Supporting Information

Chemical soil-biological engineering theoretical foundations, technical means and technology for safe intra-soil waste recycling and long-term higher soil productivity

1,2Valery P. Kalinitchenko*, 2Alexey P. Glinushkin, 3Tatiana M. Minkina, 3Saglara S. Mandzhieva, 3Svetlana N. Sushkova, 1Vladimir A. Sukovatov, 4Ljudmila P. Il’ina, 5Dmitry A. Makarenkov

1Institute of Fertility of Soils of South Russia, 346493, Krivoshlykova str., 2, Persianovka, Oktyabr’skii district, Rostov Region, Russia

2All-Russian Phytopathology Research Institute RAS, Institute str., 5, Bolshiye Vyazemy, Odintsovskii district, Moscow Region, 143050, Russia

3Southern Federal University, 344090, prosp. Stachki, 194/1, Rostov-on-Don, Russia

4Southern Scientific Center RAS, 344006, prosp. Chekhova, 41, Rostov-on-Don, Russia

5Institute of Chemical Reagents and High Purity Chemical Substances of National Research Centre Kurchatov Institute, 107076, Bogorodsky rampart, 3, Moscow, Russia, 107076

*Corresponding author (email: kalinitch@mail.ru)
1. Method details

Soil and vadose zone samples were analyzed by standard methods. The water extraction of soluble salts was fulfilled under water to soil ratio 5:1 and following 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±0.2°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 Cl−, Ca2+ and Mg2+, SO42−, and Na+ content was measured by standard chemical methods: chloride ion was analyzed by the argentometric method with potassium chromate; Ca2+ + Mg2+ total content was detected by complexometric titration, Ca2+ was detected in another aliquot complexometrically; content of Mg2+ was calculated as a difference of Ca2+ + Mg2+ and Mg2+; sulfates were analyzed by BaSO4 sedimentation; Na+ content was analyzed by flame photometric detection using a flame photometer PFP7 (JENWAY, UK).

The soil Pb total content 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 Pb 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.

2. Plants organogenesis and Pb2+ passivation

The better will be agrophysical conditions for soil physicochemical properties improvement by phosphogypsum, the better will be the plant growth. The more CO2 will be consumed by the plants from atmosphere, the more soil CO2 will be produced by the plant roots in rhizosphere, the higher will be the soil partial CO2 pressure, and the greater will be a buffering chemical influence of amphoteric H2CO3 acid produced from the biologically originated CO2 in the surrounding plant root hair nutrition zone soil rhizosphere biome. This process is capable to sustain the soil solution pH close to neutral. Such conditions are preferable for plant growth. At the same time, this is a positive circumstance for the PbOH+, Pb(OH)20 and PbCO30, Pb(CO3)22−, PbHCO3+ formation. The following successful Pb2+ passivation, provides soil remediation.

The Ca2+ containing in phosphogypsum improves the soil physicochemical properties and also is acting as a nutritive source for plant and soil biota. Ca2+ acts as the soil biological carcass formation agent. In addition to inorganic ion association revealed using the ION–2 mathematical thermodynamic model, the Pb2+ binding of organic complexes is highly probable in fertile soil. This is favorable for irreversible intra-soil sink of dangerous chemical element from the active ecosphere.

Contamination of phosphogypsum produced from Kovdor apatite ore with Pb is many times less compared to the US EPA hazard standards, and even to the Russian limit, which is the
strictest in the world.\textsuperscript{5,6} According the research presented, the phosphogypsum is high-quality not toxic for soil and plant substance, and its application for the soil remediation and reclamation is environmental safety priority.

3. Phosphogypsum doses justification

The data of model experiment and calculations by ION-2 using the ion association patterns justify a low risk assessment of soil pollution with HMs containing in phosphogypsum.\textsuperscript{7} Nevertheless, careful thermodynamic assessment of phosphogypsum doses in model experiments and mathematical modeling is needed for individual soil and individual ore in the focus of environmental substantiation of amelioration and remediation to ensure the high level chemical soil engineering taking into account a motive of slight reduction of Pb\textsuperscript{2+} association in soil solution after phosphogypsum application.

4. Soil environment representation by the water extract

The important methodological point of the soil environment representation by the water extract is a reliability level of the research result. This is because in hydro-chemical terms the soil water extract is a diluted soil solution. The chemical equilibriums in such soil solution are distorted to the some extent compared to the soil environment.\textsuperscript{8} Nevertheless, the soil water extract is a good base for further research in the field of soil solution thermodynamics mathematical modeling in dry environment. One more reason to apply phosphogypsum in the steppe and semiarid environment is higher soil salinity, and, in consequence, a greater number of associated ions in the soil solution.\textsuperscript{9} Phosphogypsum dose for saline soil can be higher. This statement could be extended to the low saline soil too, because in dry steppe and semiarid environment the soil moisture is low, increasing the soil solution ionic strength.

5. Soil superdispersity reducing via BGT* methodology

The soil mineral and organic material of 30–50 (in some soils 40–70) cm illuvial horizon (in anthropogenically transformed soil, it is named a layer) is subjected to soil aggregates superdispersity at the standard agronomy, soil amelioration, and irrigation practices. The superdispersity is transformation and destruction of the soil mineralogical composition under the influence of periodical excessive moistening.\textsuperscript{10,11} The physical, chemical, physicochemical and biological properties, as well as the soil mineralogical, aggregate composition and architecture, are degrading in result of superdispersity. The superdispersity effect prevention is achieved when the amendment is applied into the deeper soil layer of 30–50 cm and is mixed with soil simultaneously.\textsuperscript{12} This excludes the soil profile temporal over-moistening after precipitation or standard irrigation. The unfavorable for soil aggregates stability mineral phase superdispersity is weaken subsequently.\textsuperscript{11} The HMs mobility and bioavailability reduces.\textsuperscript{13}

6. Early organogenesis plant growth stage

Usually there is a lot of moisture in the soil at these organogenesis stages. Therefore the first biogeochemical barrier does not work, and plants are at risk of pollutant intake. In addition, young plants have less developed ability to selectively consumption of chemicals from the soil. This is partly due to insufficient development of the root system.

On the one hand, the proposed device gives an opportunity for careful soil and phosphogypsum mixing providing close contact between the soil fine particles and the fine
particles of the ameliorant substance into the treated soil layer. On the other hand, the substance placement into deeper soil layer excludes a hazardous effect of the amendment on plant growth in the early organogenesis stages.

Probable pollution flux from soil to plant is passivated in consequence of relatively low soil water matrix potential due to improved soil carcass architecture. Thus the amount decreases of pollutants capable to penetrate the plant root system over the first biogeochemical barrier.

New deep and well aggregated soil profile ensures relatively low soil moisture content at the same soil water volume compared standard plowing technology. This makes more perceptible the biogeochemical role of ion association in reliable and environmentally safe waste recycling. The soil becomes easily accessible for the vast root zone.

Plant nutrition is a superposition of a root hair and a discrete soil solution micro-basin interaction at the "micro-basin – soil structural particle" interface in the process of rhizosphere spread throughout soil architecture carcass. The plant supplies carbon dioxide into a micro-basin via the root hair during the initial stage of root feeding from this discrete micro-basin. Then plant consumes the product via this root hair, if the product contained in the chemical solution of micro-basin is appropriate for the plant. Some root hair in rhyzosphere can penetrate the micro-basin containing pollutant. The plant “analyzes” composition of the initial portion of soil solution received by this root hair, and “finds” this initial portion improper. After that, the plant shuts the soil solution consumption through this exact root hair. Thus the plant selectively prevents contaminant penetration to the root system. The soil solution consumption by some root hair ceasing is possible only if the soil water matrix potential is sufficiently low to provide formation of the soil solution discrete micro-basins. At the same time, the minimal value of soil water matrix potential is to be additionally controlled technologically to ensure the soil solution reliable consumption by plant root system. The relative pollutant content in the plant biological product decreases also due to the plant aboveground and underground biomass increment.

7. Soil layer assignment for phosphogypsum applying

Exact assignment of the soil layer for mineral, organic, and organic-mineral amendment intra-soil applying depends on many reasons. This is a subject of future modeling, including soil solution chemical thermodynamic mathematic modeling, as well as the field research in different soils and landscapes.

8. References (supporting)

1. Carter, M.R.; Gregorich, E.G. Soil Sampling and Methods of Analysis, 2nd ed. CRC Press, 2007. ISBN 9781420005271.

2. Shtiza, A.; Swennen, R. Appropriate sampling strategy and analytical methodology to address contamination by industry. Part 2: Geochemistry and speciation analysis. Open Geosciences 2011, 3(1), 53–70.

3. PND F 16.1.42-04. The methodology for measuring the mass fraction of metals and metal oxides in powder soil samples by X-ray fluorescence analysis Russia. Moscow, 2004
4. 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*(6), 2717–2728.

5. US Environmental Protection Agency. Risk-Based Screening Table – Generic Tables. [http://www2.epa.gov/risk/risk-based-screening-table-generic-tables](http://www2.epa.gov/risk/risk-based-screening-table-generic-tables) (date of access 2020-01-30)

6. Maximum permissible concentrations of chemical substances in soil. Russian Health Standards 2.1.7.2042-06, 2006

7. Endovitsky, A.P.; Kalinichenko, V.P.; Bakoyev, S.Y.; Ivanenko, A.A.; Sukovatov, V.A.; Radevich, E.V. Certificate of the state registration of computer program “ION-2”. RU No 2009612162, published on 11/3/2009

8. Batukaev, A.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 solonetz as a driver of terrestrial carbon sink. *Solid Earth* **2016**, *7*(2), 415–423.

9. 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. Problems* **2015**, *2*(2), 136–153

10. Barre, P.; Berger, G.; Velde, B. How element translocation by plants may stabilize illitic clays in the surface of temperate soils. *Geoderma* **2009**, *151*, 22–30.

11. Topunova, I.V.; Prikhodko, V.E.; Sokolova, T.A. Influence of irrigation on the content and mineralogical composition of the clay fraction of the chernozem of the Rostov region (Bagaevsky-Sadkovsky irrigation system). *Moscow Univ. Bul. Ser. 17: Soil Sci.* **2010**, *1*, 3–10.

12. Kalinitchenko, V.P. Optimizing the matter flow in biosphere and the climate of the Earth at the stage of technogenesis by methods of biogeoecosystem technique (problem-analytical review). *Int. J. Environ. Problems* **2016**, *4*(2), 99–130.

13. Anisimov, V.S.; Kochetkov, I.V.; Dikarev, D.V.; Anisimova, L.N.; Korneev, Y.N. Effects of physical-chemical properties of soils on $^{60}$Co and $^{65}$Zn bioavailability, *J. Soils Sediments* **2015**, *15*(11), 2232–2243.

14. Rykhlik, A.E.; Bezuglova, O.S. Method of Intra-Soil Pulse Continuous-Discrete Moistening (Model Experiment). *Biogeoecosystem Technique* **2017**, *4*(1), 39–65.

15. Grassian, V.H. Physical Chemistry of Environmental Interfaces: Aerosols, Nanomaterials and Indoor Surfaces. *The Chemist* **2019**, *91*, 13–17.