Application of Callopian clay to improve the productivity of zinc-contaminated soils in lawn ecosystems

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Abstract. Pollution of lawn soils with heavy metals leads to the suppression of life and activity of living organisms inhabiting these ecosystems. The use of various means of soil detoxification will make it possible to neutralize the effect of technogenic pressure on the functional properties of urban ecosystems. The article presents data on the sorption-fertilizing properties of Callovian clay when used in zinc-contaminated soils of lawn ecosystems. The study used a small-plot field experiment, which simulated artificial contamination of agro-gray soil with zinc. The article discusses 2 methods of tillage and 4 doses of fertilizer-sorbent. It was found that the use of Callovian clay led to an increase in the production of raw and dry phytomass of lawn grasses by 3.7 - 33.2%, microbiological activity of soils by 0.9 - 132.5 times, as well as a decrease in zinc toxicity by 10 - 25%. The sorption-fertilizing effect and the optimal doses of the applied Callovian clay were determined by the time when the Callovian clay was introduced into the soil (autumn or spring).

1. Introduction

Lawn ecosystems are part of the green infrastructure of urban areas and perform such important ecological functions as the conservation of biological diversity, sequestration of atmospheric CO₂ [1], storage of organic carbon [5;9], oxygen production [1], protection of anthropogenic pollutants. In addition, lawn ecosystems make it easy to combine natural and man-made components in the design of urban landscapes. Pollution of urban soils with heavy metals does not allow lawn ecosystems to fully realize their ecosystem services [7].

At present, a significant number of technologies have been developed and implemented in the field of urban soil detoxification from heavy metal pollution and increasing the productivity of lawn ecosystems. Among such technologies, phytoremediation, chemical soil purification, physical soil purification, and sorption detoxification of soils are often used [3;4;6]. Agrotechnical and agrochemical methods are actively used to increase the aesthetic appeal of lawns. A very promising and rational technology for increasing the environmental sustainability of soils in lawn ecosystems will be a technology based on the use of natural materials as a fertilizer-sorbent, which are waste from the mining industry (overburden). Callovian clay, an overburden rock of marine origin from the Mikhailovsky iron ore basin of the Kursk magnetic anomaly, which has a slightly alkaline reaction of the medium, contains up to 4% organic matter, and is rich in potassium and microelements, can serve as one of such fertilizer-sorbents for soils of lawn ecosystems.

The aim of the work was to evaluate the sorption and fertilization properties of Callovian clay when used in zinc-contaminated soils of lawn ecosystems.
2. Materials and methods

The study was conducted in the growing season of 2021 on the experimental sites of the Agrobiological Station of KSU. The soil cover is represented by agro-gray medium loamy soils on heavy loess-like loam. Scheme of the structure of the soil profile: AU (25 cm) - AEL (31 cm) - BEL (72 cm) - BT (104 cm). A small-scale field experiment was laid. The size of each experimental plot was 0.5×0.5 m$^2$. The protective strip between the plots was 0.5 m. Crushed (up to a fraction of no more than 1 mm) Callovian clay (fertilizer-sorbent) was applied in dry form, embedding into the soil of experimental plots to a depth of 20 cm. Doses were 250, 500, 750, 1000 g/m$^2$. To determine the optimal method of tillage with Callovian clay, it was introduced into the soil in autumn (September 2020) and spring (April 2021). In the spring of 2021, the soils of the plots were artificially contaminated with zinc. Zinc was introduced in dissolved form in the form of zinc nitrate. The dose of pollution was tested equal to 10 maximum allowable concentrations for loamy soils. Plots uncontaminated with zinc and not treated with Callovian clay served as control. In all control and experimental plots, lawn grass was planted, represented by a mixture of seeds of cereal crops: perennial ryegrass 40%, red fescue 35%, bluegrass meadow 20%. According to the seeding rate recommended by the manufacturer. The experiment was repeated four times. Determination of dry and wet biomass of cereal crops (lawn grass) was carried out at the heading stage in the third decade of June. Determination of the physical and chemical properties of soils was carried out according to standard methods: pH (KCl GOST 26483-85), humus content (according to Tyurin GOST 26213-91), nitrogen content (according to Kornfield), phosphorus (GOST 26204-91) and potassium (GOST 26204 -91). The microbiological activity of soils was determined by growing groupings of soil microorganisms (bacteria, fungi, actinomycetes) on nutrient media (HMF agar, Czapek's medium, Gauze I medium). The mobile forms of Zn were determined by atomic absorption spectroscopy. Mobile forms of Zn were extracted by extracting ammonium acetate buffer pH = 4.8 (RD 52.18.289-90). Statistical data processing was carried out using the tools of the Microsoft Excel package.

3. Results

The content of humus in the studied agro-gray soils did not change after the introduction of Callovian clay both in autumn and in spring. This is due to the relatively low application of fertilizer-sorbent - a maximum of 0.4% of the total soil mass in each plot (table 1).

The studied soils were characterized by a very high availability of mobile phosphorus. Callovian clay had no effect on the content of available phosphorus. There were no significant differences in the content of P$_2$O$_5$ between the variants of the experiment. Within the framework of the proposed agricultural practices, the applied fertilizer-sorbent contributed to the maintenance of phosphorus concentrations in the soil solution at a high level, which can be explained by the organo-mineral chemical composition of Callovian clay [8]. In addition, the consistently high content of mobile phosphorus in the soil solution is due to relatively stable and close to neutral values of the exchangeable acidity index (5.6 < pH < 6.4) [10]. Callovian clay, due to its neutral reaction of the medium, did not affect the index of exchangeable acidity. However, it is worth noting the decrease in the pH value in the experimental variants in which the soil was artificially contaminated with zinc. Soil acidification is associated with the introduction of a large dose of zinc nitrate. The addition of zinc in the nitrate form also led to the accumulation of easily hydrolysable nitrogen in the studied agro-gray soils; this effect was previously noted in the works of other authors [2]. The increase in the content of N shch.g. by 22 - 42 mg/kg in all variants of the experiment with artificial pollution. The sorbent fertilizer had a significant effect on the content of exchangeable potassium in the soil. In the experimental variants with the application of Callovian clay in autumn, an increase in the K$_2$O content by 2.8–13.4% was noted in contaminated soils treated with clay doses of 250, 500 and 750 g/m$^2$. In other variants of the experiment with the autumn application of Callovian clay, the content of K$_2$O significantly decreased relative to the control, which is explained by the adsorption of potassium by soil colloids and the adsorption of swelling clay minerals in the interplanar spaces in the composition of the introduced Callovian clay. When clay was introduced in the spring, a somewhat different
picture was observed. In uncontaminated soils, an increase in the studied indicator (K₂O) by 2.6–22.5% was noted, and in contaminated soils it decreased by 10.0–13.6% relative to the control.

Table 1. Influence of the dose and time of soil treatment with Callovian clay on the physicochemical and chemical properties of zinc-contaminated agro-gray soils.

| Indicator | Control without treatment with Callovian clay | 250 g/m² | 500 g/m² | 750 g/m² | 1000 g/m² |
|-----------|---------------------------------------------|----------|----------|----------|-----------|
| Humus, %  | 3.5± 3.4± 3.2± 3.1± 3.2± 3.1± 3.4± 3.1± 3.3± |          |          |          |           |
| pH (KCl)  | 5.6± 6.1± 5.8± 6.1± 5.8± 6.2± 5.7± 6.3± 5.8± 6.4± |          |          |          |           |
| K₂O, mg/kg| 472±9 524±7 605±8 448±5 539±9 468±14 564±8 493±7 443±6 475±13 |          |          |          |           |
| P₂O₅, mg/kg| 602±8 609±7 631±9 619±12 627±8 598±21 609±8 596±5 606±5 598±11 |          |          |          |           |
| N w.g., mg/kg| 134±3 98±5 136±9 94±6 132±7 92±4 109±5 87±3 112±8 85±9 |          |          |          |           |
| Zn p.f., g/kg| 2.0± 0.04± 1.7± 0.06± 1.5± 0.08± 1.8± 0.02± 1.8± 0.02± |          |          |          |           |

Soil cultivation with Callovian clay in the spring of 2021

| Indicator | Control without treatment with Callovian clay | 250 g/m² | 500 g/m² | 750 g/m² | 1000 g/m² |
|-----------|---------------------------------------------|----------|----------|----------|-----------|
| Humus, %  | 3.5± 3.4± 3.5± 3.9± 4.2± 3.5± 3.2± 3.5± 3.6± 3.5± |          |          |          |           |
| pH (KCl)  | 5.6± 6.1± 5.8± 6.1± 5.8± 6.2± 6.0± 6.2± 5.9± 6.3± |          |          |          |           |
| K₂O, mg/kg| 472±9 524±7 467±7 676±10 453±9 554±4 465±6 547±15 463±9 538±12 |          |          |          |           |
| P₂O₅, mg/kg| 602±8 609±7 618±8 600±6 598±9 613±11 609±6 593±5 586±9 589±6 |          |          |          |           |
| N w.g., mg/kg| 134±3 98±5 129±4 97±5 120±7 95±8 118±7 95±3 116±9 91±5 |          |          |          |           |
| Zn p.f., g/kg| 2.0± 0.04± 1.9± 0.03± 2.0± 0.02± 1.9± 0.03± 1.9± 0.02± |          |          |          |           |

A distinct detoxifying effect of Callovian clay with respect to zinc was observed only during soil cultivation in autumn and was expressed in a decrease in the content of mobile zinc in soils by 10–25%. The maximum immobilizing effect was recorded in the variant of the experiment with a clay application dose of 500 g/m².

The introduction of Callovian clay into agro-gray soil led to an increase in the biomass of the main studied groups of soil microorganisms relative to the control variant, regardless of soil contamination with zinc and the time of clay application (table 2).

The biological activity of bacteria during the spring application of the fertilizer-sorbent was higher (at all doses) by 7.4–132.5 times in uncontaminated agro-gray soils and 0.9–2.3 times in zinc-contaminated agro-gray soils than with autumn application. Callovian clays. When comparing the biomass of bacteria in contaminated and uncontaminated soils, it was noted that the values of this indicator varied and depended on the time of application of Callovian clay. During autumn tillage, the microbiological activity of bacteria in zinc-contaminated soils prevailed over the microbiological activity of bacteria in uncontaminated soils. During the spring tillage of soils with clay, a diametrically opposite situation was observed. Spring tillage also increased the microbiological activity of micromycetes more strongly. The biomass of micromycetes in uncontaminated soils treated with Callovian clay in spring was 5.2–88.3 times higher than in autumn treatment. In contaminated soils,
the spring application of clay increased the biomass of micromycetes by 12.3–35.0 times compared to the autumn application. In the experimental variants with fertilizer-sorbent doses of 750 g/m² and 1000 g/m², the biomass of micromycetes was the highest. In most variants of the experiment, the biomass of actinomycetes was also 1.3–2.6 times higher with spring tillage than with autumn tillage. As a rule, in soils contaminated with zinc, the microbiological activity of micromycetes was higher than in soils with a background content of Zn. The maximum biological activity of actinomycetes was observed in the variant of the experiment with a fertilizer-sorbent application dose of 1000 g/m² and reached 25.8 × 10⁶ CFU/g of soil.

Table 2. Influence of the dose and time of soil treatment with Callovian clay on the microbiological activity of zinc-contaminated agro-gray soils.

| Indicator                  | Control without treatment with Callovian clay | Dose of application of Callovian clay, g/m² |
|----------------------------|---------------------------------------------|-------------------------------------------|
|                            | Zn 10 MPC field                             | 250 | 500 | 750 | 1000 |
| Bacteria, n × 10⁶ cfu/g soil | 1.6± 0.7±                                    | 5.2± | 1.9± | 1.3± | 1.4± | 5.5± | 0.8± | 1.2± | 0.2± |
| Mushrooms, n × 10⁵ cfu/g soil | 1.1± 0.4±                                    | 1.1± | 3.4± | 2.0± | 1.7± | 1.6± | 2.3± | 8.7± | 0.3± |
| Actinomycetes, n × 10⁶ CFU/g soil | 7.1± 2.8±                                  | 8.0± | 11.2± | 10.4± | 4.4± | 10.2± | 5.4± | 25.8± | 3.7± |

Soil cultivation with Callovian clay in the spring of 2021

| Indicator                  | Control without treatment with Callovian clay | Dose of application of Callovian clay, g/m² |
|----------------------------|---------------------------------------------|-------------------------------------------|
|                            | Zn 10 MPC field                             | 250 | 500 | 750 | 1000 |
| Bacteria, n × 10⁶ cfu/g soil | 1.6± 0.7±                                    | 12.0± | 14.0± | 1.5± | 41.1± | 6.4± | 21.2± | 1.5± | 26.5± |
| Mushrooms, n × 10⁵ cfu/g soil | 1.1± 0.4±                                    | 13.5± | 17.8± | 13.4± | 24.2± | 56.0± | 2.5± | 1.9± | 38.5± |
| Actinomycetes, n × 10⁶ CFU/g soil | 7.1± 2.8±                                  | 13.9± | 17.3± | 13.9± | 3.9± | 18.5± | 14± | 6.8± | 3.2± |

Soil treatment with Callovian clay in autumn, as a rule, led to an increase in biomass production by the studied lawn grasses (figure 1).

With the introduction of certain doses of Callovian clay, an increase in the values of indicators of wet and dry plant biomass was noted both in variants with zinc contamination and in variants with a background zinc content. The most optimal dose for autumn application was 500 g/m², which contributed to an increase in wet and dry weight by 22.8% and 28.1%, respectively, in uncontaminated soils and by 33.2% and 25.1% in soil contaminated with zinc (figure 1).

During the spring tillage of soils with Callovian clay, the stimulating effect on the accumulation of biomass by plants was observed only in soils with a background content of zinc (figure 2).

In uncontaminated soils, the spring application of Callovian clay led to an increase in the values of the wet biomass index by 3.7–15.6%, and dry biomass, by 15.2–28.7%. In zinc-contaminated soils, these indicators significantly decreased. The decrease in wet biomass reached 17%, dry biomass - 27.3%.
Figure 1. Dependence of the production of raw and dry biomass by lawn grasses on zinc pollution and treatment with Callovian clay applied to soils in autumn 2020.

Figure 2. Dependence of the production of raw and dry biomass by lawn grasses on zinc pollution and treatment with Callovian clay applied to soils in the spring of 2020.

4. Discussion
The use of Callovian clay had a positive environmental effect, which was expressed both in the aspect of increasing soil fertility and in the aspect of increasing the biological productivity of lawn grasses. The sorbent fertilizer made it possible to increase the ecological stability of agro-gray soils using the mechanism of stabilizing the concentrations of mobile phosphorus in the soil, increasing the content of exchangeable potassium in the soil solution, through maintaining the acidity of the environment, increasing the microbiological activity of soils, and due to the fixation of mobile forms of the pollutant element (zinc). It should be noted that the detoxifying effect of Callovian clay was manifested under conditions of severe soil pollution of 10 MPC, it is likely that under conditions of low and medium levels of pollution, the efficiency of the studied fertilizer-sorbent will be much higher. It should be
assumed that Callovian clay in the aftereffect (prolonged effect) will also have a positive effect on the content of soil organic matter and increase the water resistance of soil aggregates due to the significant content of silt and clay fractions. The increase in the biological productivity of lawn grasses, noted in the framework of the experiments, will significantly increase the ability of lawn ecosystems to sequester carbon dioxide from the atmosphere, which will bring modern urban areas closer to achieving a zero carbon balance. Obviously, the time of soil treatment with Callovian clay must be selected selectively, based on the natural and anthropogenic features of each individual urban landscape and those of its properties that need to be optimized.

5. Conclusion
Thus, the following conclusions can be drawn:

- Soil cultivation with Callovian clay contributed to the improvement of the environmental sustainability of soils. The effect depended both on the dose of the fertilizer-sorbent and on the time of its application. In the autumn application, the most optimal dose was 500 g/m$^2$ of soil, in the spring - 750 g/m$^2$ of soil.
- Autumn application of Callovian clay led to a decrease in the content of mobile forms of zinc by 10-25%.
- Soil treatment with Callovian clay made it possible to increase the biological productivity of lawn grasses up to 33.2%.

Acknowledgments
The work was supported in part by a grant from the Innovation Promotion Foundation, the UMNIK program, contract (agreement) No. 15096GU/2020.

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