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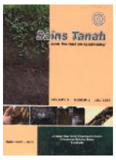

Ecotoxicological assessment of Zn, Cu and Ni based NPs contamination in Arenosols

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ABSTRACT

Nanoparticles are increasingly used in many industrial fields because of their special properties. In this context, several questions arise related to possible negative consequences associated with nanoparticle (NPs) entrance into the ecosystem. The adsorption of NPs by soil can adversely influence its biological properties. In the present article, the influence of Cu, Zn, and Ni NPs on the biological characteristics of Arenosol is considered. Research aimed to study the effect of Cu, Zn, Ni NPs on the biological characteristics of sandy loam chernozem. Copper, Zn, and Ni NPs were added to the soil in concentrations of 100, 1,000, and 10,000 mg kg^{-1}. The effect of NPs on the biological properties of Arenosol was evaluated after 10-day incubation. The biological indices of the ecological condition of the soil, including the germination of radish, the length of the roots, the bacteria population, *Azotobacter* sp. count, the catalase activity, and dehydrogenases were studied. As a result of this study, it was revealed that the degree of indices changes depending on the concentration of Cu, Zn, and Ni NPs in the Arenosols. Microbiological characteristics (bacteria population, and *Azotobacter* sp. count) and phytotoxic feature (length of roots and radish germination) properties were most sensitive to contamination compared to the enzyme activity of Arenosol. Based on the soil integral index of a biological state, the strongest inhibitory effect on biological parameters of Arenosols relative to the control was exerted by Cu NPs (lower than control by 48-72%), while the greatest stability in Arenosol was found for Ni NPs (lower than control by 30-55%). The studied biological parameters allow characterizing the severity of nanoparticle exposure on Arenosols. Early diagnostics of the severity of soil contamination by NPs can be successfully used to quickly assess their impact on the soil condition and prevent possible adverse consequences.

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1. INTRODUCTION

Because of their multiple special characteristics, nanoparticles (NPs) are applied in many industries, such as agriculture (Acharya et al., 2020; Adisa et al., 2020; Faizan et al., 2020), medicine (Patra et al., 2018; Shende et al., 2021), cosmetology (Pastrana et al., 2018), industry (Ali et al., 2021; Ameta et al., 2020), etc. However, large-scale synthesis and application of NPs cause a threat of adverse consequences of their release into the environment (Rajput, Minkina, Fedorenko, et al., 2021; Rajput, Minkina, Kumari, et al., 2021; Ranjan et al., 2021; Shende et al., 2021). Once in the soil, NPs change its fertility, the population of soil microflora, as well as physiology and metabolism of important plants (Ali et al., 2021; Iqbal et al., 2019; Rai & Ingle, 2012; Rajput, Singh, et al., 2021). However, the research results on the effect of NPs on the environment are not consistent. Some scientists have identified adverse effects on plants (Minkina et al., 2020; Usman et al., 2020; Zoufan et al., 2020), animals (Rajput et al., 2017; Rajput et al., 2018), and soil characteristics (Kolesnikov, Minnikova, et al., 2021). At the same time, the other researchers confirmed the absence of any adverse effects (Faizan et al., 2021; Samarajeewa et al., 2017) or even note a positive effect (Acharya et al., 2020; Faizan et al., 2020; Shekhawat et al., 2021). Nanoparticles entering the soil are distributed differently depending on soil fertility, structure, and composition. The behavior of NPs depending on soil thickness (Khanna et al., 2021; Tourinho et al., 2012). However, studying a single soil parameter is not enough to understand the effect of NPs. Experiments are needed to study the distribution of NPs depending on other soil parameters, for example, such as the granulometric composition and the soil response. Such information would provide many chances to develop methods for remediation and rebuild soil fertility depending on its type, structure, and composition.

The goal of the present work is to evaluate the impact of Cu, Zn, and Ni NPs on the biological properties of Arenosols.

2. MATERIALS AND METHODS

2.1. Study area

In this research, the soil was classified as sandy loam black soil. The soil samples were taken at Verkhnekundryuchenskaya village, the Rostov Region, Russia (47°46'0.57" N; 40°51'41.69" E). This type of soil is characterized by a sandy loam granulometric composition, poor structure, a mean organic matter content of 2.3%, and a neutral soil reaction, pH = 6.8. For the experiment, the top layer of Arenosols (0-20 cm) was chosen, since it is here that heavy metals are deposited (Kabata-Pendias, 2010).

2.2. Experimental design

The present study aimed to provide a comprehensive evaluation of the effect of Cu, Zn, and Ni NPs on the phytotoxicity, microbial, and fermentation activity of Arenosol. The sizes of the Cu, Ni and Zn NPs for modeling were 50-100, 70-80, and 90-150 nm, respectively. The selection of metals was due to the fact that they are most often used in various fields of nanotechnology, and therefore the risk of their entering the soil is more likely than NPs of other elements. Polluting substances were introduced into the soil in the contents of 100, 1000, 10000 mg kg^{-1}. The soil was placed in plastic containers at a temperature of 22-25 °C and soil humidity of 60%. The effect of Cu, Zn, and Ni NPs on the biological characteristics of Arenosols in a model experiment was evaluated after 10 days of incubation.

2.3. Measurement procedures

Experimental tests were carried out using methods confirmed in ecology, biology, and soil science (Table 1). The soil condition was studied based on phytotoxic characteristics of the soil (root length and germination rate), the total bacteria count, *Azotobacter* sp. count, the catalase and dehydrogenases activity. Soil toxicity was evaluated using the germinating ability of radish seeds and root length (n = 180: 3 incubation vessels, 3 soil samples, x 20 seeds).

Microflora studies were carried out by the fluorescence microscopy method for evaluation of bacterial abundance in the soil according to Zvyagintsev et al. (2005) (n=720: 3 incubation vessels with soil x 3 soil samples x 4 square centimeters on slides x 20 microscope fields of view). *Azotobacter* sp. abundance was taken into account by fouling soil lumps method on non-acidified Ashby medium (n = 180: 3 incubation vessels with, 3 soil samples, 20 fouling lumps). Catalase activity was measured using hydrogen peroxide decomposition rate (n = 36: 3 incubation tubes with soil x 3 soil samples x 4 repetitions), dehydrogenases activity by the conversion rate of triphenyl tetrazolium chloride to triphenylformazane (n = 36: 3 incubation vessels with soil x 3 soil samples x 4 repetitions).

Biological indices are the first to respond to chemical contamination of the soil. Therefore, it is appropriate to apply exactly biological indices to assess the ecological condition of soils (Kolesnikov et al., 2019). To diagnose the soil condition after chemical contamination, it is advisable to use informative and sensitive biological indices as the most effective. The degree of the instructive value of the index was determined by the closeness of correlation between the index and the pollutant concentration in the soil. The sensibility of the indices was determined by analyzing the level of decrease in the contaminated soil compared to the blank soil.

To combine a large number of indices, the method of determining the integral index of the biological state of soils (IIBS) was used (Kolesnikov, Minnikova, et al., 2021; Kolesnikov, Timoshenko, et al., 2021).

2.4 Statistical analyses

for validation of the results, a variance and correlation analysis were performed, and then the means were compared using the least significant difference (LSD) at $p \le 0.05$. The data were obtained by three-fold reduplication. Statistical data were processed using the Statistica software package (version 12.0).

Table 1. Measurement and methods of biological properties.

No	Biological Indices	Unit	Method
1	The total number of bacteria	10^9 bacteria in a gram of soil dry weight	luminescent microscopy with the solution of acridine orange, 40X
2	*Azotobacter* sp. Abundance	% of the mud balls surrounded by *Azotobacter* mucus	the method of fouling lumps on the Ashby medium
3	Catalase activity	ml O_2 per gram of soil dry weight in 1 min	by the rate of decomposition of hydrogen peroxide
4	Dehydrogenases activity	mg of triphenylformazane (TPF) per gram of soil dry weight per hour	according to the rate of conversion of triphenyltetrazolium chloride (TPC) to TPF
5	The germination rate of radish seeds	% of germination seeds of control	the germination rate of radish (*Raphanus sativus* L.) after 7 days of the experiment
6	Radish roots length	millimeters	of roots length of the radish (*Raphanus sativus* L.) after 7 days of the experiment

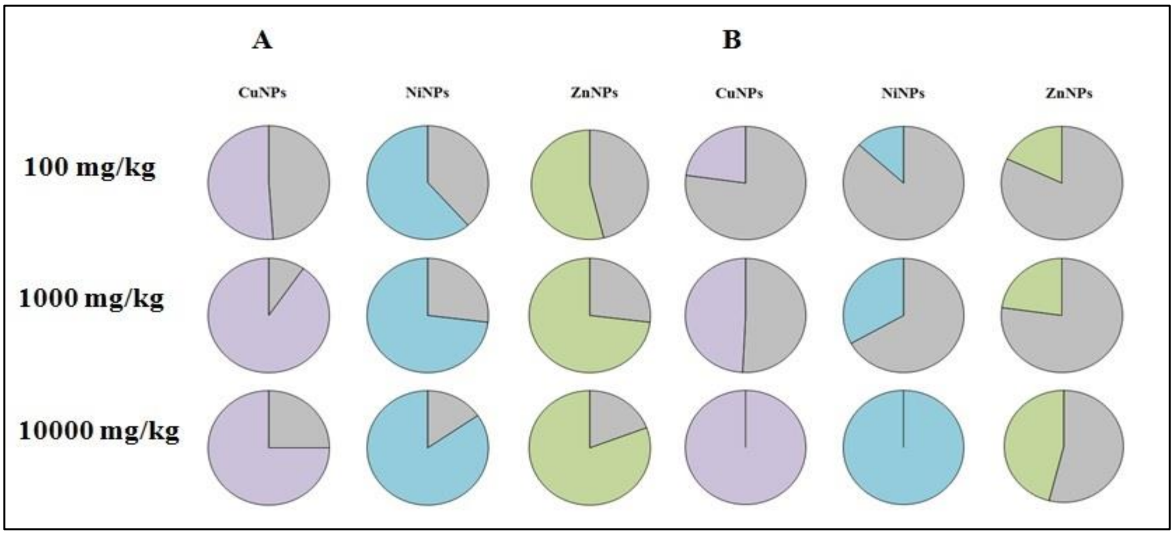


Figure 1. Change in microbiological indices of Arenosols by Cu, Ni, Zn NPs pollution, % of control
Notes: A) the total number of bacteria; B) *Azotobacter* sp. abundance

3. RESULTS

3.1. Influence of Cu, Ni, and Zn NPs on microbiological publication of the soil

Application of NPs at concentrations of 100, 1000, and 10000 mg kg^{-1} decreased in the total bacteria number (Fig. 1A) and the *Azotobacter* sp. count of Arenosol (Fig. 1B). The Cu and Zn NPs had a higher effect. The Ni NPs were less toxic than the Cu and Zn NPs. When contaminated with Cu NPs, there was a tendency to restore the total number of bacteria, which was not typical for the other two elements. In most cases, the total bacteria number in the Arenosols decreased more significantly than the *Azotobacter* sp. abundance. The 100 mg kg^{-1} concentration of Cu, Zn, and Ni NPs reduced the total bacteria number by 51, 62, and 54%, respectively, while the *Azotobacter* sp. abundance –23, 13, and 18%, respectively.

Application of Cu and Zn NPs to the Arenosols in an amount of 10000 mg kg^{-1}, decreased the *Azotobacter* sp. abundance completely. No other biological index from the studied indices decreased dramatically. The Ni NPs had significantly less toxic effects on the *Azotobacter* sp. abundance. Thus, the index of the *Azotobacter* sp. abundance turned out to be very sensitive only when contaminated with Cu and Zn NPs, and only at an extremely high concentration of 10000 mg kg^{-1}. In all other cases, the *Azotobacter* sp. abundance decreased insignificantly. This contradictory result was obtained by other researchers, which indicate that the sensibility of nitrogen-fixing bacteria to NPs is one million times higher than that of other groups of prokaryotes (Baklitskaya, 2011; Feng et al., 2013; Moll et al., 2016).

Thus, microbiological parameters in the sandy loam black soil responded negatively to contamination with Cu, Zn, Ni NPs.

3.2. Effect of Cu, Zn, and Ni NPs on enzymes activity in soil

Soil enzymes are catalyzing important metabolic processes. Their activity is determined with high accuracy and is a stable and sensitive index of soil biogenesis (Andreoni et al., 2004; Pascual et al., 2000).

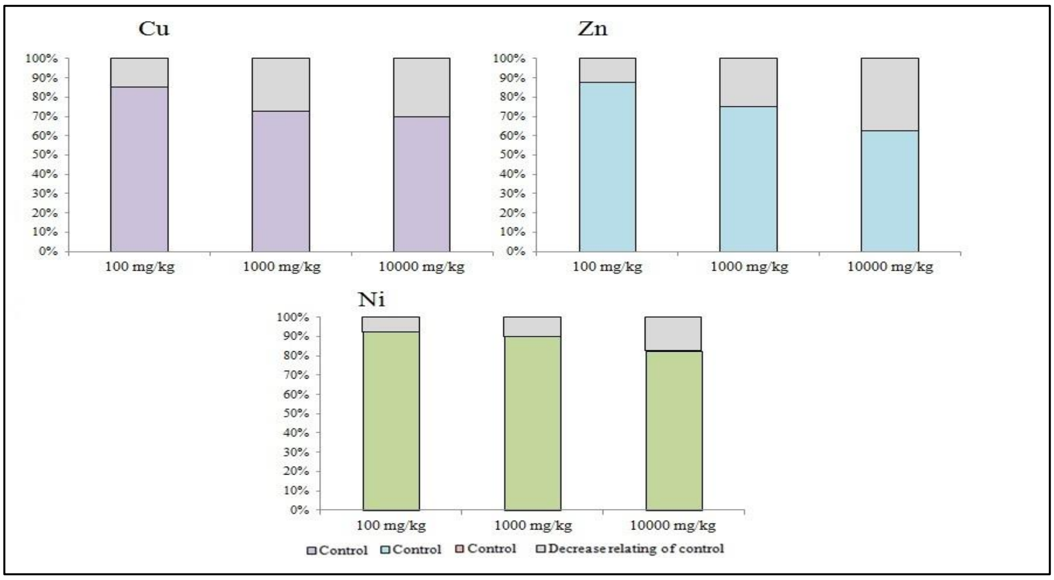


Figure 2. Change in catalase activity of Arenosols by Cu, Zn, Ni NPs pollution, % of control

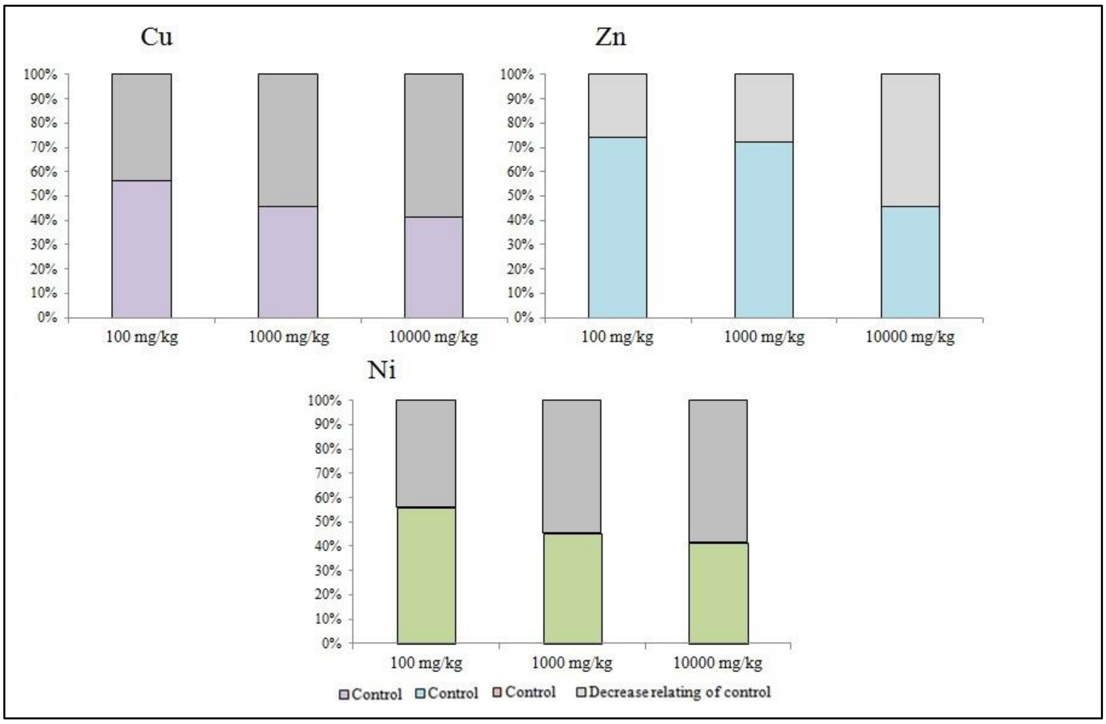


Figure 3. Change in dehydrogenases activity of Arenosols by Cu, Zn, Ni NPs pollution, % of control

The level of different concentrations effect of Cu, Ni, and Zn NPs on the activity of catalase and dehydrogenases is shown in Figure 2 and 3. The fermentation activity of Arenosol is sensitive to the presence of Cu, Zn, and Ni NPs. The sequence of metals effect on the catalase activity was as the following series: Zn ≥ Cu > Ni, while this sequence for dehydrogenases was obtained as this series: Cu > Zn > Ni.

When Cu, Zn, and Ni NPs are introduced to the soil at a concentration of 100 mg kg^{-1}, the dehydrogenase activity decreased by 44, 26, and 9%, respectively, while the catalase activity decreased by 15, 12, and 7%, respectively. Thus, the dehydrogenase activity was more sensitive to contamination by Cu, Zn, and Ni NPs than the catalase activity.

3.3. The effect of NPs on root length and germination rate of radish

The level of impact of various contents of Cu, Zn, and Ni NPs on the germination and length of radish roots is shown in Fig. 4. The toxic level of Arenosols for radish (germination and length of roots) was most affected by Cu NPs. Already at 100 mg kg^{-1} concentration, a decline in the germination of radishes by 70% relative to the control, as well as a reduction of the length of the roots by 85% was observed. Also, further enhancement in the concentration of Cu NPs decreased germination rate, and the length of the radish roots was first slightly restored and then decreases again. Zinc NPs had a slightly smaller effect on phytotoxic properties than Cu NPs.

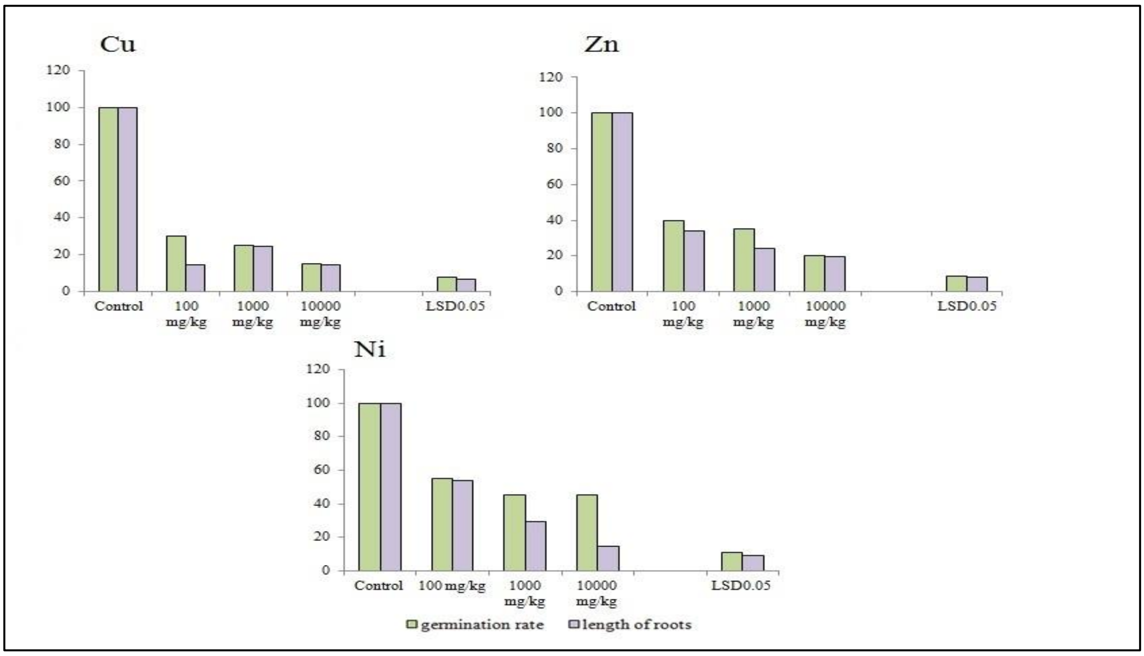


Figure 4. Change in phytotoxity indices of Arenosols by Cu, Ni, Zn NPs addition, % of control

At the concentration of 100 mg kg^{-1}, the germination of radishes reduced by 60% of the control, while the length of the roots was decreased by 66%. The higher the concentration, the stronger was the toxic effect. Nickel NPs had the least effect on germination (a 45% decrease of the control at a concentration of 100 mg kg^{-1}) and radish root length (a 46% decrease of the control at a concentration of 100 mg kg^{-1}). Also, the concentrations of 1000 and 10000 mg kg^{-1} had the same effect on germination. As for the length of the radish roots, it decreased with an increase in the nanoparticle concentration. Thus, the phytotoxic properties of sandy loam black soil turned out to be sensitive to the presence of Cu, Zn, and Ni NPs.

3.4 Integral index of the biological state of Arenosols contaminated by Cu, Ni, and Zn NPs

The results of the IIBS calculations based on the analysis of the effect of Cu, Zn, and Ni NPs on the state of the Arenosol are shown in Fig. 5. The concentration of 100 mg kg^{-1} Cu, Zn, and Ni NPs, decreased IIBS by 48, 40, and 30%, respectively, while at 1000 mg kg^{-1} – by 62, 50, and 44%, respectively, and at 10000 mg kg^{-1} – by 72, 73, and 55%, respectively. Thus, in terms of the influencing degree on the biological properties of sandy loam black sands, the following series were obtained Cu > Zn > Ni. The studied NPs had the greatest effect at a concentration of 10000 mg kg^{-1}. So, there is a positive correlation between the NPs content and the degree of deterioration of the biological properties of Arenosol.

3.5 Assessment of the informative value of biological indices

The instructive value of the index can be determined by the closeness of the correlation between the index and the content of the polluting substance in the soil. Table 2 presents the correlation coefficients of the studied biological indices.

In terms of informative value (based on the closeness of the relation between the index and the concentration of the pollutant in the soil), the studied biological indices are arranged as follows.

When contaminated with Cu NPs: *total bacteria count > abundance of Azotobacter genus bacteria ≥ catalase activity > dehydrogenase activity ≥ germination > root length*.

When contaminated with Zn NPs: *abundance of Azotobacter genus bacteria > dehydrogenase activity > catalase activity > germination > total bacteria count > root length*.

When contaminated with Ni NPs: *catalase activity ≥ abundance of Azotobacter genus bacteria > dehydrogenase activity > root length ≥ total bacteria count > germination rate*.

3.6 Assessment of the sensitivity degree of biological indices

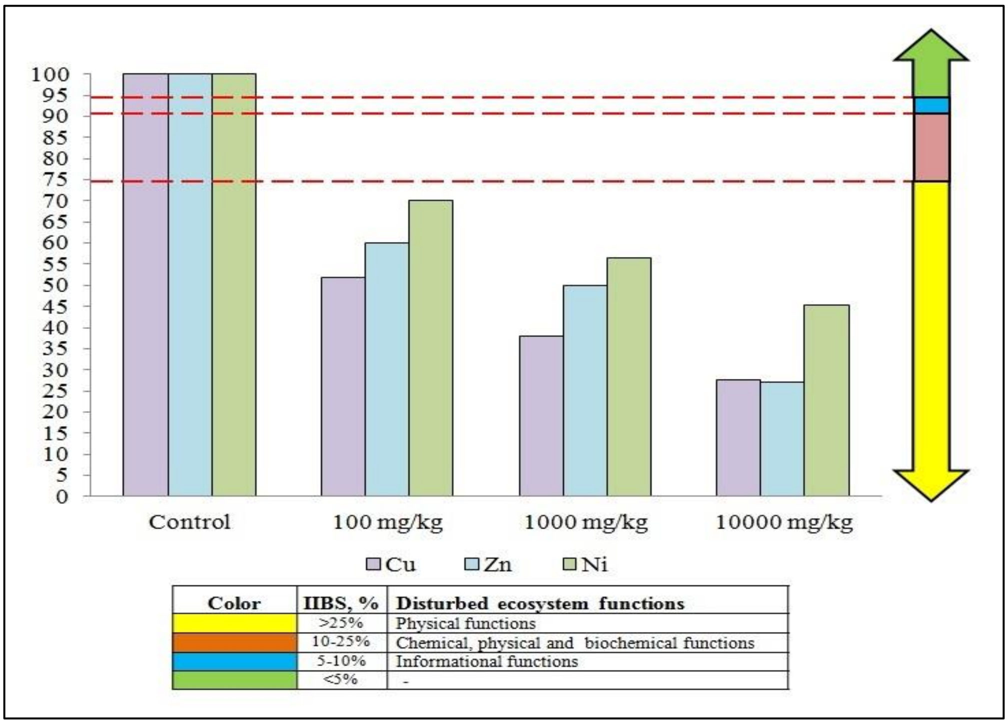
The sensitivity degree of the index was evaluated by the decrease in its value in presence of contaminants compared to the control. Table 3 shows the values of the degree of decrease in the studied biological parameters. These are the average values for all concentrations of heavy metal NPs.

In terms of the sensitivity degree (according to the decrease in values) to the presence of Cu, Ni, and Zn NPs, the studied biological parameters are arranged as follows.

When contaminated with Cu NPs: *root length > germination rate > total number of bacteria > Azotobacter sp. abundance > dehydrogenases activity > catalase activity*.

When contaminated with Zn NPs: *total number of bacteria ≥ root length > germination rate > Azotobacter sp. abundance > dehydrogenases activity > catalase activity*.

When contaminated with Ni NPs: *total number of bacteria ≥ root length > germination > Azotobacter sp. abundance > dehydrogenases activity> catalase activity*.



Color	IIBS, %	Disturbed ecosystem functions
🟨	>25%	Physical functions
🟧	10-25%	Chemical, physical and biochemical functions
🟦	5-10%	Informational functions
🟩	<5%	-

Figure 5. Change in integral index of biological state of Arenosols by Cu, Ni, Zn NPs pollution, % of control

Table 2. Correlation coefficients (r) between the content of Cu, Ni, and Zn NPs in Arenosols.

No	Biological index	Cu	Zn	Ni	Average
1	total number of bacteria	-0.90*	-0.58	-0.59	-0.69
2	*Azotobacter* sp. abundance	-0.67	-0.92*	-0.83*	-0.80
3	catalase activity	-0.64	-0.85*	-0.85*	-0.78
4	dehydrogenases activity	-0.54	-0.85*	-0.83*	-0.74
5	germination rate of radish seeds	-0.52	-0.59	-0.47	-0.53
6	length of the radish roots	-0.42	-0.50	-0.68	-0.53
7	IIBS	-0.62	-0.75*	-0.69	-0.69

Note: * $p < 0.05$ compared to the control

4. DISCUSSION

It was confirmed that Cu, Zn, and Ni NPs decreased the germination rate and length of radish roots. Other works have also noted negative impacts of Cu and Zn on plant condition (Ghosh et al., 2016; Hossain et al., 2015; Ranjan et al., 2021). However, some studies have noted a stimulating effect of Cu on plant conditions (Polischuk et al., 2019).

The toxicity mechanisms of heavy metal NPs with respect to plants are associated with the inhibition of major physiological processes, like photosynthesis, mineral nutrition, and water-binding (Minkina et al., 2020; Yadav et al., 2014). In addition, due to the high redox capacity, the ions of HM NP can participate in the redox reactions in cells and, through the Haber-Weiss and Fenton reactions, lead to the formation of reactive oxygen species, like superoxide radicals, hydrogen peroxide, and hydroxyl radicals. Besides, as noted above, HM NPs cause the inactivation of enzymes as a result of interaction with sulfhydryl groups of proteins, which leads to metabolic disorders and causes chlorosis, necrosis, and growth retardation of shoots and roots (Manceau et al., 2008).

It was confirmed that the ecotoxicity of Cu, Zn, and Ni NPs on soil microorganisms increases with increasing concentration. The results of other works have indicated that NPs can penetrate directly into the cell and cause more damage than macroparticles. This concerns interference with DNA and protein synthesis, redox, and organoid functions (Slavin et al., 2017; Yoo et al., 2021).

The mechanism of the inhibitory effect of metal NPs on enzymes seems to be due to their interaction with sulfhydryl groups (Manceau et al., 2008; Metryka et al., 2021; Slavin et al., 2017). The degree of ecotoxicity of NPs depends not only on the dose but also on the class of the enzyme. In the present study, it was revealed that dehydrogenase activity is less sensitive to contamination by Cu, Zn, and Ni NPs than catalase activity. Previous studies have shown both the negative impact of NPs on the activity of enzymes (Kolesnikov, Timoshenko, et al., 2021; Peyrot et al., 2014; Shende et al., 2021) and the positive effect (Asadishad et al., 2017).

The present work is consistent with the hypothesis that the higher the content of NPs in the soil, the more pronounced are toxic effects on biological parameters of the soil (the activity of enzymes, total bacteria count, and phytotoxic indices). According to the obtained biological indices of the state of soil contaminated with Cu, Zn, and Ni NPs, their information value and sensitivity were evaluated.

The indices of enzymatic activity and microbiological indices turned out to be the most informative in terms of reflecting the status of the studied black soil contamination with Cu, Zn, and Ni NPs, while the indices of phytotoxicity were less informative. Microbiological and phytotoxicity indices were the most sensitive to contamination by Cu, Ni, and Zn NPs. The indices of enzymatic activity were less sensitive. A similar result was obtained earlier for oxides and water-soluble salts of heavy metals, including Cu, Zn, and Ni (Vodyanitskii, 2016). Also, the sensitivity of the index depended on the nature of the metal. Copper and Zn NPs showed greater toxicity than Ni ones. This does not support the existing hypothesis that the toxicity of NPs depends on their size and does not depend on the chemical nature of the element. A slightly different pattern was observed for oxides and water-soluble salts of these heavy metals. Thus, Cu and Ni NPs were more toxic than Zn NPs (Abdel-Khalek et al., 2015; Iqbal et al., 2021).

Because some indices are sensitive, while others are informative, it is advisable to use the IIBS. In terms of influencing the biological properties of sandy loam black soil, metal NPs form the following series: Cu > Zn > Ni. First, this does not consistent with the existing hypothesis that the NPs toxicity depends only on their size and does not depend on the chemical nature of the element. Secondly, the oxides and water-soluble salts of these metals are characterized by a slightly different pattern, namely, Cu and Ni are more toxic than Zn.

Table 3. Degree of decrease in biological parameters of Arenosols upon contamination with Cu, Zn and Ni NPs, % of control (average values for three doses of NPs).

No	Biological index	Cu	Zn	Ni	Average
1	total number of bacteria	28	27	31	29
2	*Azotobacter* sp. abundance	43	51	71	55
3	catalase activity	76	75	88	80
4	dehydrogenases activity	48	64	72	61
5	the germination rate of radish seeds	23	32	48	34
6	the length of the radish roots	18	26	33	26
7	IIBS	54	58	67	60

Based on the results obtained, one can state that further study of the effect of NPs on the properties of the soil is necessary. Most publications related to NPs are devoted to their synthesis and application. At the same time, an increase in the scope of applications and the utilization capacity of NPs leads to the threat of their release into the environment and soil contamination. The potential risk and environmental impact are difficult to quantify and are not fully studied. Knowledge of the ultimate effects of NPs on the environment should be expanded, and appropriate guidelines should be developed to prevent contamination.

5. CONCLUSION

The degree of reduction in biological characteristics of the soil depends on the content of contaminating NPs. It was revealed that the total bacteria count, the length of radish roots and germination are the most sensitive indices to the presence of Cu, Zn, and Ni NPs. These indices have shown significant changes (more than 50%) caused by the impact of even a small pollutant dose of 100 mg kg^{-1}. The activity of enzymes was the least sensitive index to the presence of Cu, Zn, and Ni NPs. However, a significant decrease was noted in these indices when the studied pollutants were introduced. The presence of Cu, Zn, and Ni NPs led to a decrease in the IIBS of sandy loam black soil. According to the results of the IIBS, Cu NPs had the strongest effect on the soil, while Ni NPs had the least effect. The conducted research confirmed the need for further study of the effect of NPs on the biological characteristics of different types of soils. This study confirmed the need for further study of the effect of NPs on the biological properties of soils in order to identify possible negative effects. For a better understanding of the negative consequences of the ingress of NPs into the soil, it is necessary to study a large number of pollutants, indices, soil types, as well as the mechanisms of their influence.

Declaration of Competing Interest

The authors declare no competing financial or personal interests that may appear and influence the work reported in this paper.

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