Production and Use of Selenium Nanoparticles as Fertilizers

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1. INTRODUCTION

Trace element selenium is indispensable for the functioning of most living creatures.1 Se is found in soil, water, crops, animals, and food.2 The soil Se content varies greatly throughout the world. The selenium content of soils varies greatly from 0.005 to 1200 μg g⁻¹; and most commonly between 0.1 and 10 μg g⁻¹.3−6 The concentration of Se in an individual living organism highly depends on Se consumption.7−9 Se nanoparticles enhance the plant disease suppressing ability and manifest the antifungal properties,10,11 Se is a part of mammal protein, which is commonly named as selenoproteins.12 There are 25 known selenoproteins. At least 12 selenoproteins are antioxidant enzymes largely involved in the redox homeostasis of the organism along with other enzyme antioxidants.13,14 The most known proteins of this kind are glutathione peroxidase (GSH-Pxs), thioredoxin reductase (TrxR), and selenoprotein P (SePP). The last molecule contains up to 10 Se atoms.15 Enzymes have a tetrameric form and contain one Se per subunit.16 Selenoproteins form an antioxidant barrier for the protection of organisms from the damaging effect of the cellular metabolism harmful products including reactive oxygen species.17,18 The enzymes decompose hydrogen peroxide and organic hydroperoxides, protecting the tissue from oxidative...
damage. The TrxRs are involved in the cell redox potential determination and signaling. SePP is an extracellular antioxidant. Selenoprotein activity depends on the Se concentration in tissues. Normalizing Se balance in the organism is an important task. For this, selenium content correction is carried out in food products. The Se balance in food could be corrected, if needed, by Se containing fertilizer application to the soil. The Se-balanced food manufacturing technology is simple. This allows us to overcome the Se imbalance problem in the vast agricultural lands completely. The problem of soil Se concentration normalization has been tried to be solved for more than half a century. Organic (selenium-containing amino acids, chelates, etc.) and inorganic (oxides, salts, and selenium minerals) selenium compounds are used as fertilizers. The peculiarity of both classes of fertilizers is that the Se introduced into the soil remains in the upper fertile layer until one or, at best, a few harvests only. Then, inorganic selenium compounds are leached along with rains into the lower soil infertile horizons. The organic Se compounds are not actively leached but degraded rather quickly after applying. The zero-valent Se nanoscale state is a concomitant additive to fertilizers. These nanoparticles do not dissolve in water and aqueous solutions and are not leached from the soil slowly. Different methodological approaches are used for producing Se nanoparticles. Se is supplied from the soil to plants via nanoparticle surface gradual oxidation and oxide release to the soil solution.

This paper is a development of our previous studies. The technology for producing Se zero-valent-state nanoparticles has been discussed. The Se zero-valent-state nanoparticles were investigated as fertilizers and antioxidants. The synergy problem is discussed linking Se nanoparticles and plant oxidative stress reduction. The study has synergistic focus. It has opened up the possibility not only to produce but also to apply the Se zero-valent-state nanoparticles based on the Biogeosystem Technique (BGT*) methodology for long-term improvement of the soil system and for higher agricultural efficacy of Se nanoparticles.

The aims of the research are as follows: Se nanoparticle zero-valent-state study, Se nanoparticle technology of laser ablation in water development, experimental study of Se nanoparticle influence on the plant growth, and effective agricultural application of Se nanoparticles via the BGT* methodology.
2. RESULTS AND DISCUSSION

2.1. Se Nanoparticle Properties. The Se nanoparticles obtained by ablation of a bulk Se target in still water with power fiber laser have relatively large sizes, around 700–800 nm. The resulting nanoparticles were nearly monodisperse in size and mass. This is due to the fact that Se is a brittle material, and the ablated particles are composed of small entities in the course of “classical” ablation. These are particles detached from the target because of thermal shock. The latter particles are larger and should be used for the tests. The laser fragmentation process has been applied for particle size reduction. The individual particles were melted under the laser pulse, and thus, the average size of the individual particles gradually decreased. Fragmentation time of the mass distribution function of Se particles subjected to laser fragmentation is shown in Figure 1a. The 0 min curve showed the just-generated Se particle content. The gradual decrease of the average size of individual particles matches the high probability of the above-mentioned antioxidant potential manifestation of Se nanoparticles in plant products. The transmission electron microscopy (TEM) view of Se nanoparticles after laser fragmentation is shown in Figure 1b. The main Se nanoparticle fraction after fragmentation is less than 100 nm.

The main nanoparticle mass is contained in the particles of 800 nm diameter. The main particle mass part shifted to a small particle size correspondingly when the laser fragmentation time gradually increased and arrived finally to a size less than 500 nm according the X-ray diffractograms of Se particles (Figure 2). The value 500 nm corresponds to the generally accepted notion that nanoparticles have a size of 100 nm. The last fraction of nanoparticles was widely present in the product. Fragmented Se nanoparticles are amorphous (Figure 2a). This fact corresponds to the previous observations. Relatively large Se particles preserve a crystallographic orientation of the initial target (Figure 2b). Smaller Se nanoparticles have no distinct crystalline structure. However, it can be supposed that a structural difference does not affect the possibility of successful soil application of the Se nanoparticles as stimulants and antioxidants because a great part of the product is formed from the active nanoparticles of size about 100 nm. A positive circumstance is that the biological activity of amorphous nanoparticles is higher compared to that of crystalline nanoparticles. This feature can be discussed concerning the greater size particle fraction. On the one hand, this fraction can be supposed that it consisted of crystalline nanoparticles with amorphous nanoparticles on the surface. On the other hand, larger size particles can be presented as those associated with amorphous nanoparticles. In both cases, the association of Se nanoparticles to the complexes with soil mineral matter is believed to be reduced. The fragmentation provides prolonged functioning of associated Se nanoparticles because of the rather stable "associated Se nanoparticle-soil solution" interface. Se nanoparticles influence the seedlings, plant growth, biochemical characteristics, and yield.

2.2. Se Nanoparticle Effect on Plants. The effect of Se nanoparticles at different concentrations on plant development was studied using the climate chamber. It has been revealed that Se nanoparticles did not affect the plant growth very significantly under unchanged artificial climate for the first 10 days of organogenesis (Figure 3). The plant’s growth and habitat were slightly better with a Se nanoparticle dose of 10 μg kg⁻¹. For more complete assessment, we calculated the plant leaf plate surface area using Green Image software. The biggest difference in indicators was registered in an experiment conducted on the 30th day after the beginning of the plant growth. The plant leaf plate surface area was 30 ± 2 cm² in the control option of the experiment. The leaf plate surface area of plants grown at a Se nanoparticle concentration of 1 μg kg⁻¹ was about 32 ± 3 cm² and correspondingly the leaf plate area for 5 μg kg⁻¹ was 37 ± 2 cm², 10 μg kg⁻¹ was 38 ± 3 cm², and 25 μg kg⁻¹ was 28 ± 4 cm².

The high-temperature stress alleviation by Se nanoparticles was shown for Sorghum. Hyperthermia inhibited the development of radish plants (Figure 4). The plant leaf plate surface area was only about 14 ± 3 cm² in the control option of the experiment 30 days after planting. Hyperthermia has stressed the plants grown at a Se nanoparticle concentration of 1 μg kg⁻¹. The plant leaf plate surface area was 16 ± 4 cm² at a Se nanoparticle concentration of 1 μg kg⁻¹, and correspondingly, the leaf plate area for 5 μg kg⁻¹ was 27 ± 3 cm²; 10 μg kg⁻¹ was 29 ± 3 cm², and 25 μg kg⁻¹ was 15 ± 3 cm². The stressed plant’s growth rate was the highest in Se nanoparticle concentrations of 5 and 10 μg kg⁻¹. The plant leaf plate surface area after Se nanoparticle application was almost 2 times larger compared to the stressed plants grown without Se nanoparticle addition to the soil. It was observed that such a pattern was observed when growing at least three radish generations on the same soil. This is a preliminary proof of the possible prolonged action of Se nanoparticles. Consequently, further studies are of high priority on the Se nanoparticle application to the soil for effective preservation. Because the effectiveness does not differ much in the Se nanoparticle concentrations of 5 and 10 μg kg⁻¹, we decided to use the Se nanoparticle concentration of 10 μg kg⁻¹ only in the subsequent experiments. Tentatively, the potential time for Se leaching from soil could be increased at higher Se nanoparticle concentrations.

The plant organogenesis proceeds in different ways after heat stress of the plants grown in the untreated soil and of the plants grown in the soil with the Se nanoparticle concentration of 10 μg kg⁻¹ (Figure 5). The Se nanoparticles did not affect the development of chilli peppers compared to the control option after hyperthermia. The plant organogenesis was satisfactory in both options.
also experimented with barley (*Hordeum vulgare*) and cabbage (*Brassica oleracea*) seedlings. Cabbage did not survive the hyperthermia in both conditions, that is, being grown on the soil with the addition of Se nanoparticles at a concentration of 10 μg kg⁻¹ and grown in the untreated soil (control option). Only few barley plants (about 10% of the seedling initial number) of a series survived in the soil with Se nanoparticles. After exposure to hyperthermia, the eggplant grown on the soil with the Se nanoparticle addition at a concentration of 10 μg kg⁻¹ showed almost twice the plant leaf plate surface area compared to the eggplant plant leaf plate area grown in the untreated soil. Similar results were obtained with the leaf plate area of tomato plants. The leaf plate surface area of the cucumber plant grown using Se nanoparticles increased almost by 50% compared to the experimental control option. The antioxidant potential manifestation of Se nanoparticle can almost by 50% compared to the experimental control option. The soil organic matter (SOM) is stimulated with Se nanoparticles as the other nanoparticle, HS, and SOM functioning in the soil are linked to organic matter degradation. Organic matter degradation is controlled by microbial communities significantly influencing soil fertility. Bacteria within specific habitats are not a faceless mixture of the once acquired participants but are structurally strictly ordered polymicrobial communities in which each participant takes its specific functional role. The occurrence of polymicrobial communities, structures, and composition of polymicrobial biofilms in soil is an important objective for controlled soil evolution. The soil is a sophisticated bioreactor whose performance provides acceleration of manifold biodegradation processes. This acceleration is achieved by sustaining, promoting, and steering of preselected polymicrobial consortia. Thus, the soil microbiome functioning in distinct areas should be distinguished and expanded. The soil is not a perfect bioreactor as a mammal colon. We insist that the soil bioreactor function has to be improved. The standard agricultural technology fails to achieve this goal.

In our experiment, we mixed Se nanoparticles at the soil granulometric composition microlevel using forced soil and solution introduced to soil mixing. A good contact of Se nanoparticles and the soil provided the needed result. In standard agronomic practice, ploughing or other soil cultivation procedures do not provide the formation of the soil aggregate system needed for proper Se nanoparticle functioning. The soil clods are of a transverse dimension up to 100 mm after standard ploughing. Thus, the Se nanoparticles will fall into the gaps between large soil aggregates and thus will be excluded from the active soil biological process.

Another concern of the Se nanoparticle as well as other nanoparticle, HS, and polymicrobial biofilm function in the standard agrarian technology framework is soil moisturizing. It is a well-known fact that the soil water content must be suitable for the plant growth and for the functions of nanoparticles, HS, polymicrobial biofilms. The soil water content should not be too high, preventing leaching of the nanoparticles and other soil matter. However, standard irrigation is incapable to decide this task because the soil humidity is high after standard watering. This determines the soil interface degradation and water and matter loss to the preferential water flux from the soil to the vadose zone.

The nanoparticles used in agriculture has an important issue which is the strict dosage and distribution control. Both are impossible under the current agrarian technology. Thus, the assessment of the environmental risk of nanoparticle application in the soil and/or to the plant (seeds) for plants, animals, and humans is defined as high.
Se nanoparticles are the pronounced low-dose stimulant. The Se standard fertilizer form application is assessed as less efficient compared to the Se nanoparticles concerning biological processes and the yield in the soil and plants.42-44 Nanoparticle dosage prescription demands precaution because excessive nanoparticle doses are toxic to plants and the soil.45 The nanoparticle doses for foliar or soil applications are different because of soil sorption capability.46 The recommended Se nanoparticle dosage is about 0.1–0.4 g ha\(^{-1}\).42,47 But this dose, as well as a tenfold and even hundred times higher doses, is not capable to be supplied using standard agricultural equipment. Thus, the Se nanoparticle application to the field crops is possible now only on small experimental plots.47 A manual mixing and application to the soil and/or plant (seeds) is practiced in the absence of a suitable robotic system.

Stability of nanoparticles over time is commonly regarded as acceptable. In our opinion, this point of view is an exaggeration. Being a result of the natural product heavy transformation, the nanoparticles have a finite term of existence. There is an urgent need to produce the nanoparticles immediately before the application in the soil and to plants. In addition to the above-mentioned motives, this task ensures a suitable robotic system synthesis.

The problems mentioned can be solved using the BGT* methodology.32 Active intrasoil milling of the 20–45 cm soil layer can provide a fine aggregate soil system of an initially compacted soil subarable horizon.48,49 This improves the soil and ensures a possibility to supply the Se nanoparticles, HS, and polymicrobial biofilm starters into the soil while soil milling.50 New abundant soil interfaces ensure a high rate of soil biological process in the multilevel soil architecture system. Because of their high surface energy, nanoparticle aggregates into the complexes with soil matter. Therefore, nanoparticles after application into the soil are no longer the initial substances. BGT* overcomes this circumstance because of the priority rhizosphere development. The probability is higher in the interactions on the internal surface of the soil where nanoparticles are located—root system interface. This provides a high rate of Se nanoparticle supply to the plants. On the contrary, the mean rate of soil passivation of Se nanoparticles is lower because of the reduction in the interaction period of Se nanoparticles and the internal surface of the soil. The BGT* intrasoil pulse continuous-discrete watering paradigm provides water supply to the soil without leaching the soil substances.54 The soil matrix potential value is from −0.2 to −0.4 MPa after intrasoil pulse continuous-discrete watering application. This potential is much less than that of standard irrigation. However, at the same time, this soil matrix potential value is a priority for the plants and soil biome organogenesis. It is very important for the soil matter turnover because the water spread throughout the soil is strictly controlled. This eliminates the water preferential flux to the vadose zone, soil matter leaching and provides the Se nanoparticles, HS, polymicrobial biofilm starters an expanded development, as well as the soil biological process and high productivity of the soil.52

For the first time, the synergistic efficacy was shown for the Se zero-valent-state nanoparticles, and a new procedure has been proposed for this substance to be applied to the soil based on the BGT* methodology.52 This synergy will provide a long-term fertility to the soil system and high stable plant productivity.53 The soil, plant, and environmental health will be improved.54–56

3. STUDY IMPLICATIONS AND OUTLOOK

In this paper, a developed technology has been shown for producing Se nanoparticles using laser ablation. The prepared Se nanoparticles consisted of zero-valent Se and had the same characteristic size. The prepared Se nanoparticles do not significantly affect the development of plants under reference conditions. The prepared Se nanoparticles effectively leveled the adverse effect of hyperthermia in eggplant, tomato, and cucumber seedling organogenesis. The prepared Se nanoparticle concentration of 10 μg kg\(^{-1}\) in the soil is the most effective for the antioxidant potential manifestation of Se nanoparticles and plant growth improvement. The BGT* methodology for the intrasoil milling of 20–45 cm soil layer for soil multilevel aggregate system formation and intrasoil pulse continuous-discrete watering for controlling soil water regime has a perspective for better functioning of Se nanoparticles in the real soil. This will provide a synergy effect of soil mechanical processing, nanoparticles, HS, and polymicrobial biofilms on the soil fertility.

4. METHODS

4.1. Selenium Nanoparticle Production. Se nanoparticles were produced in water using the laser ablation process. For the irradiation of the solid Se target, the following lasers were used: a fiber ytterbium laser with a wavelength between 1060 and 1070 nm, pulse repetition rate of 20 kHz, pulse duration of 80 ns, and average power of 20 W and a copper vapor laser with wavelengths of 510.6 and 578.2 nm and an average power of 8 W.

In the first series of studies, the Se target was exposed to laser irradiation in a still water medium. In the second series of studies, a flowing cell reactor was used. This kind of reactor provides the just-generated nanoparticle screening action reduction in the course of target laser irradiation. The Se nanoparticle generation rate was about 0.8 mg/min in still water and 2.4 mg/min in a flowing cell reactor.57 The generated Se nanoparticle size was determined using analytical measuring centrifuge DC24000 (CPS Instruments). The nanoparticle morphology was acquired using the TEM Carl Zeiss 200FE accounting for electron energy loss spectrometry. The nanoparticle crystalline structure was determined on X-ray diffractometer Bruker AXS P4.

4.2. Vegetation Tests. The Se nanoparticle water suspension was introduced into the soil. The soil Se nanoparticle concentration was about 1, 5, 10, and 25 μg kg\(^{-1}\). To apply the Se nanoparticle in ultralow doses, the original colloidal solution of nanoparticles was diluted with water to provide a dose of 100 g of diluted solution per kg of the soil, air-dried at 22 °C. For that, forced soil mechanical mixing was applied in the course of diluted solution, by adding the soil to achieve the uniform distribution of nanoparticles into the soil. The experiments were carried out in a climate chamber using the following procedures.

1. Plants are grown in the soil imitating the standard organogenesis environment conditions: illumination of 16 h per day, temperature of 22 °C, soil humidity of 25% SDW, and an experiment duration of 30 days.

2. Plants are grown in the soil under changing organogenesis environment conditions. The standard environmental conditions for the first 10 days are as follows: illumination of 16 h day\(^{-1}\), temperature of 22 °C, and soil humidity of 25% SDW. The plant stress for 5 days in
hyperthermia of 40 °C. The standard environmental conditions for the next 15 days are as follows: illumination of 16 h day⁻¹, temperature of 22 °C, and soil humidity of 25% SDW. It was assumed that the plant development rate under the stress could reduce compared to the standard organogenesis conditions in the second series of experiments.²⁸

The plant species under experiment were radish (Raphanus sativus var. sativus), arugula (Eruca sativa), eggplant (Solanum melongena), cucumber (Cucumis sativus), tomato (Solanum lycopersicum), and chili pepper (Capsicum annum). The plant seedlings were grown in the vegetation vessel with a diameter of 6 cm and a height of 10 cm. The plant seedling leaf surface area calculation was performed using Green Image software.²⁹

The studied parameters were determined in triplicates. Calculations of the statistical significance of the data and the associated errors were performed with Statistica v.10.0.1011, developed by StatSoft (USA). All data presented are statistically significant at the level of p < 0.05.

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Notes
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■ REFERENCES

(1) Gissel-Nielsen, G. Selenium content of some fertilizers and their influence on uptake of selenium in plants. J. Agric. Food Chem. 1971, 19, 564–566.
(2) Rosenfeld, I.; Beath, O. A. Selenium: Geobotany, Biochemistry, Toxicity and Nutrition; Academic Press: New York, London, 1964.
(3) Oilfield, J. E. Selenium e-World Atlas; STDA: Grimbergen, Belgium, 1999.
(4) Bagrintseva, O. V.; Mazo, V. K.; Khotimchenko, S. A.; Shatrov, G. N. In to the question of selenium using in case of foodstuffs enrichment. Vopr. Pitan. 2012, 81, 4–12.
(5) Zachara, B. A. Selenium in Complicated Pregnancy. A Review. Adv. Clin. Chem. 2018, 86, 157–178.
(6) Alexander, J. Selenium. Handbook on the Toxicology of Metals, 4th ed.; Academic Press, 2015; Chapter 52, Vol II, pp 1175–1208
(7) Borawska, M. H.; Witkowska, A. M.; Hukalowicz, K.; Markiewicz, R. Influence of Dietary Habits on Serum Selenium Concentration. Ann. Nutr. Metab. 2004, 48, 134–140.
(8) Levander, O. A. Scientific rationale for the 1989 recommended dietary allowance for selenium. J. Am. Diet. Assoc. 1991, 91, 1572–1576.
(9) Adadi, P.; Barakova, N. V.; Muravyov, K. Y.; Krivoshapkina, E. F. Designing selenium functional foods and beverages: A review. Food Res. Int. 2019, 120, 708–725.
(10) Nandini, B.; Hariprasad, P.; Prakash, H. S.; Shetty, H. S.; Geetha, N. Trichogenic-selenium nanoparticles enhance disease suppressive ability of Trichoderma against downy mildew disease caused by Sclerospora graminicola in pearl millet. Sci. Rep. 2017, 7, 2612.
(11) Joshi, S. M.; De Britto, S.; Jogaiah, S.; Ito, S.-i. Mycogenic Selenium Nanoparticles as Potential New Generation Broad Spectrum Antifungal Molecules. Biomolecules 2019, 9, 419.
(12) Varlamosova, E. G.; Cheremushkina, I. V. Contribution of mammalian selenocysteine-containing proteins to carcinogenesis. J. Trace Elem. Med. Biol. 2013, 39, 76–85.
(13) Sharapov, M. G.; Novoselov, V. I.; Gudkov, S. V. Radio-protective Role of Peroxiredoxin 6. Antioxidants 2019, 8, 15.
(14) Ulrich, K.; Jakob, U. The role of thiols in antioxidant systems. ree Radical Biol. Med. 2019, 140, 14–27.
(15) Steinbrenner, H.; Speckmann, B.; Klotz, L.-O. Selenoproteins: Antioxidant selenoenzymes and beyond. Arch. Biochem. Biophys. 2016, 595, 113–119.
(16) Zachara, B. A. Mammalian selenoproteins. J. Trace Elem. 1992, 6, 137–151.
(17) Lyakhovich, V. V.; Vavilin, V. A.; Zenkov, N. K.; Menshchikova, E. B. Active defense under oxidative stress. The antioxidant responsive element. Biochemistry 2006, 71, 962–974.
(18) Sharapov, M. G.; Novoselov, V. I. Catalytic and Signaling Role of Peroxiredoxins in Carcinogenesis. Biochemistry 2019, 84, 79–100.
(19) de Lorgeril, M.; Salen, P. Selenium and antioxidant defences as major mediators in the development of the chronic heart failure. Heart Failure Rev. 2006, 11, 13–17.
(20) Mostert, V. Selenoprotein P: Properties, Functions, and Regulation. Arch. Biochem. Biophys. 2000, 376, 433–438.
(21) Asri-Rezaei, S.; Nourian, A.; Shalizlar-Jalali, A.; Najafi, G.; Nazarizadeh, A.; Koohestani, M.; Karimi, A. Selenium supplementa-
tion in the form of selenium nanoparticles and selenite sodium improves mature male mice reproductive performances. Iran. J. Basic Med. Sci. 2018, 21, 577–585.
Cluster Bean Cyamopsis tetragonoloba.

Nanoparticles on Growth, Biochemical Characteristics and Yield of aggregates in soils. OA 2017, 60, No. e1760452, DOI: 10.1590/1678-4324-201760452.

Sowndarya, P.; Ramkumar, G.; Shivakumar, M. S. Green synthesis of selenium nanoparticles conjugated Cusnea dentata plant leaf extract and their insecticidal potential against mosquito vectors. Sci. Cells, Nanomed., Biotechnol. 2017, 45, 1490–1495.

Gudkov, S.; Glazkov, P.; Zavalin, A.; Kovaleva, T.; Nikulina, E.; Glushko, A.; Dubinok, N.; Shafee, G.; Davydov, R. Production and application of selenium nanoparticles to prevent ionizing radiation-induced oxidative stress. IOP Conf. Ser.: Earth Environ. Sci. 2019, 390, 012031.

Kuzmin, P. G.; Shafee, G. A.; Voronov, V. V.; Raspopov, R. V.; Ariana, E. A.; Trushina, E. N.; Gmoshinski, I. V.; Khotimchenko, S. A. Bioavailable nanoparticles obtained in laser ablation of a selenium target in water. Quantum Electron. 2012, 42, 1042–1044.

Shafee, G.; Barmina, E.; Valiullin, L.; Simakin, A.; Osyvanka, A.; Demin, D.; Kosolapov, V.; Korshunov, A.; Denisov, R. Soil fertilizer based on selenium nanoparticles. IOP Conf. Ser.: Earth Environ. Sci. 2019, 390, 012041.

Simakin, A.; Baimler, I.; Uvarov, O.; Rud’, I.; Krassnovsheskov, V. Obtaining of nanoparticles of Sc, Ti, V, Cr, Mn, Fe, Co, Ni with controlled sizes and properties using laser ablation. IOP Conf. Ser.: Earth Environ. Sci. 2019, 390, 012036.

Cieschi, M. T.; Polyakov, A. Yu.; Lebedev, V. A.; Volkov, D. S.; Pankratov, D. A.; Vel'gazhina, A. A.; Perminova, I. V.; Lucena, J. J. Eco-Friendly Iron-Humic Nanofertilizers Synthesis for the Prevention of Iron Chlorosis in Soybean (Glycine max) Grown in Calcareous Soil. Front. Plant Sci. 2019, 10, 413.

Polyakov, A. Y.; Lebedev, V. A.; Shirshin, E. A.; Rumyantsev, A. M.; Volkov, A. B.; Zherebker, A.; Garshev, A. V.; Goodinl, E. A.; Perminova, I. V. Non-classical growth of water-dispersible spheroidal gold nanoparticles assisted by leonardite humate. CrystEngComm 2017, 19, 876–886.

Kalinichenko, V.; Batu'eva, A.; Zarmaa, A.; Startsev, V.; Chernenko, V.; Dikaye, Z.; Sushkova, S. Biogeosystem technique as the way to certainty of soil, hydrosphere, environment and climate. Geophys. Res. Abstr. 2016, 18, No. EU2016-3419.

Hu, T.; Li, H.; Li, J.; Zhao, G.; Wu, W.; Liu, L.; Wang, Q.; Guo, Y. Absorption and Bio-Transformation of Selenium Nanoparticles by Wheat Seedlings (Triticum aestivum L.). Front. Plant Sci. 2018, 9, 597.

Ragavan, P.; Ananth, A.; Rajan, M. R. Impact of Selenium Nanoparticles on Growth, Biochemical Characteristics and Yield of Cluster Bean Cyamopsis tetragonoloba. Int. J. Environ. 2017, 2, 2917.

Djanaguiraman, M.; Belliraj, N.; Bossmann, S. H.; Prasad, P. V. V. High-Temperature Stress Alleviation by Selenium Nanoparticle Treatment in Grain Sorghum. ACS Omega 2018, 3, 2479–2491.

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 Kastanoezom complex. J. Soils Sediments 2018, 19, 2717–2728.

Volikov, A. B.; Kholodov, V. A.; Kulikova, N. A.; Philippova, O. I.; Ponomarenko, S. A.; Lasareva, E. V.; Parfonova, 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.

Piccolo, A.; Spacini, R. L.; Savy, D.; Drosos, M.; Cozzolino, V. The Soil Humeoma: Chemical Structure, Functions and Technological Perspectives. In Sustainable Agrochemistry; Vaz, S., Jr., Ed.; Springer: Cham, 2019; pp 183–222.

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

Kalinichenko, V. P.; Glinushkin, A. P.; Sokolov, M. S.; Sharsk, V. K.; Ladan, E. P.; Minkina, T. M.; Zinchenko, V. E.; Chernenko, V. V.; Makarenkov, D. A.; Rykhlik, A. E.; Larin, G. S. Nature-Based Technologies of Biogeosystem Technique. Agrochemistry 2020, 2, 61–68.

Shipelin, V. A.; Gmoshinski, I. V.; Khotimchenko, S. A. Risk assessment of silver nanoparticles. IOP Conf. Ser.: Mater. Sci. Eng. 2015, 98, 012010.

Chernikova, O.; Mazhayshkyu, Yu.; Ampleeva, L. Selenium in nanoform as an alternative to microfertilizers. Agron. Res. 2019, 17, 974–981.

Pestovsky, Y. S.; Martinez-Antonio, A. The Use of Nanoparticles and Nanoformulations in Agriculture. J. Nanosci. Nanotechnol. 2017, 17, 8699–8730.

Tremblay, G. F.; Bélanger, G.; Lajeunesse, J.; Chouinard, P. Y.; Charbonneau, É. Timothy response to increasing rates of selenium fertilizer in Eastern Canada. Agron. J. 2015, 107, 211–220.

Rajput, V.; Minkina, T.; Sushkova, S.; Behal, A.; Maksimov, A.; Blicharska, E.; Ghazaryan, K.; Movsesyan, H.; Barsova, N. ZnO and CuO nanoparticles: a threat to soil organisms, plants, and human health. Environ. Geochim. Health 2020, 42, 147–158.

Ljashenko, G. M.; Kalinichenko, V. P. Soil and air pollution of plant leaves with lead //Proceedings of higher educational institutions. North Caucasian region. Nat. Sci. 2006, 512, 124–130.

Ampleueva, L. E.; Konkov, A. A.; Radnaya, A. V. Selenium nanoparticles suspension influence on the corn “Obsky 140” seeds qualitative and quantitative indicators. Bull. P. A. Kostychev Royzhan Agrotechnological Univ. 2012, 3, 33–35.

Kharitonova, G. V.; Shein, E. V.; Krutikova, V. O.; Ostrouhova, A. V. Calcium Carbonate Formations in Edaphic Components of Ecosystems. Biogeosystem Tech. 2018, 5, 197–212.

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.

Kalinichenko, V. P. Device for application of substance while intra-soil milling. RU 2387115 C2, Published on March 27, 2010.

Keesstra, S. D.; Bouma, J.; Wallinga, J.; Tittonell, P.; Smith, P.; Fresco, L. O. The significance of soils and soil science towards realization of the United Nations Sustainable Development Goals. Front. Plant Sci. 2019, 1042; 29; American Chemical Society: San Diego, CA, 2019https://plan.core-apps.com/acs_sdx2019/abstract/6dc4fdd9-0f1c-41b3-a54e-a4ce18736726.

Glinushkin, A. P.; Kudayarov, V. N.; Sokolov, M. S.; Zinchenko, V. E.; Chernenko, V. N. Nature-Similar Technologies of the Biogeosystem Technique in Solving a Global Social and Environmental Problem. Biogeosystem Tech. 2018, 5, 159–196.

Kot, F. S.; Farran, R.; Fujiiwara, K.; Kharitonova, G. V.; Kochva, M.; Shavu, A.; Sugo, T. On boron turnover in plant-litter-soil system. Geoderma 2016, 268, 139–146.

Keestra, S. D.; Bouma, J.; Wallinga, J.; Tittonell, P.; Smith, P.; Cerdà, A.; Montanarella, L.; Quinton, J. N.; Pachepsky, Y.; van der Putten, W. H.; Bardgett, R. D.; Moolenaar, S.; Mol, G.; Jansen, B.; Fresco, L. O. The significance of soils and soil science towards realization of the United Nations Sustainable Development Goals. Soil 2016, 2, 113–128.

De Melo, B. A. G.; Motta, F. L.; Santana, M. H. A. Humic acids: Structural properties and multiple functionalities for novel technological developments. Mater. Sci. Eng. C 2016, 62, 967–974.

Kalinichenko, V. P.; Glinushkin, A.; Sokolov, M.; Batu'eva, A.; Minkina, T.; Zinchenko, V.; Chernenko, V.; Startsev, V.; Mandzhieva, S.; Sushkova, S.; Makarenkov, D.; Il’ina, L.; Larin, G.; Rykhlik, A.
(57) Ayyyzhy, K. O.; Voronov, V. V.; Gudkov, S. V.; Rakov, I. I.; Simakin, A. V.; Shafeev, G. A. Laser Fabrication and Fragmentation of Selenium Nanoparticles in Aqueous Media. *Phys. Wave Phenom.* 2019, 27, 113–118.

(58) Veselov, A. P. Simulation Model of a Possible Trigger for Reversible Switching of the Stress Regime in Plants. *Russ. J. Plant Physiol.* 2001, 48, 104–110.

(59) Astashev, M.; Beloshapkina, O.; Kvitko, A.; Matasov, A.; Zakharyan, R.; Bogun, I. Development of software for plant leaf area estimation. *IOP Conf. Ser.: Earth Environ. Sci.* 2019, 390, 012029.