originated from Kovdor apatite ore in the Belorechensk

chemical plant (Figure 3, red mark) as a byproduct of phosphorus fertilizer production by the end-of-pipe sulfuric acid technology. The raw material was the Kovdor apatite ore. Technological stages are as follows: phosphogypsum mechanical removal after P_2O_5 extraction; phosphogypsum sludge acid residue neutralizing with lime milk to pH 5.0–5.3; and pulp transportation to open sludge ponds. The ponds are the source of soil, surface runoff, ground water, and the pollution of rivers Ganza, Pshekha, and Belya (Figure 4). The total Pb^{2+} content in phosphogypsum is of 55.98 mg kg⁻¹ SDW, and the water-soluble form Pb^{2+} content is of 10.48 mg kg⁻¹ SDW. The total content of Cd^{2+} in the phosphogypsum is of 2.76 mg kg⁻¹ and the content of Cd^{2+} water-soluble form is of 0.33 mg kg⁻¹.⁴¹ The F total content is of 0.12%.⁷⁹

4.1.2. Model Experiment. The application of the phosphogypsum to Haplic Chernozem 20–45 cm soil layer in doses of 0 (control), 10, 20, and 40 t ha⁻¹ was simulated in the model experiment.

Soil was sampled from the 20–40 cm illuvial horizon. This soil layer was appointed for chemical reclamation as inclined to natural and technogenic compaction because of soil heavy granulometric composition, bad soil structure, soil porous media adverse architecture, and Na content in the soil adsorption complex (SAC).⁸⁰ The used methodological approach provides direct apply of amendment to the target soil layer. This reduces excess of anthropogenic HMs in the upper soil layer.

Soil samples were ground and sieved through a screen with 2 mm wire mesh. The sifted soil was mechanically mixed with phosphogypsum in the abovementioned doses.

Every soil sample was humidified to 25–30% SDW after phosphogypsum application and placed in the hermetic

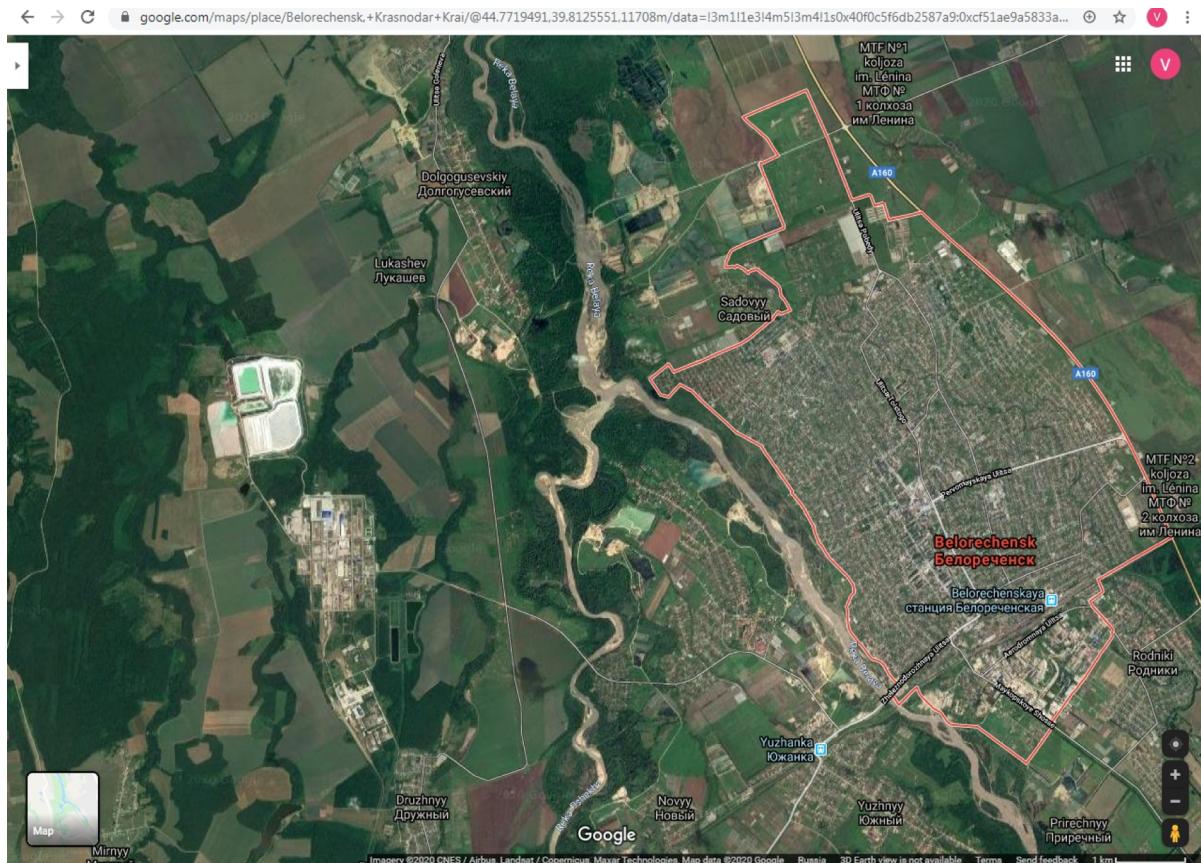


Figure 4. Belorechensk chemical plant (bottom left) with phosphogypsum ponds (left). Satellite Maps. 2020.

container for a week to carry out the soil and phosphogypsum physicochemical equilibrium for further analyses. The time term is sufficient to establish equilibrium.⁴⁶

The model experiment was performed in triplicate.

4.2. Methods. Soil and vadose zone samples were analyzed by standard methods (for details, see *Supporting Information*).

4.2.1. Soil Solution Thermodynamic Model. Application of soil phosphogypsum doses were substantiated based on the soil solution thermodynamics point of view.

The thermodynamics of macroion and microelement-free and associated ion molar fractions in soil solution chemical equilibrium is influenced by CCE. The CCE in its turn is altered by ion's association and depends on soil-liquid phase chemical composition, pH, Eh, buffering properties, dissolution, migration, and precipitation of carbonates in soil profile, and landscape. The ion exchange processes are important at the interfaces of soil solid, liquid, and gaseous phases.^{1,66,68,81} The CCE influences the gas exchange in the "soil-atmosphere" system, partial pressure, and seasonal cycles of soil CO₂. The ion pairs can exist in the soil solution in the form of CaCO₃⁰; CaSO₄⁰, MgCO₃⁰, MgSO₄⁰ (neutral), and the CaHCO₃⁺, MgHCO₃⁺, NaCO₃⁻, NaSO₄⁻, CaOH⁺, and MgOH⁺ (charged) ion pairs.

Soil solution thermodynamic mathematical model ION-2 considers the fundamental laws of the electrolyte theory.^{11,43,44}

The higher is the ionic strength of the solution, the number of ion passes in the form of associated ions. The CCE system of soil solution includes dynamic equilibria: adsorption-hydration; solution balance between the gas phase and bioorganic phase; carbonic acid dissociation stages; CCE between soil solution, soil absorbing complex, CaCO₃, and solid phase sedimentation; and water ion equilibrium. Soil solution ionic strength, ion

equilibrium constants, and free and bounded macroion form interactions are accounted depending on the macroion origin.

The free anions and macroion pair equilibrium concentrations [CO₃²⁻], [HCO₃⁻], [SO₄²⁻], [Cl⁻], and [OH⁻] influence the Pb²⁺ soluble form content in water extract. The Pb content can be calculated taking into account the thermodynamic stability constants of Pb²⁺ forms in the given soil solution using the free and bounded macroion forms.

A potentially hazardous HM in soil can be considered as the microelement.¹ We proposed to characterize the thermodynamic state of the microelement in soil solution by microelement association coefficient *k*_{as(ME)}. This coefficient indicates a degree of potentially hazardous HM binding into associates and complexes with soil solution main ions. The phrase "coefficient of ion association *k*_{as}" meaning suits electrolyte thermodynamics framework, as well as the empirical data of experiments *in vitro* and *in situ*.⁴⁶

The equation for the microelement can be written as follows (eq 3)

$$C_{(ME)} = (1 + k_{as(ME)})[C_{(ME)}] \quad (3)$$

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 Pb²⁺ ion is as follows (eq 4)

$$k_{\text{asPb}} = \frac{[\text{CO}_3^{2-}]}{K_{\text{PbCO}_3}} + \frac{[\text{CO}_3^{2-}]^2}{K_{\text{Pb}(\text{CO}_3)_2}} + \frac{[\text{HCO}_3^-]}{K_{\text{PbHCO}_3}} + \frac{[\text{SO}_4^{2-}]}{K_{\text{PbSO}_4}} \\ + \frac{[\text{Cl}^-]}{K_{\text{PbCl}}} + \frac{[\text{OH}^-]}{K_{\text{PbOH}}} + \frac{[\text{OH}^-]^2}{K_{\text{Pb}(\text{OH})_2}} \quad (4)$$

where $[\text{CO}_3^{2-}]$ and other are the equilibrium concentrations of macroelement ions; $K_{(\text{PbCO}_3)}$ and other are the equilibrium constants.

The free and bound microelement (HM) ion molar fractions were taken into account. Coefficients of ion association are as follows (eq 5)

$$\nu_{\text{free}} = 1/(1 + k_{\text{as(ME)}})100, \% \\ \nu_{\text{bound}} = 100 - \nu_{\text{free}} \quad (5)$$

Eq 2 can be rewritten for the Pb^{2+} content as follows (eq 6)

$$\text{Pb}^{2+} = [\text{Pb}^{2+}] \left(1 + \frac{[\text{CO}_3^{2-}]}{K_{\text{PbCO}_3}} + \frac{[\text{CO}_3^{2-}]^2}{K_{\text{Pb}(\text{CO}_3)_2}} + \frac{[\text{HCO}_3^-]}{K_{\text{PbHCO}_3}} \right. \\ \left. + \frac{[\text{SO}_4^{2-}]}{K_{\text{PbSO}_4}} + \frac{[\text{Cl}^-]}{K_{\text{PbCl}}} + \frac{[\text{OH}^-]}{K_{\text{PbOH}}} + \frac{[\text{OH}^-]^2}{K_{\text{Pb}(\text{OH})_2}} \right) \quad (6)$$

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

The Pb content in the soil and Pb concentration in soil solution as well are many times less compared to macroion concentration. Thus, the influence of the Pb content is insignificant on formal and effective soil solution ionic strength values. For this reason, eq 6 was not included to the equation system for macroions. The use of equation for the trace element separately simplifies the calculation procedure and increases the reliability of mathematical modeling. The unstable associates of Pb^{2+} were not considered. The thermodynamic stability constants of Pb^{2+} associates were borrowed from Sposito (1989) PbCO_3^0 , PbHCO_3^0 , $\text{Pb}(\text{CO}_3)_2^{2-}$, and PbHCO_3^{+} , and Lurie (1986) PbSO_4^0 , PbCl^+ , PbOH^+ , and $\text{Pb}(\text{OH})_2^{011,82}$.

The CCE thermodynamic mathematical model, algorithm, and program ION-2 are presented in detail in our publications.^{1,7,41–43}

Heuristic synthesis of the soil mechanical processing and amendment applying new methodology; device for high-level chemical soil engineering.

Heuristic synthesis of the new device for soil mechanical processing and simultaneous application of the soil amendment and waste has been the focus of the higher level chemical soil engineering. By the term “heuristic synthesis”, we mean as a nonstandard and new knowledge-based approach to technological development. We presumed that the soil processing system is not to be the imitative but transcendental to some extent to provide the technology new quality compared to the natural or the anthropogenic approach known at the moment.

There is need for soil mechanical processing methods which are capable to provide the soil structure loosening and the soil macroaggregates and microaggregates mixing with applied material for enriched stable biogeochemical turnover.^{50–52} This provides multilevel heterogeneous soil architecture synthesis (Lin, 2012) and preferable conditions for polymicrobial biofilms and soil organic matter synthesis and function.^{67,69}

The tasks of heuristic synthesis of technosoil were an upper horizon of 0–25 (or 0–30) cm after the soil mechanical

processing remains intact; a horizon of 25–50 (or 30–70) cm is crushed via 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 mixture of water and phosphogypsum and other waste (the pulp form is acceptable) is supplied to a soil horizon of 25–50 (or 30–70) cm and is mixed with soil mass during its mechanical processing. Soil layers of 25–50 (or 30–70) cm are discussed focusing on different plant rhizosphere depths.

The deviation of processing the horizon depth in every case of soil processing is linked to regional soil properties. Heuristic synthesis was based on the BGT* methodology of soil processing devices synthesis, laboratory research, soil processing equipment tests in soil channel, and long-term field intrasoil processing trials and experiments, as well as on the own patents.^{3,53,59,83,84}

4.3. Data Statistical Processing. The studied parameters were determined 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 presented in the tables and in the text are statistically significant at the level of $p < 0.05$. On this basis, the data in the text are not accompanied by measures of dispersion (variance or standard deviation) for not to clutter up the paper.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.0c02014>.

Method details, plant organogenesis and Pb^{2+} passivation, phosphogypsum dose justification, soil environment representation by the water extract, soil superdispersity reducing via the BGT* methodology, early organogenesis plant growth stage, soil layer assignment for phosphogypsum application, and references ([PDF](#))

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Endovitsky, A. P.; Kalinichenko, V. P.; Minkina, T. M. Carbonate calcium equilibrium in soil solution as a driver of heavy metals mobility. *Int. J. Environ. Probl.* **2015**, *2*, 136–153.
- (2) Bech, J.; Korobova, E.; Abreu, M.; Bini, C.; Chon, H.-T.; Pérez-Sirvent, C. Soil pollution and reclamation. *J. Geochem. Explor.* **2014**, *147*, 77–79.
- (3) Kalinichenko, V. P. Optimizing the matter flow in biosphere and the climate of the Earth at the stage of technogenesis by methods of biogeosystem technique (problem-analytical review). *Int. J. Environ. Probl.* **2016**, *4*, 99–130.
- (4) Kalinichenko, V. P. Effective use of phosphogypsum in agriculture. *Bull. Plant Nutr.* **2017**, *1*, 2–33.
- (5) Xiong, T.; Leveque, T.; Shahid, M.; Foucault, Y.; Mombo, S.; Dumat, C. Lead and cadmium phytoavailability and human bioaccessibility for vegetables exposed to soil or atmospheric pollution by process ultrafine particles. *J. Environ. Qual.* **2014**, *43*, 1593–1600.
- (6) Dastyar, W.; Zhao, M.; Yuan, W.; Li, H.; Ting, Z. J.; Ghaedi, H.; Yuan, H.; Li, X.; Wang, W. Effective Pretreatment of Heavy Metal-Contaminated Biomass Using a Low-Cost Ionic Liquid (Triethylammonium Hydrogen Sulfate): Optimization by Response Surface Methodology—Box Behnken Design. *ACS Sustainable Chem. Eng.* **2019**, *7*, 11571–11581.
- (7) Batukaev, A.-M. A.; Endovitsky, A. P.; Andreev, A. G.; Kalinichenko, V. P.; Minkina, T. M.; Dikaev, Z. S.; Mandzhieva, S. S.; Sushkova, S. N. Ion association in water solution of soil and vadose zone of chestnut saline solonetza as a driver of terrestrial carbon sink. *Solid Earth* **2016**, *7*, 415–423.
- (8) Glazko, V. I.; Galzko, T. T.; Galzko, T. T. Conflicts of biosphere and agroecosystems. *Int. J. Environ. Probl.* **2015**, *1*, 4–16.
- (9) Pardo, T.; Clemente, R.; Epelde, L.; Garbisu, C.; Bernal, M. P. Evaluation of the phytostabilisation efficiency in a trace elements contaminated soil using soil health indicators. *J. Hazard. Mater.* **2014**, *268*, 68–76.
- (10) Lehman, R.; Cambardella, C.; Stott, D.; Acosta-Martinez, V.; Manter, D.; Buyer, J.; Maul, J.; Smith, J.; Collins, H.; Halvorson, J.; Kremer, R.; Lundgren, J.; Ducey, T.; Jin, V.; Karlen, D. Understanding and Enhancing Soil Biological Health: The Solution for Reversing Soil Degradation. *Sustainability* **2015**, *7*, 988–1027.
- (11) Sposito, G. Green water and global food security. *Vadose Zone J.* **2013**, *12*, 1.
- (12) Motuzova, G. V.; Minkina, T. M.; Karpova, E. A.; Barsova, N. U.; Mandzhieva, S. S. Soil contamination with heavy metals as a potential and real risk to the environment. *J. Geochem. Explor.* **2014**, *144*, 241–246.
- (13) Lisetskii, F.; Stolba, V. F.; Marinina, O. Indicators of agricultural soil genesis under varying conditions of land use, steppe Crimea. *Geoderma* **2015**, *239–240*, 304–316.
- (14) Kalinichenko, V. P.; Glinushkin, A. P.; Sokolov, M. S.; Zinchenko, V. E.; Minkina, T. M.; Mandzhieva, S. S.; Sushkova, S. N.; Makarenkov, D. A.; Bakoyev, S. Y.; Il'ina, L. P. Impact of soil organic matter on calcium carbonate equilibrium and forms of Pb in water extracts from Kastanozem complex. *J. Soils Sediments* **2018**, *19*, 2717–2728.
- (15) Sheudzhen, A. K.; Bondareva, T. N.; Syetov, V. P.; Lebedovsky, I. A.; Osipov, M. A.; Bezsonov, V. O. The contents and forms of lead compounds in leached chernozem of the Western Ciscaucasia in terms of agricultural soil genesis. *KubGAU Sci. J.* **2018**, *140*, 131–141.
- (16) US Environmental Protection Agency. Risk-Based Screening Table—Generic Tables. <http://www2.epa.gov/risk/risk-based-screening-table-generic-tables> (date of access Jan 30, 2020).
- (17) Favas, P. J. C.; Pratas, J.; Gomes, M. E. P.; Cala, V. Selective chemical extraction of heavy metals in tailings and soils contaminated by mining activity: environmental implication. *J. Geochem. Explor.* **2011**, *111*, 160–171.
- (18) da Costa, C. H. M.; Crucioli, C. A. C. Long-term effects of lime and phosphogypsum application on tropical no-till soybean-oat-sorghum rotation and soil chemical properties. *Eur. J. Agron.* **2016**, *74*, 119–132.
- (19) Tayibi, H.; Choura, M.; López, F. A.; Alguacil, F. J.; López-Delgado, A. Environmental impact and management of phosphogypsum. *J. Environ. Manage.* **2009**, *90*, 2377–2386.
- (20) Goswami, M.; Nand, S. Management of Phosphogypsum. *Proceedings of the IFA Global Safety Summit, Canada, Vancouver*, 2015.
- (21) Pérez-López, R.; Macías, F.; Cánovas, C. R.; Sarmiento, A. M.; Pérez-Moreno, S. M. Pollutant flows from a phosphogypsum disposal area to an estuarine environment: An insight from geochemical signatures. *Sci. Total Environ.* **2016**, *553*, 42–51.
- (22) Wang, T.; Zhou, Y.; Lv, Q.; Zhu, Y.; Jiang, C. safety assessment of the new Xiangyun phosphogypsum tailings pond. *Miner. Eng.* **2011**, *24*, 1084–1090.
- (23) Bituh, T.; Vučić, Z.; Marović, G.; Prlić, I. A new approach to determine the phosphogypsum spread from the deposition site into the environment. *J. Hazard. Mater.* **2013**, *261*, 584–592.
- (24) Hentati, O.; Abrantes, N.; Caetano, A. L.; Bouguerra, S.; Gonçalves, F.; Römbke, J.; Pereira, R. Phosphogypsum as a soil fertilizer: Ecotoxicity of amended soil and elutriates to bacteria, invertebrates, algae and plants. *J. Hazard. Mater.* **2015**, *294*, 80–89.
- (25) Yang, L.; Zhang, Y.; Yan, Y. Utilization of original phosphogypsum as raw material for the preparation of self-leveling mortar. *J. Cleaner Prod.* **2016**, *127*, 204–213.
- (26) Rychkov, V. N.; Kirillov, E. V.; Kirillov, S. V.; Semenishchev, V. S.; Bunkov, G. M.; Botalov, M. S.; Smyshlyayev, D. V.; Malyshev, A. S. Recovery of rare earth elements from phosphogypsum. *J. Cleaner Prod.* **2018**, *196*, 674–681.
- (27) Saadaoui, E.; Ghazel, N.; Ben Romdhane, C.; Massoudi, N. Phosphogypsum: potential uses and problems – a review. *Int. J. Environ. Stud.* **2017**, *74*, 558–567.
- (28) Lapin, A. V.; Lyagushkin, A. P. The Kovdor apatite-francolite deposit as a prospective source of phosphate ore. *Geol. Ore Deposits* **2014**, *56*, 61–80.
- (29) *Contaminants and the Soil Environment in the Australasia-Pacific Region*; Naidu, R., Kookana, R. S., Oliver, D. P., Rogers, S., McLaughlin, M. J., Eds.; Kluwer Academic Publishers, 1996.
- (30) Hilton, J. Phosphogypsum (PG): Uses and Current Handling Practices Worldwide. 2010, [https://www.parlimen.gov.my/images/webuser/jkuasalam/pMemoranendum/Kertas kerja Phosphogypsum \(PG\) -UsesandCurrentHandlingPracticesWorldwide/Phosphogypsum\(PG\)-Uses&CurrentHandlingPracticesWorldwide-JulianHilton.pdf](https://www.parlimen.gov.my/images/webuser/jkuasalam/pMemoranandum/Kertas kerja Phosphogypsum (PG) -UsesandCurrentHandlingPracticesWorldwide/Phosphogypsum(PG)-Uses&CurrentHandlingPracticesWorldwide-JulianHilton.pdf).
- (31) Gázquez, M. J.; Mantero, J.; Mosquera, F.; Bolívar, J. P.; García-Tenorio, R. 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.* **2014**, *137*, 79–87.
- (32) Bezuglova, O. S. Current state of the Chernozems of the Rostov Region and problems of monitoring. Collection of scientific papers of the State Nikitsky Botanical Garden, 2019; Vol. 148, pp 34–41.
- (33) Nayak, S.; Mishra, C. S. K.; Guru, B. C.; Rath, M. Effect of phosphogypsum amendment on soil physico-chemical properties, microbial load and enzyme activities. *J. Environ. Biol.* **2011**, *32*, 613–617.
- (34) Amari, T.; Ghnaya, T.; Abdelly, C. Nickel, cadmium and lead phytotoxicity and potential of halophytic plants in heavy metal extraction. *S. Afr. J. Bot.* **2017**, *111*, 99–110.
- (35) Enamorado, S.; Abril, J. M.; Delgado, A.; Más, J. L.; Polvillo, O.; Quintero, J. M. Implications for food safety of the uptake by tomato of

- 25 trace-elements from a phosphogypsum amended soil from SW Spain. *J. Hazard. Mater.* **2014**, *266*, 122–131.
- (36) Akanova, N. I. Neutralized phosphogypsum – a promising agrochemical means of agriculture intensifying (based on the materials of EuroChem OJSC workshops). *Fertility* **2013**, *1*, 2–7.
- (37) Crusciol, C. A. C.; Artigiani, A. C. C. A.; Arf, O.; Carmeis Filho, A. C. A.; Soratto, R. P.; Nascente, A. S.; Alvarez, R. C. F. Soil fertility, plant nutrition, and grain yield of upland rice affected by surface application of lime, silicate, and phosphogypsum in a tropical no-till system. *Catena* **2016**, *137*, 87–99.
- (38) Hilton, J. Building Reputational Capital: the Independent Global Phosphogypsum Study and the IFA PG Handbook, *IFA Global Safety Summit, Canada: Vancouver*, March 23–26, 2015.
- (39) Kalinichenko, V. P. Renewal of Energy and Life in the Biosphere. *Eur. J. Renew. Energy* **2017**, *2*, 3–28.
- (40) Kalinichenko, V. P.; Glinushkin, A.; Sokolov, M.; Batukaev, A.; Minkina, T.; Zinchenko, V.; Chernenko, V.; Startsev, V.; Mandzhieva, S.; Sushkova, S.; Makarenkov, D.; Il'ina, L.; Larin, G.; Rykhlik, A. Biogeosystem Technique for Healthy Soil, Water and Environment. In *ACS Fall 2019 National Meeting and Exposition, Chemistry and Water, August 25–29, 2019. San Diego, CA*, 2019.
- (41) Batukaev, A.; Endovitsky, A.; Kalinichenko, V.; Mischenko, N.; Minkina, T.; Mandzhieva, S.; Sushkova, S.; Bakoyev, S.; Rajput, V.; Shipkova, G.; Litvinov, Y. Cadmium status in chernozem of the Krasnodar Krai (Russia) after application of phosphogypsum. *Proc. Est. Acad. Sci.* **2017**, *66*, 501–515.
- (42) Kalinichenko, V. P.; Glinushkin, A. P.; Sokolov, M. S.; Zinchenko, V. E.; Minkina, T. M.; Mandzhieva, S. S.; Sushkova, S. N.; Makarenkov, D. A.; Bakoyev, S. Y.; Il'ina, L. P. Impact of soil organic matter on calcium carbonate equilibrium and forms of Pb in water extracts from Kastanozem complex. *J. Soils Sediments* **2018**, *19*, 2717–2728.
- (43) Endovitsky, A. P.; Kalinichenko, V. P.; Bakoyev, S. Y.; Ivanenko, A. A.; Sukovatov, V. A.; Radovich, E. V. Certificate of the State Registration of Computer Program "ION-2". RU No 2009612162, published on March 11, 2009.
- (44) Sposito, G. *The Chemistry of Soils*; Oxford University Press: New York, 1989.
- (45) Mays, D. A.; Mortvedt, J. J. Crop Response to Soil Applications of Phosphogypsum. *J. Environ. Qual.* **1984**, *15*, 78–81.
- (46) Endovitsky, A. P.; Batukaev, A. A.; Minkina, T. M.; Kalinichenko, V. P.; Mandzhieva, S. S.; Sushkova, S. N.; Mischenko, N. A.; Bakoyev, S. Y.; Zarmaev, A. A.; Jusupov, V. U. Ions association in soil solution as the cause of lead mobility and availability after application of phosphogypsum to chernozem. *J. Geochem. Explor.* **2017**, *182*, 185–192.
- (47) Sukovatov, V. A. Duration of reclamation of the solonetzic complex of chestnut soils. Dissertation for the degree of candidate of agricultural sciences; Don State Agrarian University. Persianovska, 2009; p 140.
- (48) Kwasniewska, J. Molecular cytogenetics serves environmental monitoring In *Abstract Book of the 3rd ScienceOne International Conference on Environmental Sciences*, 2014; p 25.
- (49) Peries, R.; Gill, J. S. Subsoil manuring in the high rainfall zone: a practice for ameliorating subsoils for improved productivity. In *Proceedings of the 17th ASA Conference, 20–24 September, 2015, Hobart, Australia*, 2015.
- (50) Mishchenko, N. A.; Gromyko, E. V.; Kalinichenko, V. P.; Chernenko, V. V.; Larin, S. V. Ecological and recreational phosphogypsum recycling in chernozem on example of the Krasnodar Territory. *Fertility* **2009**, *6*, 25–26.
- (51) Totsche, K. U.; Amelung, W.; Gerzabek, M. H.; Guggenberger, G.; Klumpp, E.; Knief, C.; Lehndorff, E.; Mikutta, R.; Peth, S.; Prechtel, A.; Ray, N.; Kögel-Knabner, I. Microaggregates in soils. *J. Plant Nutr. Soil Sci.* **2018**, *181*, 104–136.
- (52) Neuman, J. *Soil Organic Matter Maintenance in No-Till and Crop Rotation Management Systems. Soil Organic Matter. Reference Module in Earth Systems and Environmental Sciences*; Elsevier, 2017.
- (53) Coleman, D. C.; Callaham, M. A., Jr.; Crossley, D. A., Jr. Secondary Production: Activities of Heterotrophic Organisms—Microbes. *Fundamentals of Soil Ecology*, 3rd ed; Academic Press, 2018; Chapter 3, pp 47–76.
- (54) Lin, H. Understanding Soil Architecture and Its Functional Manifestation across Scales. Part I: Overviews and Fundamentals. *Hydropedology*; Academic Press, 2012; Chapter 2, pp 41–74.
- (55) Kalinichenko, V. P. Device for application of substance in process of rotary subsoil tillage. RU 2387115 C2, published on April 27, 2010.
- (56) De Gryze, S.; Jassogne, L.; Six, J.; Bossuyt, H.; Wevers, M.; Merckx, R. Pore structure changes during decomposition of fresh residue: X-ray tomography analysis. *Geoderma* **2006**, *134*, 82–96.
- (57) Shein, E. V.; Kharitonova, G. V.; Milanovsky, E. Yu. Aggregation of natural disperse formations: Value of organic matter, soluble salts and diatoms. *Biogeosystem Tech.* **2016**, *7*, 77–86.
- (58) Haider, K. M.; Guggenberger, G. Organic matter. Genesis and Formation. *Encyclopedia of Soils in the Environment*; Elsevier, 2005; pp 93–101.
- (59) Kalinichenko, V. P.; Sharshak, V. K.; Mironchenko, S. F.; Chernenko, V. V.; Ladan, E. P.; Genev, E. D.; Illarionov, V. V.; Udalov, A. V.; Udalov, V. V.; Kippel, E. V. Changes in the properties of soils in a solonet soil complex thirty years after reclamation. *Eurasian Soil Sci.* **2014a**, *47*, 319–333.
- (60) Kalinichenko, V. P.; Glinushkin, A. P.; Sokolov, M. S.; Kozyrev, S. G.; Savostyanov, A. P.; Ilin, V. B. Complex of utilization of gasification wastes. 2692718C1, published on June 26, 2019.
- (61) Lisetski, F. N.; Stolba, V. F.; Goleusov, P. V. Modeling of the evolution of steppe chernozems and development of the method of pedogenetic chronology. *Eurasian Soil Sci.* **2016**, *49*, 846–858.
- (62) Lisetski, F.; Zelenskaya, E.; Rodionova, M. Geochemical features of fallow land in ancient plots in the flora of Chersonesos. *Geosciences* **2018**, *8*, 410.
- (63) Zhao, F.-J.; Ma, Y.; Zhu, Y.-G.; Tang, Z.; McGrath, S. P. Soil Contamination in China: Current Status and Mitigation Strategies. *Environ. Sci. Technol.* **2015**, *49*, 750–759.
- (64) Fang, L.; Yan, F.; Chen, J.; Shen, X.; Zhang, Z. Novel Recovered Compound Phosphate Fertilizer Produced from Sewage Sludge and Its Incinerated Ash. *ACS Sustainable Chem. Eng.* **2020**, *8*, 6611–6621.
- (65) Jiang, N.; Cai, D.; He, L.; Zhong, N.; Wen, H.; Zhang, X.; Wu, Z. A Facile Approach To Remediate the Microenvironment of Saline-Alkali Soil. *ACS Sustainable Chem. Eng.* **2015**, *3*, 374–380.
- (66) Grassian, V. H. Physical Chemistry of Environmental Interfaces: Aerosols, Nanomaterials and Indoor Surfaces. *The Chemist* **2019**, *91*, 13–17.
- (67) Swidsinski, A. 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.
- (68) Volikov, A. B.; Kholodov, V. A.; Kulikova, N. A.; Philippova, O. I.; Ponomarenko, S. A.; Lasareva, E. V.; Parfyonova, A. M.; Hatfield, K.; Perminova, I. V. Silanized humic substances act as hydrophobic modifiers of soil separates inducing formation of water-stable aggregates in soils. *Catena* **2016**, *137*, 229–236.
- (69) Kamjunke, N.; Hertkorn, N.; Harir, M.; Schmitt-Kopplin, P.; Griebler, C.; Brauns, M.; von Tümpeling, W.; Weitere, M.; Herzsprung, P. Molecular change of dissolved organic matter and patterns of bacterial activity in a stream along a land-use gradient. *Water Res.* **2019**, *164*, 114919.
- (70) Roth, V.-N.; Lange, M.; Simon, C.; Hertkorn, N.; Bucher, S.; Goodall, T.; Griffiths, R. I.; Mellado-Vázquez, P. G.; Mommer, L.; Oram, N. J.; Weigelt, A.; Dittmar, T.; Gleixner, G. Persistence of dissolved organic matter explained by molecular changes during its passage through soil. *Nat. Geosci.* **2019**, *12*, 755–761.
- (71) Olk, D. C.; Bloom, P. R.; Perdue, E. M.; McKnight, D. M.; Chen, Y.; Farenhorst, A.; Senesi, N.; Chin, Y.-P.; Schmitt-Kopplin, P.; Hertkorn, N.; Harir, M. Environmental and Agricultural Relevance of Humic Fractions Extracted by Alkali from Soils and Natural Waters. *J. Environ. Qual.* **2019**, *48*, 217–232.

(72) Withers, P. J. A.; Sylvester-Bradley, R.; Jones, D. L.; Healey, J. R.; Talboys, P. J. Feed the Crop Not the Soil: Rethinking Phosphorus Management in the Food Chain. *Environ. Sci. Technol.* **2014**, *48*, 6523–6530.

(73) Akulova, T. V.; Maltsev, A. V.; Kalinichenko, V. P.; Eremenko, V. N. Occurrence and abundance of earthworms in biotopes with different chemical load at Crop Protection. *Proceedings of higher educational institutions. North Caucasus region. Series: Natural Science*, 2010; Vol. 3, pp 81–84.

(74) Mindubaev, A. Z.; Voloshina, A. D.; Kulik, N. V.; Ryzhikov, D. V.; Barsukova, T. A.; Akosah, Y. A.; Minzanova, S. T.; Mironova, L. G. Biodegradation of White Phosphorus – a Dangerous Industrial Contaminant. *Biogeosystem Tech.* **2019**, *6*, 91–101.

(75) Wang, Y.-Y.; Jing, X.-R.; Li, L.-L.; Liu, W.-J.; Tong, Z.-H.; Jiang, H. Biototoxicity Evaluations of Three Typical Biochars Using a Simulated System of Fast Pyrolytic Biochar Extracts on Organisms of Three Kingdoms. *ACS Sustainable Chem. Eng.* **2017**, *5*, 481–488.

(76) Kalinichenko, V. P.; Starcev, V. F. Recycling of poultry litter by method of Biogeosystem technique. *Int. J. Environ. Probl.* **2015**, *1*, 17–38.

(77) Kalinichenko, V. P.; Starcev, V. F.; Batukaev, A. A.; Zarmaev, A. A. Device for killing, processing of farm animals and recycling slaughter house wastes. RU 2584022 C2, published on May 20, 2016.

(78) Caldararu, S.; Purves, D. W.; Palmer, P. I. Phenology as a strategy for carbon optimality: a global model. *Biogeosciences* **2014**, *11*, 763–778.

(79) Belyuchenko, I. S. Features of mineral waste and the expediency of their use in the formation of complex composts. *KubSAU Sci. J.* **2014**, *101* (7), 1–21.

(80) Khitrov, N. B. Choice of diagnostic criteria for the existence and severity of the solonetz process in soils. *Eurasian Soil Sci.* **2004**, *1*, 18–31.

(81) Tenno, T.; Rikmann, E.; Zekker, I.; Tenno, T.; Daija, L.; Mashirin, A. Modelling equilibrium distribution of carbonaceous ions and molecules in a heterogeneous system of CaCO_3 –water–gas. *Proc. Est. Acad. Sci.* **2016**, *65*, 68–77.

(82) Lurie, J. *Handbook of Analytical Chemistry*; Mir Publishers: Moscow, 1975; p 488, ASIN: B0007AK7F6.

(83) Kalinichenko, V. P.; Il'in, V. B.; Endovitsky, A. P.; Chernenko, V. V. Method of substance synthesis inside supracolloidal system. 2476055C2, published on February 27, 2013.

(84) Kalinichenko, V. P.; Zinchenko, V. E.; Sharshak, V. K.; Illarionov, V. V.; Ladan, E. P.; Genev, E. D.; Chernenko, V. V.; Lohmanova, O. I.; Lemeshko, M. A.; Kozlov, V. B. Device for subsoil rotary milling with forced cleaning of mechanical drive and its cutting element from soil. RU 2517859C1, published on June 10, 2014.