Bulletin of University of Agricultural Sciences and Veterinary Medicine Cluj-Napoca. Agriculture

Open Access

The Effects of Heavy Metals on Soil Biology

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REVIEW

Abstract

Heavy metal pollution is a global environmental issue threatening food security and the environment. It is caused by the rapid growth of agriculture and industry. The development of new industries and the increasing number of people have also contributed to the rise in these conditions. Heavy metals that contaminate soils are mercury (Hg), cadmium (Cd), lead (Pb), and chromium (Cr), these toxic substances are retained by the soil and act as a filter for their properties. The aim of this paper was to review the impact of heavy metals on soil, as well as the methods to combat their toxicity in agricultural ones. In order to achieve this goal, data belonging to national and international databases were used (Science Direct, NCBI). The finding of different strategies to combat pollution, particularly on the soil represented the goals for the majority of the studies. As such, bioremediation is a promising choice to reduce heavy metal concentrations.

Keywords: heavy metals, soil, contamination

Received: 26 December 2022
Accepted: 27 February 2023
Published: 15 May 2023

DOI:
10.15835/buasvmcn-agr:2022.0019

INTRODUCTION

Heavy metals are natural elements defined by their high density greater than 5 g cm^{-3} and high atomic weight (Zhang et al., 2019). They are toxic metals used in industrial processes and can affect soil, plant and animal life at low concentrations. The fact that some soils and irrigation water are contaminated with heavy metals represents more than a problem, it is a threat to the environment, food safety and human and animal health (Gonzales and Ghneim-Herrera, 2021). Maintaining the activity and diversity of soil biomass (SMB) and microflora is fundamental to sustainable soil management (Isam, 2001). The structure and activity of the soil microbial community depend to a large extent on the state of their habitat. In this one, soil organisms feed, breathe, compete, cooperate, and respond to environmental changes (Allison et al., 2008). Due to the processing of minerals, and natural factors, including rock weathering and volcanic activity, large amounts of lead (Pb), zinc (Zn) cadmium (Cd), mercury (Hg) and chromium (Cr) have been released into the environment, affecting soils, plants and people, with the appearance of various diseases. Simultaneously, some plants can be genetically adapted to survive and reproduce in soils contaminated with heavy metals (Kruckeberg, 1967). However, specific ecotypes are capable of tolerating toxic conditions in uncontaminated soil. This means that the plant populations that grow in contaminated sites are different from those that live in uncontaminated areas (Assunção et al., 2003). Thus, the consumption of contaminated plants is correlated with the appearance of different types of cancer and neurological damage (Mudgal et al., 2010). From these metals, Zn, in small quantities, is essential for the growth and development of plants.(Ahmed et al., 2020). It is toxic only in large quantities. Heavy metals also occur from agriculture. Hence, fertilizers, pesticides, wastewater, and livestock manure are the sources related to the agricultural sector (Li et al., 2014). They can cause degradation and contamination of the surrounding area (Srivastava et al., 2017). The accumulation of heavy metals in the soil can vary depending on their nature and the environment.

In Romania, one of the most polluted areas with heavy metals is Baia-Mare and the territories in the immediate vicinity. Hence, due to the heavy metal pollution, the average life expectancy has dropped to 65 years old, in the areas previously mentioned (Maramureș Environment Protection Agency).

The aim of this paper was to review the impact of heavy metals on soil, as well as the methods to combat their toxicity in agricultural ones.

THE RESISTANCE OF SOIL MICROORGANISMS TO HEAVY METALS

Heavy metals are a very studied element, mostly because of their high persistence, and bioaccumulation. Many studies demonstrate a high sensitivity of microbial communities to metal pollution (eg, declining microbial diversity) while others show resistance/tolerance to metal exposure in long-term polluted soils (Zhao et al., 2019). Also, an important thing to mention is that even if the microbial composition is sensitive to a disturbance, the community can still be resistant and quickly return to its pre-disturbance composition (Azarbad et al., 2016). Many microorganisms have rapid growth rates, so if their abundance is suppressed by a disorder, they have the potential to recover rapidly. Thus, they have a high degree of physiological flexibility (eg nonsulfur purple bacteria, which can be phototrophic under anoxic conditions and heterotrophic under aerobic conditions). Even if the relative abundance of some taxa initially decreased, they can physiologically adapt to the new abiotic conditions and Cuzepan, 2014; Rock-Moses, 2016). In many locations it has been found that the populations of some species are decreasing due to their vulnerability to climatic and anthropogenic changes (Burnaz, 2007; Török, 2010; Rock-Moses, 2021). In a study by Török, (2010) it is shown that there are at least 13 vulnerable taxa of the family Lycaenidae and Nymphalidae.

At national level, the Romanian legislation recognizes the need to protect an even more important number of butterfly species, and with the protection of these species, the need for unaltered conservation of the natural ecosystems in which these insects can be found is implicitly recognized (Rákosy, 2003, 2005; Schmitt and Rákosy, 2007). return to their original abundance (Azarbad et al., 2016) (Figure 1).

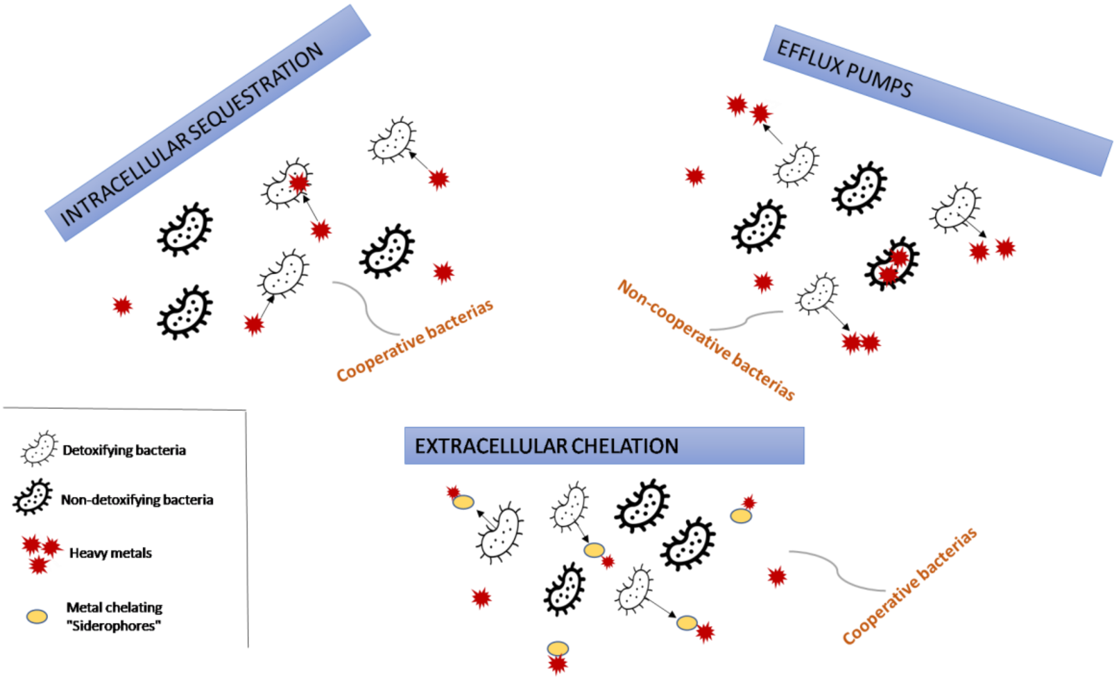

Figure 1. Upon intracellular sequestration, detoxifying bacteria receive and store heavy metals in their cells. Through efflux pumps, detoxifying bacteria pump heavy metals from their cells. In this way, the environment becomes more toxic. Thus, the non-detoxifying microorganisms cannot cope with increased toxicity. At extracellular chelation, detoxifying bacteria produce metal chelating molecules called siderophores. These molecules bind to heavy metals and prevent them from diffusing into cells. Therefore, the concentration of free-floating heavy metals in the environment is low (Adapted after O'Brien et al., 2015).

In terms of microorganism's examples resistant to heavy metals, there are:

- *Ralstonia pickettii* which are resistant to Cu, Ni, Fe and Zn;
- *Cupriavidusgilardii*, resistant to Cu (De La Rosa-Acostaet al., 2015);
- *Vibrio harveyi* bioluminescent is tolerant of numerous heavy metals (Thakre and Shanware, 2015).

Fungal species are also resistant to heavy metal toxicity. Moreover, they have the ability to remove them from the soil, through biosorption or bioaccumulation, binding metals on their surfaces. *Penicillium simplicissimum* is known to remove Pb and Cu in liquid media, throughout the biosorption process (Iskandar et al., 2011). Another example of fungal species that uses the same process is *Trichoderma asperellum*, it can tolerate Cd, Pb, Cu and Cr (Puglisi et al., 2012).

Beside the fungal species and bacteria, yeast is also a ubiquitous microorganism that can potentially react to heavy metals (Bahafid et al., 2017). Regarding protozoa, studies show that some species are also tolerant to heavy metals from metal-rich industrial wastewater. An example of protozoa that showed high tolerance to heavy metals is *Peranema sp*. (Kamika et al., 2013). In the next section, we will discuss the sources and the effects of heavy metals on agricultural soil.

THE EFFECTS OF HEAVY METALS ON AGRICULTURAL SOIL

The soil that has more needs than usual, is the agriculture one. It is a non-renewable natural resource. The cause of heavy metals contamination of soil is industrial activity and agriculture. The usage of urban wastewater that has been treated for agricultural irrigation, solid waste disposal, vehicle exhaust and industrial activities represent a major source of heavy metals soil contamination (Khan et al., 2013; Srivastava et al., 2016; Toth et al., 2016; Sharma et al., 2017; Woldetsadik et al., 2017). Consequently, this results in exceeding the recommended limits of heavy metals in drinking water, represents the main source of human exposure to heavy metals, and causes worldwide high mortality and morbidity.

Sources of heavy metals are:

- different pesticides and anti-corrosive paint.
- waste products of numerous industrial processes (cellulose industry releases mercury) (Tutic et al., 2015) (Table 1);
- urban settlements (sewerage water; lead on roads);

Important sources of industries that emit heavy metals are presented in Table 1.

Table 1. Industrial sources of heavy metals

Industrial branch	Cd	Cr	Cu	Hg	Pb	Ni
Paper industry	-	+	+	+	+	+
Petrochemistry	+	+	-	+	+	-
Production of chlorine	+	+	-	+	+	-
Fertilizer industry	+	+	+	+	+	+
Ironworks and steelworks	+	+	+	+	+	+

Cd-cadmium; Cr-chromium; Cu-copper; Hg-mercury; Pb-lead; Ni-nickel; + (yes)- means that the industrial branch releases that heavy metal; - (no)-means that the industrial branch doesn't release the heavy metal. We can observe that ironworks, steelworks and fertilizer industry are the most toxic industrial branch, where all 6 heavy metals are released into the environment, compared to the paper industry, petrochemistry and production of chlorine release 4 and 5 heavy metals into the environment

With all the strategies adopted for pollution by industries, the concentration of heavy metals remains high, particularly in urban areas. (Moolenaar, 1998; Guinee et al. 1999). Therefore, EU member states must respect the stability limit values for heavy metals in the soil, according to the EU directive on the protection of the environment and land (86/278/EEC) (Table 2).

The excessive use of fertilizers can result in the accumulation of heavy metals in agricultural soils. This can reduce the fertility of the soil and decrease the productivity and growth of plants (Ai et al., 2020). Cd, Pb and Zn in high concentrations are the most common heavy metals in agricultural soil. Cd belongs to the category of non-essential heavy metals, which affect both soil pH and the content of organic matter (Ai et al., 2020). Low concentrations of Pb can lead to high levels of toxic chemicals in the soil. The main source of this contamination is the geogenic contribution of Pb. This process can reduce the microbial activities in the soil, which can also affect the soil's fertility and nutrients (Dotaniya et al., 2020). Zn is known to play an important role in the plant's physiological and metabolic processes. However, the toxicity of Zn high concentrations can negatively affect the soil's microbial activities. This issue can lead to the reduction of the soil's fertility and nutrients (Mertens et al., 2013). The following paragraph reflects the soil health and fertility concerning heavy metal pollution.

Table 2. Limit values of heavy metals (mg*kg^{-1}).

Parameters	Limit values
Cadmium	13
Copper	50-140
Nickel	30-57
Lead	50-300
Zinc	150-300
Mercury	1-1,5
Chromium	37

In this table, we can observe that Zn and Pb have the highest values, compared to Hg, Cd, Cr and Ni which have the lowest values. Cu is somewhere in the middle, as far as the classification of limit values is concerned.

SOIL HEALTH AND FERTILITY

Soil resources together with the other components of the environment are directly or indirectly involved in all aspects of social-economic life. Soils are an essential source for development and therefore their quality is important. Their preservation must be a permanent concern of sustainable development. Preserving the soil cover is a vital requirement because it has a determining role in creating the food base, and the process of its formation or regeneration requires a long time.

The highest pollution in the soil is in intensive agricultural areas (Ionescu, 1973).

The most common potentially polluting sources in this area are:

- impurities from fertilizers;
- sludge from wastewater;
- organic residues from the intensive breeding of animals, especially pigs and birds;
- pesticides;
- waste from composts (not necessarily used in agriculture);
- the exploitation of forests;
- corrosion of metal objects;
- industrial activities, and persistence of pollution from current/past mining and metallurgy;
- car traffic exhaust;
- municipal waste and waste landfills.

Most agricultural and horticultural soils in technologically advanced countries are regularly fertilized with chemical and organic fertilizers. In addition, the concentration of heavy metals from amendments and composts is high. Another thing that we have to take into account is soil biology. Before all this, we have to start with the beginning and that is represented by microorganisms. They are an essential component of the ecosystem (Harris, 2009) due to their important role in maintaining soil fertility, but at the same time, they are negatively affected by heavy metal pollution (Schimel et al., 2007; Paz-Ferreiro and Fu, 2016). The following paragraph is showing the indicators of soil health and phytoremediation.

Indicators of soil health and phytoremediation

As we previously mentioned, one of the most important indicators is represented by soil microorganisms. It acts as a biological engine of the earth. *Rhizobium* and other populations of nitrifying bacteria are indicators of soil quality. These microorganisms absorb the carbon by the generation of greenhouse gases like oxides of nitrogen and methane (Hermans et al., 2017; Van Bruggen and Semenov, 2000; Visser and Parkinson, 1992. They can change their persistence and characteristics due to the increasing levels of heavy metals in the soil (Djukic and Mandic, 2006; Ulea, et al., 2017). Therefore, this is the reason that finding efficient combating methods for heavy metals is essential. The following bacteria are used as indicators of heavy metal pollution: *Thiobacillus sp.* can transform mercury into methyl and dimethyl mercury (Sumampouw and Risjani, 2014). Also, they are capable to convert toxic forms of Hg into nontoxic ones through mer genes (Brock and Madigan, 1991).

In the case of Cd and Pb pollution, Pseudomonas *spp.* represent the main indicator. Moreover, they can also indicate the presence of Hg (Das et al., 2009; Selvin et al., 2009). In addition, the parameter for Pb and Cd is represented by Serratia *marcescens* (Cristani et al., 2012). Another example of a heavy metal pollution parameter is *Vibrio spp.* (Djukic and Mandic, 2006) (Figure 2). In the last section, we discuss the results of soil contamination with heavy metals in Romania, Baia mare.

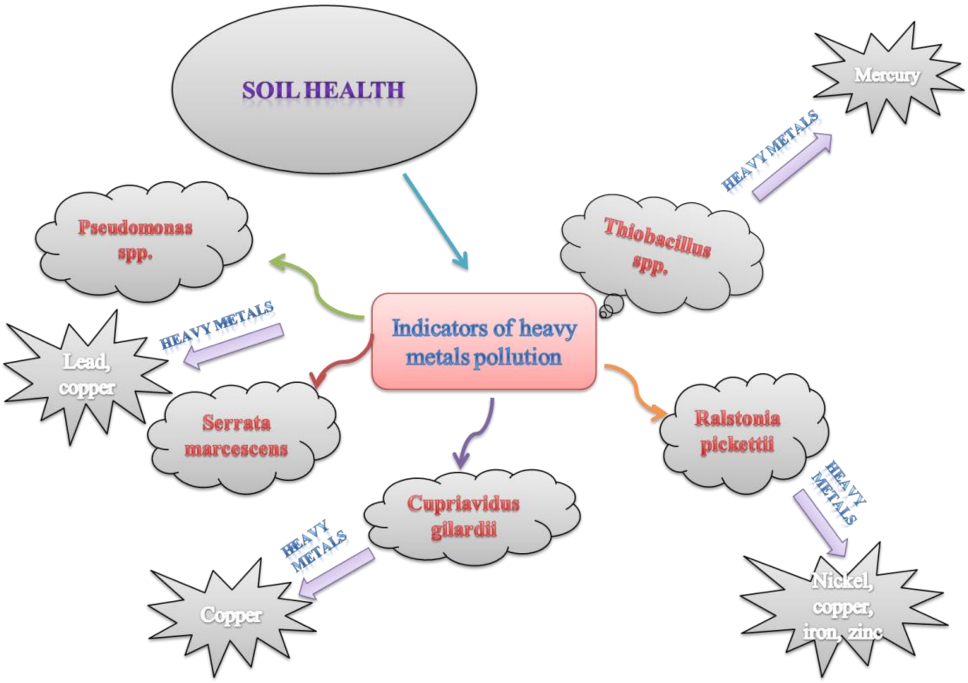

Figure 2. The bacteria are used as indicators for soil pollution. *Serrata marcescens* and *Pseudomonas spp.* are both indicators for Pb and Cu. *Cupriavidus gilardii* indicates Cu, and *Thiobacillus spp.* is indicator for Hg. *Ralstonia pickettii* is an indicator for Ni, Cu, Fe and Zn.

THE SOIL CONTAMINATION WITH HEAVY METALS IN BAIA MARE, ROMANIA

Managing contaminated sites aims to lessen any adverse effects where environmental damage is suspected or proven and to reduce potential threats to human health, water bodies, soil, habitats, food products and biodiversity. The main sources of soil pollution in Maramureș County, and a historical character are S.C. Romplumb SA Baia Mare, S.C. Cuprom Bucharest - Baia Mare Branch (formerly Phoenix S.A.), the tailings ponds of the non-ferrous ore preparation plants, the ore tailings resulting from mining activities, mine waters that are discharged from the existing galleries (Maramureș Environment Protection Agency). Although all activities are no longer practiced today, sites are currently inactive in the problem area.

From 2008-2010 the concentrations of heavy metals in the soil in the vicinity of the former plants were very high (Integrated Urban Development Strategy Baia Mare, Baia Mare, Romania, 2020). Unfortunately, these high concentrations affect local ecosystems and human health (Coman et al., 2010; ProEnvironment, 2009). Also, in Baia Mare soils the concentrations of heavy metals are very high for Cu: 22–118 mg·kg^{-1}, Zn: 89–308 mg·kg^{-1} and Pb: 32–165 mg·kg^{-1} (Damian et al., 2010) (Table 4).

Table 4. Concentrations of heavy metals in Baia mare soils (mg·kg^{-1})

Heavy metals	Concentrations
Cu	22-118
Zn –high concentrations	89-308
Pb	32-165

Cu- copper; Zn-zinc; Pb-lead. Regarding this table, it is very clear that Zn has the highest value, followed by Pb. Zn is considered toxic only in high concentrations. Cu has the lowest value.

In the vicinity of the former plants, they increase for Cu: 54–750 mg·kg^{-1}, Zn 252–1325 mg·kg^{-1}, Pb: 425–995 mg·kg^{-1} (Damian et al., 2010; Fazakas et al., 2020) (Table 5).

Table 5. Concentrations of heavy metals in the vicinity of the former plants in 2010 (mg*kg^{-1})

Heavy metals	Concentrations
Cu	54-750
Zn-high concentrations	252-1325
Pb	425-995

Cu- copper; Zn-zinc; Pb-leadAs can be seen, there is a big difference between the values of Zn, Pb and Cu concentrations. Zn is considered toxic only in high concentrations.

In 2015-2017 the concentrations for Pb, Cu, and Zn were higher in the vicinity of the former plant's area in comparison with 2010 (Weindorf et al., 2015; Coroian et al., 2017). High concentrations were identified for: Cu: 400–5823 mg·kg^{-1}, Zn: 4513.2–6122 mg·kg^{-1} and Pb: 982–6565 mg·kg^{-1} (Damian et al., 2008) (Table 6).

Table 6. Concentrations of heavy metals in the vicinity of the former plants in 2015-2017 (mg·kg^{-1})

Heavy metals	Concentrations
Cu	400-5823
Zn-high concentrations	4513.2–6122
Pb	982–6565

Cu- copper; Zn-zinc; Pb-lead. In this table, all 3 heavy metals have very high values with small differences between them, but the highest value is represented by Zn. Zn is considered toxic only in high concentrations.

Unfortunately, in 2020, the levels for Pb ranged from 43.69 mg·kg^{-1} dry weight (dw) for the pilot site "Craica 1" and 417. 97 mg·kg^{-1} dw for the pilot site "Urbis". Concerning Cu, were registered levels from 21.13 mg·kg^{-1} dw for the pilot site "Romplumb" to 128.96 mg·kg^{-1} dw for the pilot site "Craica 2". All 5 sites exceeded the normal value (20 mg·kg^{-1}). As for Zn, the levels were between 62.85 mg·kg^{-1} for the pilot site "Craica 2" and 385.22 mg·kg^{-1} dw for the pilot site "Craica 1". All sites exceeded the normal value (100 mg·kg^{-1}) (Table 7) (SPIRE, 2020).

Table 7. Concentrations of heavy metals in SPIRE pilot sites

Pilote Sites	Pb (20 mg*kg)	Cu (20 mg*kg)	Zn (100 mg*kg)
"Romblumb"	117.32-171.39	21.13-27.00	84.57-113.88
"Ferneziu"	119.77-288.05	25.45-38.82	105.20-152.67
"Colonia Topitorilor"	114.92-123.81	32.27-64.44	125.69-160.57
"Urbis"	342.98-417.97	22.45-24.06	88.43-115.68
"Craica 1"	43.69-46.36	86.33-128.78	270.09-385.22
"Craica 2"	50.59	124.31-128.96	349.86-62.85

Pb-lead; Cu-copper; Zn-zinc. In this table, Pb and Zn have the highest values, compared to Cu which has the lowest value. All of them exceed the normal value. Zn is considered toxic only in high concentrations.

Regarding bioremediation strategies based on plants, the most effective is phytoremediation. There are various techniques that are used for soil remediation. They are: phytoextraction, phytostabilization, rhizofiltration, phytodegradation, and phytovolatilization. Not all plants are equally effective at performing these procedures. The goal of phytoextraction is to absorb pollutants throughout the roots and then into the plant. Highly efficient plants with fast growth and high biomass are known to perform better in this process. The phytostabilization process aims to reduce the mobility of the contaminants in the soil and prevent them from leaking. The substances then accumulate in the rhizosphere (SPIRE, 2021). Rhizofiltration can effectively remove contaminants from the soil by mobilizing them within the rhizosphere. This process is commonly used for the decontamination of sediments and water. In the phytodegradation process, the pollutants are broken down by the plant or through the release of enzymes by the roots. Phytovolatilization is a process commonly used for soil remediation that involves taking up the pollutants from the plant and then transforming them into less toxic substances (SPIRE, 2021).

CONCLUSIONS

Heavy metals have a negative impact on soil. A promising strategy to reduce their concentration is bioremediation. This method is based on the capacity of microorganisms and bacteria for compound sequestration and transformation. Studies show that Agrobacterium*, Bacillus, Klebsiella, Enterobacter, Microbacterium, Pseudomonas, Rhodococcus and Mesorhizobium* have very high tolerance levels. More than that, they offer different biochemical and molecular mechanisms associated with promoting plant growth. One important thing to mention is that the most important effective microorganisms are *Klebsiella* and Enterobacter for bioremediation and phytoremediation in soils contaminated with arsenic, cadmium, and lead. Ultimately, the use of mechanisms and the applicability of remedial strategies based on plants and microorganisms are the most effective way to treat contaminated agricultural soils. Identifying the challenges and the prospect of implementing large-scale bioremediation strategies is also a very important step to combat heavy metal contamination.

Author Contributions: B.P., R.V. and C.M. Conceived and designed the analysis; B.P. Collected the data; R.V. and C.M. Contributed data or analysis tools; R.V. Performed the analysis; B.P. Wrote the paper.

Funding Source: This research received no external funding.

Acknowledgments

SPIRE-Smart Post-Industrial Regenerative Ecosystem Baia Mare (Project UIA04-138) supported this work. The European Regional Development Fund through the Urban Innovative Actions Initiative is the co-financier of this project."

Conflicts of Interest

The authors declare that they do not have any conflict of interest.

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