

Review Article

# A Review on the Impact of Nanoparticles on Heavy Metals in the Soils

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**Abstract** - Manufactured nanomaterials (MNMs) are witnessing an increasing use in industrial and consumer products in modern times. Many publications stated that metal and Nanoparticles (NPs) are utilized in various industries, including sunscreens, cosmetics, paints, electronics, and water treatment. The widespread use of product-based metals has dramatically increased the quantity of Heavy metals (HMs) in the environment. It is necessary to examine the impact of NPs on HMs in the soil environment and the interaction between them. This paper discussed nanoparticles' impact on environmental heavy metal accumulation, bioavailability, and biomagnification. It also highlighted the importance of soil parameters in the interaction between NPs and HMs. The article explored NPs and HMs, highlighting toxicants' harmful effects and various aspects. The manuscript's originality focused on explaining the synergistic toxicity of NPs and HMs in soil and providing an overview of the bioaccumulation and biomagnification of those pollutants in plants and the human body.

**Keywords** - Bioavailability, Biomagnification, Nanomaterials, Heavy metals, Soil.

## 1. Introduction

Manufactured nanomaterials (MNMs) are witnessing an increasing use in industrial and consumer products in modern times. Many publications state that metal and oxide NPs are employed in a wide range of industrial applications and technologies, including sunscreens, cosmetics, paints, surface coatings, electronics, soil remediation, and water treatment, as indicated in Table 1 [1–5]. These manufactured nanoproducts may be discharged into the environment (air, water, soil, and sediment) during and after production. The application of NPs has attracted enormous interest due to their unique features and advantageous applications in various agricultural and allied areas. Excessive usage of engineered nanoparticles (ENPs) and their discharge into the environment have raised serious concerns among environmentalists, scientists, and policymakers. The constant infiltration of ENPs into the environment has increased throughout time, given their widespread use in different fields. Many studies on various organisms in soil or water have been undertaken to understand better the effects of NPs in the environment [6–8]. These studies found that the concentrations are significantly higher than the allowable environmental threshold and can cause microbial strains or prevent plant growth.

The soil is treated by wastewater, stormwater, and surface runoff among various natural habitats, serving as fatty deposits for multiple contaminants, including ENPs [8]. NPs have a high surface-area-to-volume ratio, strong surface

reactivity, and an excellent affinity for absorbing and concentrating chemical pollutants. These properties eventually change the contaminant's fate, behaviour, bioavailability, and toxicity. Due to their nanoscale characteristics, NPs can potentially affect the mobility, bioavailability, and toxicity of co-existing pollutants in the soil environment, such as HMs and toxic organics. [10–12]. The permissible threshold of ENPs in the environment ranges from 0.00004 to 0.619 g/kg for silver nanoparticles (Ag NPs), from 0.0001 to 0.1 g/kg for cerium dioxide nanoparticles (CeO<sub>2</sub> NPs), and from 0.0002 to 24.5 g/kg for titanium dioxide nanoparticles (TiO<sub>2</sub> NPs) [13]. For example, TiO<sub>2</sub> NPs, the most extensively studied metal oxide NPs, have frequently been investigated at ppm or mg/L levels. [14]. According to Adams et al., TiO<sub>2</sub> NPs (330 nm) have a 0%, 75%, and 95% inhibition action on the growth of *Bacillus subtilis* at 500, 1000, and 2000 ppm, respectively, while concentrations between 10 and 100 ppm had no damaging effect on *Bacillus subtilis* development [8,15]. The predicted environmental concentration range of TiO<sub>2</sub> NPs in water in the United States is 0.7-16 mg/L; in surface water in the EU, it is 0.40-1.4 mg/L, the content of photostable TiO<sub>2</sub> NPs is 0.6-100 ng/L, and in Danish surface water, it is 0.05-7 ng/L for TiO<sub>2</sub> NPs photocatalytic. The studies have shown higher levels than the predicted ones in the environment [8,16,17]. For example, it revealed that the highest concentrations of NPs were detected in sediment in Europe and the United States in the mg/kg range [3,18].



The concentration of HMs is the most prominent contaminant in soil and water environments [19]. HMs are metallic elements with a density value of 4 to 5 g/cm<sup>3</sup>. Their concentration in the environment (soil, water, air, and organisms) is precipitated by anthropogenic activities (industry, transportation, and agriculture) and natural phenomena (volcanism and primary mineral alteration) discharged into the environment. They are redistributed in soil profiles through pedogenesis and ecosystems via bio-assimilation and bio-concentration processes [20,21]. Some

researchers have shown that those pollutants harm soil and water microorganisms [22]. The toxicity of HMs is studied in some aquatic organisms (*Daphnia Magna*, algae, *Mytilus galloprovincialis*, and *Tetrahymena thermophile*) [12,23]. Several studies have found that NPs dramatically increased the bioaccumulation and toxicity of Pb, Cu, As, Zn, and Cd in zebrafish (*Danio rerio*), larvae, and carp (*Cyprinus carpio*) [23–25].

**Table 1. Types of nanoparticles and their applications**

Type of NPs	Application of Nanoparticles	References
Metal oxides NPs		
Titanium dioxide (TiO <sub>2</sub> )	UV-A protection, Paints, Food additives, Disinfecting agent	[26–28]
Alumina (Al <sub>2</sub> O <sub>3</sub> )	Solar cells	
Silica (SiO <sub>2</sub> )	Additives for polymer composites	
Zinc dioxide (ZnO <sub>2</sub> )	Anti-fungal activity properties	
Zirconia (ZrO <sub>2</sub> )	Additives for scratch resistance coatings	
Iron Oxide (Fe <sub>3</sub> O <sub>4</sub> , Fe <sub>3</sub> O <sub>3</sub> )	Photocatalytic Degradation of Dyes	
Metals NPs		
Silver (Ag)	Broad-spectrum plant protectant, control of yield-robbing diseases, Broad-spectrum antimicrobial applications	[29,30]
Nickel (Ni)	A conductive electrolytic layer of proton exchange membrane fuel cells	
Iron (Fe)	Drug delivery, magnetic separation and labelling of biological materials	
Gold (Au)	Bio-imaging of tumour cells, explosive sensing and detection of microbial cells	
Copper (Cu)	Use as an anti-fungal agent with growth enhancer and improve root vigour properties.	
Platinum (Pt)	Anti-fungal Applications	
Palladium (Pd)	Catalysts for the Stille coupling reaction in an aqueous solvent and hydrochlorination of chloroarenes in water	
Organic NPs		
Fullerenes	mechanical and tribological applications/additives to grease	[31–34]
Graphenes	Solar panels, hydrogen fuel cell technology, transport, medicine, electronics, energy, defence, desalination;	
Carbon Nanotubes	Additives for polymer composites, mechanical performance, conductivity, electronic field emitters, Batteries, Fuel cells	
Quantum dots NPs		
Cadmium sulfide (CdS)	Biosensor, bio-imaging, nano-medicine, molecular pathology, antimicrobial activities, photovoltaic cells, semiconductor, and drug delivery.	[17,23,35]
Cadmium selenide (CdSe)	Solar cells, light-emitting diodes, and fluorescent tagging	
Cadmium telluride (CdTe)	Biomedical applications due to their tunable photoluminescence	
Zinc selenide (ZnSe)	Laser and optical instruments	
Indium phosphide (InP)	Solar cells, photodiodes, photodetectors, light-emitting diodes (LEDs) and field effect transistors (FETs).	

HMs are ionic species in the aqueous phase and are categorized into five fractions: carbonate, iron-manganese oxide, exchangeable, organic matter, and residual. However, the influence of NPs on heavy metal toxicity in aquatic organisms remains unclear. HMs are widely

distributed in sediments as NPs and are considered significant co-existing pollutants. Previous research on nanoparticle toxicity focused primarily on their direct effects. In contrast, their potentially indirect effects,

especially on the ecotoxicity of conventional pollutants such as HMs, have been underestimated.

Many studies have investigated the toxic effects of NPs in water. Unfortunately, few studies have been conducted on their influence on soil and the impact of NPs and HMs. Few studies have been published on the effect of NPs on the bioavailability of co-existing pollutants in sediments (NPs and HMs). However, the interaction between NPs and co-existing contaminants in the environment remains unclear. Metallic and organic NPs influence heavy metal bioavailability in soil. The primary goal of this chapter is to describe the impact of such NPs on HMs in the soil environment. The novelty of this paper deals with the exceeded concentration of NPs and Heavy metals in soil. By showing the toxicity levels of NPs and HMs and their combined impacts in soil. To examine the interaction between NPs and HMs in soil and how NPs influence heavy metal behaviour, bioavailability, and environmental toxicity.

## 2. Nanoparticles and Heavy Metals in the Soil

### 2.1. Sources of Nanoparticles in the Environment

“Nano” refers to a billionth of a meter, or  $10^{-9}$  meters ( $1 \text{ nm} = 10^{-9} \text{ m}$ ). The term “nano” comes from the Greek word

for “remarkably little.” NPs are atom aggregates ranging in size from 1-100 nm. They are highly reactive due to their small size and high specific surface area (SSA). For instance, the bigger the surface area, the smaller the particles. The particles smaller than 10 nm have a very high specific surface area, as shown in Figure 1. The specific surface area (SSA) of NPs is calculated using the formula 1.

$$\text{SSA} = \frac{6}{\rho \times d} \quad (1)$$

Where  $\rho$  is the density of the particle and  $d$  is the diameter of the particle.

Nanoscience and nanotechnology have brought renewed interest in the recent two decades due to their novel use in a wide range of disciplines, including consumer goods, electronics, and medical and environmental services. NPs are categorized into many groups based on size, shape, and physical properties. Carbon nanotubes, fullerenes, and their derivatives, such as carbon black, nanodiamonds, graphite NPs, graphene NPs, and graphene oxide, are examples of organic-based NPs [36].

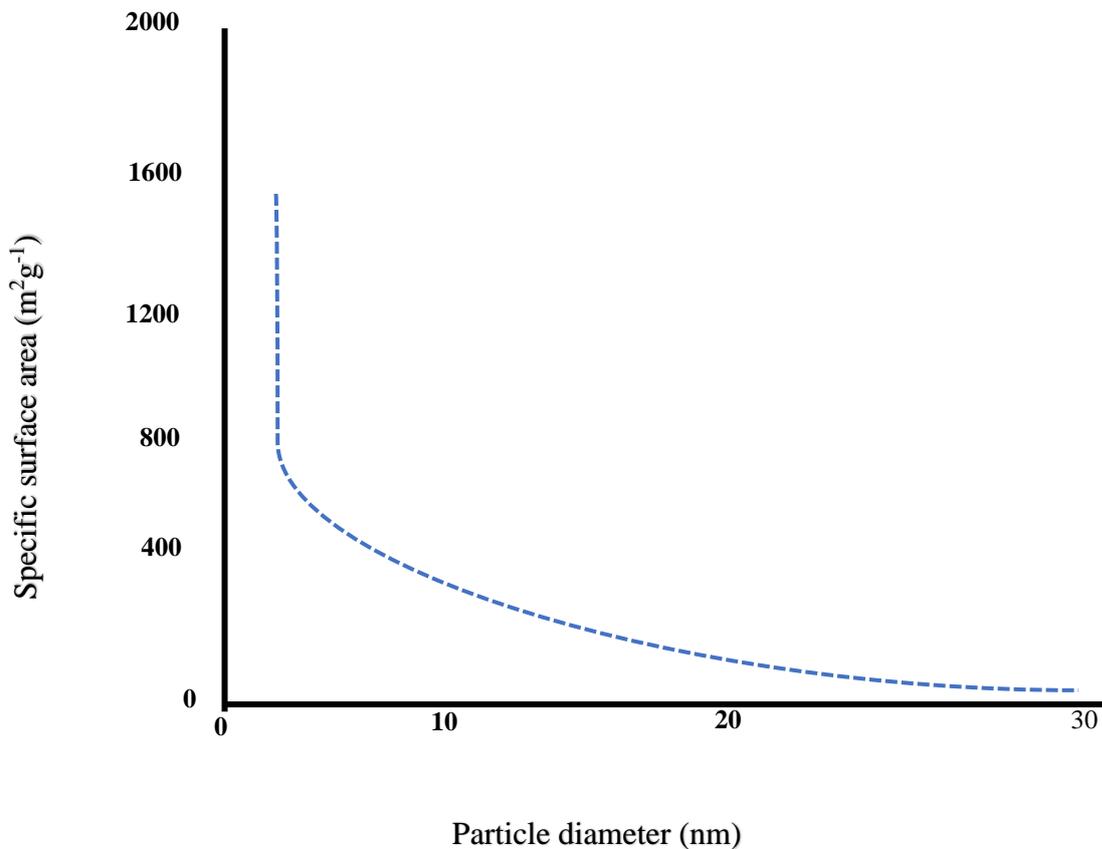


Fig. 1 The specific surface area of a nanoparticle as a function of the particle diameter

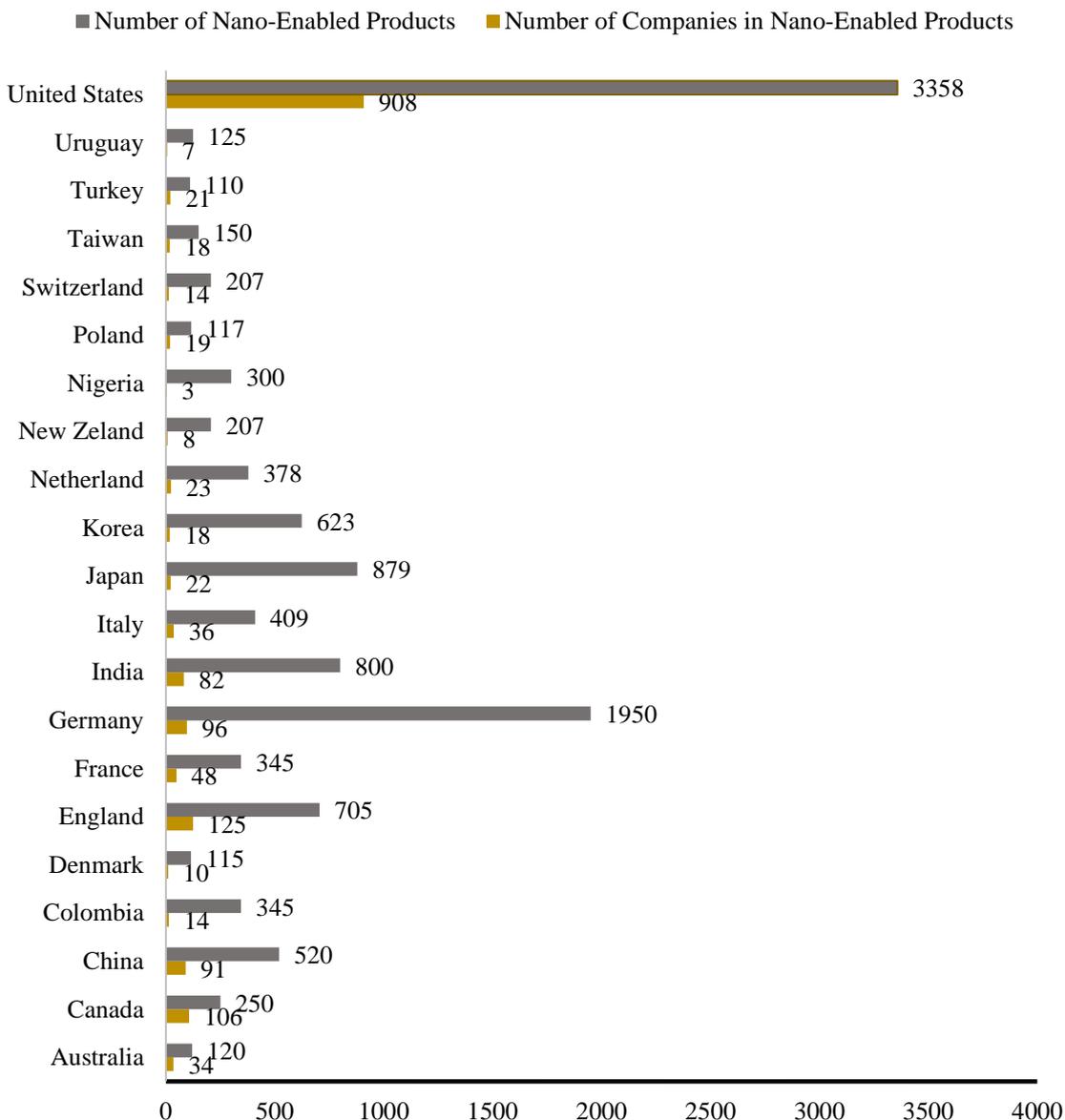


Fig. 2 Number of companies in nanoproducts and number of nanoproducts

Metal-based NPs, on the other hand (silver, zinc oxide, titanium dioxide, iron oxide, gold, and cerium dioxide), are extensively utilized in products [37]. Based on their morphology, they are subdivided into quantum dots, nanotubes, nanofibers, nanorods, nanosheets, aerogels, and nanoballs. Metallic NPs are the most commonly manufactured and used nanomaterials [38]. According to NanoWerk, NanoApex and the most recent research, about 3125 commercial goods-based NPs are created and released into the environment yearly in the most populated and industrialized countries, as shown in Figure 2 [39–41]. Bioaccumulation of NPs can potentially affect humans, aquatic life, plants, and animals.

The rising application of NPs has increased their environmental release and paid particular attention to their potential ecological implications. NPs in the environment can be both natural and manufactured. According to many investigations, the quantity of NPs in the soil is higher than

in water or air [42–44]. The environmental concentrations of NPs in sludge-treated soil have risen to levels as high as 42–89 g kg<sup>-1</sup> [45, 46]. Various anthropogenic operations contaminate the soil. Figure 3 illustrates the potential environmental releases of manufactured NPs from production to utilization and their release into the environment. Most sewage sludge is fertilized in agricultural lands [48–50]. Agricultural soils, industrial zones, and mining sites are expected to be a substantial depository for MNPs and a source of NPs in the environment and aquatic medium due to anthropogenic activities [46,50]. Agrochemical products such as synthetic fertilizers, herbicides, insecticides, and fungicides are sources of direct nanoparticles into the soil. Nano fertilizers are considered a primary source of soil and food crop pollution [51,52]. Household and pharmaceutical products are many other anthropogenic sources of MNPs in the soil [53].

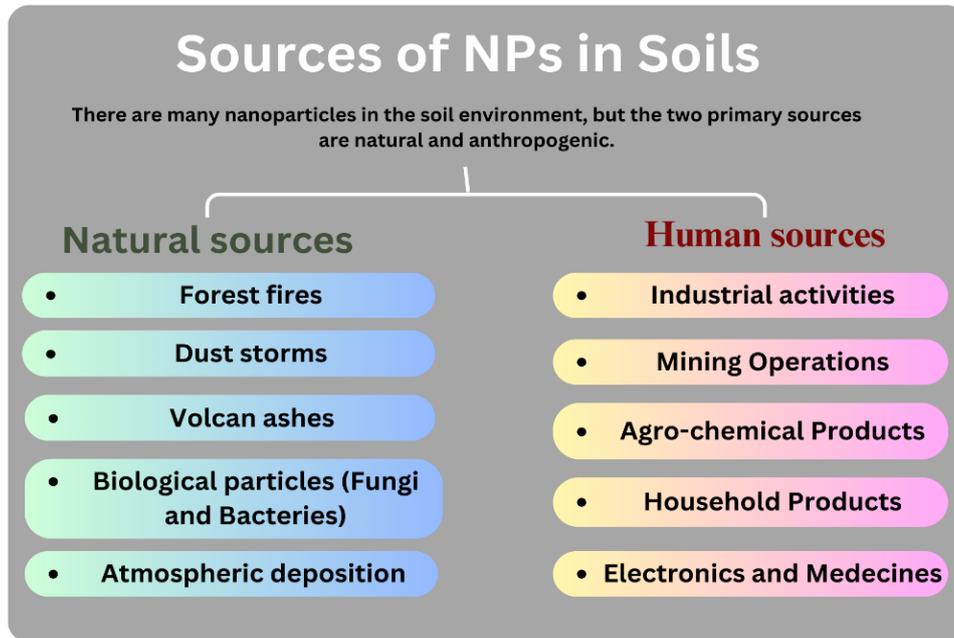


Fig. 3 The primary natural and anthropogenic sources of nanoparticles in the soil

### 2.2. Sources of Heavy Metals in the Soil

Previous research has indicated that HMs in soil and water have increased, attracting worldwide attention in recent years, particularly in developing countries [54–57]. HMs are abundant in the environment and agricultural soils due to natural (geological) and anthropogenic processes [58]. Weathering rocks, erosion, and volcanic activity are the most important natural causes of heavy metal entry into soils. Anthropogenic and natural sources include mining operations, smelting, industrial effluents, landfills, military training, pesticides, and fertilizers. Table 1 and Figure 4 reported that they are also the primary sources of HMs in soil [55,59, 61, 62]. HMs are found naturally in the earth by a geological parent material developed by the soil, known as the lithogenic source ('toxicity of heavy metals in soils and crops and its phyto-remediation ( PDFDrive.com ).pdf', no date; Järup, 2003; Brian J. Alloway, 2013; Wenzel and Alloway, 2013; Gunatilake, 2015; Deng *et al.*, 2017). They have the potential to enhance the concentrations of Ag significantly, As, Au, Ba, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se, Th, Tl, U, V, W, Zn, rare earth, and platinum (Pt)-group elements in the soils that develop on them [55,64,65]. The concentration of metals in the soil varies depending on the parent rock's lithogenic source. Black shale and oil shale are rich in organic materials and clay, as well as various HMs and other trace elements [64]. Some rocks, such as Limestones, Phosphorites, Ultramafic Rocks, and Sedimentary Ironstones, contain sufficient amounts of metal-containing minerals to be exploited as metal ores [55,66,67].

HMs are thus transported into the soil through weathering, erosion, and anthropogenic processes, constituting an essential component of the soil's ecosystem. According to Lombi and Gerzabek, Allow and Kumar *et al.*, the total concentration of HMs in the soil is calculated using the formula 2 below, which is the sum of HMs in parent

material, atmospheric deposition, fertilizers, and agrochemicals, organic waste, inorganic pollutants, crop removal, and losses by leaching and volatilization [58,68,69].

$$M = (M_{pa} + M_{atm} + M_{fer} + M_{agc} + M_{owa} + M_{ipo}) - (M_{cre} + M_{los}) \quad (2)$$

Where: "M" is the heavy metal in the soil, "pa" is the parent material, "atm" is the atmospheric deposition, "fer" is the fertilizer source, "agc" is the agrochemical source, "owa" is the organic waste sources, "ipo" are other inorganic pollutants, "cre" is crop removal, and "los" is the losses by leaching, volatilization.

This formula is essential for determining the number of HMs in the soil. The type of soil influences the formation and mobility of HMs in the environment; for example, water flowing through limestone (CaCO<sub>3</sub>) soils will produce a pH of about 8, whereas water flowing through granite, which contains main components such as quartz (SiO<sub>2</sub>) and feldspars, will produce a more acidic pH of about 6. If pyrite (FeS<sub>2</sub>) is present, mineral oxidation will form acid fluids, which will impact heavy metal solubility and may result in enhanced mobility of those metals [70].

### 3. Impacts of Soil Texture and Organic Matter on the Relationship between Nanoparticles and Heavy Metals

Soil parameters such as texture and organic matter (OM) content influence the interactions between NPs and HMs. Table 2 shows that the interactivity between NPs and TMs highly depends on the properties of the soil. Many investigations have demonstrated that in the presence of OM, clay and fulvic acid, the hazardous effects of these contaminants are significant [71–73]. This section focused on the influence of soil factors such as texture and OM in the interaction between NPs and HMs.

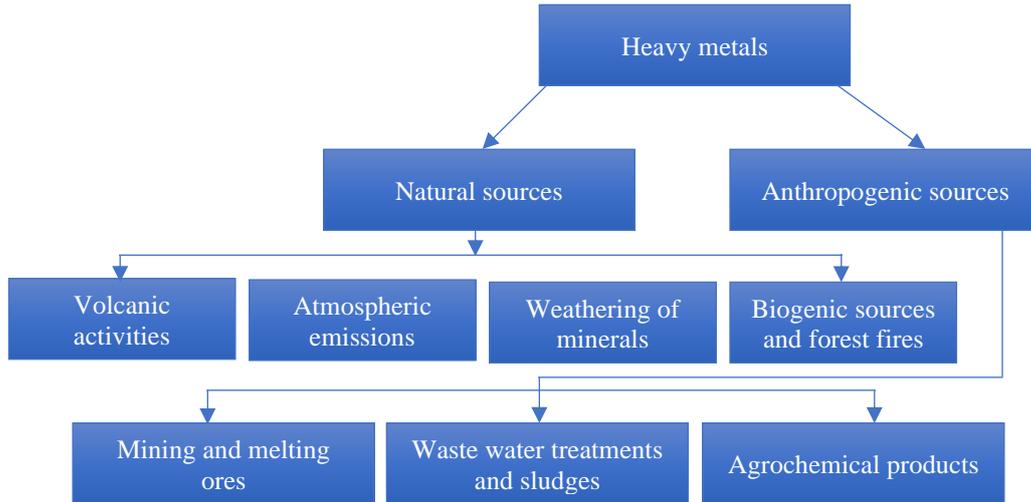


Fig. 4 The primary natural and anthropogenic sources of HMs in the soil

Table 2. Effects of soil texture and OM on the relationship between NPs and HMs.

Soil parameters	Effects on NPs and HMs	References
Soil texture (particle sizes)	The size of particles plays a crucial role in influencing the movement of nanoparticles (NPs) and heavy metals (HMs) within soil. Smaller particles act as barriers, hindering the transfer of NPs and HMs. The surface area of these particles greatly affects the deposition of pollutants in soil and their rate of movement.	[74–76]
Organic matter (OM)	The existence of organic matter (OM) within the soil has a significant impact on how soil nanoparticles (NPs) and trace metals (TMs) come together or spread out. Organic matter primarily governs the transportation and buildup of pollutants.	[28,71,77,78]

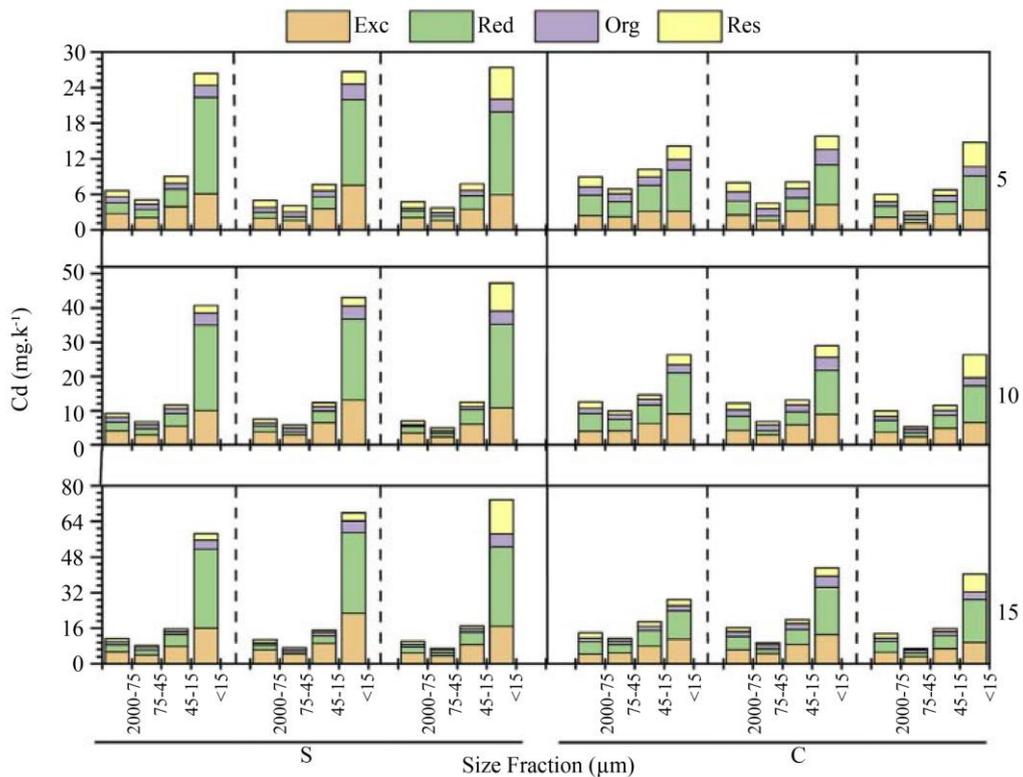


Fig. 5 Effect of particle size fraction on Cadmium accumulation in soil. (Exc: exchangeable cadmium; Red: reducible cadmium; Org: oxidizable cadmium; Res: residual cadmium; S: sandy loam; C: clay loam) [80]

The particle size of the soil is an essential aspect in controlling the movement and interaction of NPs and TMs with surrounding materials. Previous studies have shown that a smaller particle size in the medium might increase the mass transfer rate to the surface [79]. Interaction efficiency changes and large grain size can alter NPs and HMs retention. Smaller particles offer a large surface area that can be targeted for deposition, producing better adhesion sites. Advection and dispersion mechanisms are commonly used to transport NPs and co-contaminants in a porous medium in a mobile phase. While advection is the movement of NPs and HMs along the bulk flow and is directly related to flow velocity, dispersion is the spread of these elements through diffusion and mechanical dispersion [73]. Clay and OM in soil play a crucial role in the aggregation and dispersion of soil NPs and TMs. It mainly affects the transport and accumulation behaviour of the pollutants. Liu et al. demonstrated that particle sizes are significant in terms of pollutant accumulation in soil [80]. They have stipulated that cadmium concentration was significantly low with a big particle size fraction (75-45  $\mu\text{m}$ ) and highest in the particle size fraction smaller than 15  $\mu\text{m}$  in soil, as indicated in Figure 5. Other researchers confirmed this statement by discovering that the contaminants contained in the 85-50  $\mu\text{m}$  particle sizes were significantly lower than those in the finer particles (<10  $\mu\text{m}$ ) [81,82].

The biotoxicity of trace metals in soil is highly dependent on their form. According to the results of their investigation, cadmium in each particle size fraction was mainly exchangeable and reducible (61-85 %) not only in sandy loam but also in clay loam. The oxidizable and residual fractions had relatively low contents [80]. The reaction activity of the particles in response to cadmium was low in the greater particle size range (2000-45  $\mu\text{m}$ ) because the minerals in the large soil particles were primarily silicon dioxide and gravel [83]. It was evident that the particle sizes and OM significantly affect the bioactivity, accumulation, bioavailability and interactivity of NPs and HMs in the soil.

### 3. Effects of Metal Oxide Nanoparticles on Toxic Metals in the Soil

NPs could interact with metals in sediments, influencing their bioavailability. Thus, understanding how ENPs alter HMs bioavailability is essential for understanding the potential ecological damage of these elements. The aggregation and dissolution behaviour of ENPs has been proven to have significant implications for environmental fate and toxicity [8,84–87]. Soil properties influence the interactions between NPs and HMs. The fate and behaviour of NPs in the soil can be controlled by soil parameters such as pH, ionic strength of the soil solution, OM, and soil clay level, as shown in section 2 above [37,88]. Seeing as soil clay is negatively charged and can react with soil metals that are positively charged. It plays a vital role in interacting with NPs with HMs. Many studies have suggested that diverse soil factors such as clay, organic matter, pH, and ionic strength may impact the mobility and properties of NPs [8,30,89,90]. These features vary greatly depending on the soil type. According to current data, the

behaviour of NPs toward HMs in clay soil, organic matter soil, and humic acid may differ from that previously investigated in sand soil medium [89,91]. The influencing effects of NPs on HMs in soil are studied in this section.

Numerous studies have demonstrated that titanium dioxide NPs ( $\text{TiO}_2$  NPs) have an amazing capacity for heavy metal adsorption.  $\text{TiO}_2$  NPs' potential effects on HMs may influence their behaviour and toxicity. However, the effects of  $\text{TiO}_2$  NPs on the behaviour and toxicity of HMs should be investigated. According to these reasons, Wang et al., Chen et al., Miao et al., and Wang et al. investigated the physicochemical interaction of  $\text{TiO}_2$  NPs with HMs to fully understand the basic mechanisms of synergistic toxicity in the environment.

At acidic pH levels, Saripalli et al. revealed that the interaction between  $\text{TiO}_2$  NPs and HMs, such as metal element absorption in soil, is strong on the anatase form of  $\text{TiO}_2$  NPs [92]. Tel et al. demonstrated that the solubility of  $\text{TiO}_2$  NPs is low; its point of zero charges (pHpzc) in the middle of the pH scale allows them to investigate  $\text{TiO}_2$  adsorption on positively and negatively charged surfaces over a wide pH range [93]. Humic acids (HA) have a high complexation ability with metal ions, greatly influence metal ions' behaviour, and have a high affinity to oxide NPs. Several research studies have shown that the coexistence of  $\text{TiO}_2$  NPs with HMs could amplify metals' toxicity in soil. Hu et al. have demonstrated that metal oxide NPs like  $\text{TiO}_2$  NPs and graphene oxide NPs could intensify arsenic toxicity to soil organisms, causing a decrease in biomass and species destruction [94]. These properties must affect the coexistent contaminants such as toxic metals (TMs), organic pollutants, etc. Metal oxide NPs might interact with TMs in sediments and then influence the bioavailability of these metals. Metal oxide NPs are widely distributed in the soil and TMs, and these pollutants are known as co-existing contaminants. These results suggest that  $\text{TiO}_2$  NPs increase the bioconcentration of lead, which leads to the disruption of the thyroid endocrine and neuronal systems in zebrafish larvae [25]. So, the interaction of oxide NPs on coexistent contaminants depends on the soil types and characteristics that may differ from aquatic systems due to the unique biological, physical, and chemical factors of soil that vary from sand and water systems.

### 4. Synergetic effects of nanoparticles and heavy metals on plants

The widespread use of nanomaterials and product-based metals has dramatically increased the amount of NPs and HMs in terrestrial and aquatic environments. These can lead to co-contaminant overload in the environment, which can have a negative impact on the soil ecosystem. Although the effects of nano products and product-based metals on plant growth are currently unknown, some symptoms of the toxicity of the conjugated effect of NPs and HMs on plants are known, including the toxicity mechanism involving membrane disruption, protein oxidation, cytotoxicity, and release of toxic elements in the environment, as indicated in Table 3. Increasing the co-pollutant concentration resulted in a significant decrease in the plants' enzymatic activity,

growth, and photosynthetic pigmentation. Karthick et al. demonstrated that the synergistic effect of NPs and HMs could affect plant growth parameters. They also confirmed that it could have caused trophic plant transfer, which is the movement of toxic elements through the food chain via human and organism ingestion [95]. The assessment of trophic transfer is critical because contaminants may enter

into organisms at low levels over time and accumulate at higher levels in organisms and humans, causing health problems. Trophic transfer of HMs in the food chain has been observed since the early 2000s. Due to their small sizes and specific surface area to interact with their medium, NPs trophic transfer in environment organisms is receiving much attention.

**Table 3. Conjugated effects of nanoparticles and heavy metals on plants**

<b>NPs and HMs in mg/kg</b>	<b>Plant species</b>	<b>Effects</b>	<b>References</b>
CuO (100–600) and Cr (100)	Cucumber	Inhibition of seed germination up to 23.3%	[54]
TiO <sub>2</sub> (40) and Hg (25)	Capsicum annum L.	Affected nutritional quality; reduced Zn by 55% in leaves and 47% in fruits. The	[96]
CuO (0–8) and Pb (40)	Soybeans	Reduced/stopped root growth at high concentration, deforming the root cap surface and meristematic zone.	[97]
ZnO (10-1000) and Cu (400)	Radish and calendula Officinalis	Reduction in chlorophyll and protein level, with lower production in yield	[71,98]
Cu (500) and Cr (100)	Peppers	Cr over 100 mg kg <sup>-1</sup> Cr in soil-induced biomass, root and shoot length reduction	[99,100]
CeO <sub>2</sub> (250) and Co (300)	Giant reed	Reduction maximal of root length and changes in the rhizosphere	[71]
ZnO (10-90) and Cu (100)	Spinacia oleracea	Reduced root length and shoot length	[101]

## 5. Effects of biomagnification of nanoparticles and heavy metals on human and organism health

The applicability of nanomaterials has improved the industrialized sector while generating new challenges due to many unidentified environmental threats. Due to their tiny sizes, NPs are active at the atomic scale, and their presence in the environment and exposure to species could threaten the ecosystem [102]. At the same time, the concentration of HMs in the environment has increased due to the unavoidable manufacture of metal-based products and their use in various fields. However, the concept of HMs is a problematic one because some metals, such as copper (Cu), iron (Fe), manganese (Mn), nickel (Ni) and zinc (Zn), are needed at trace concentrations by organisms [71]. These elements are known as micronutrients, and their concentrations can be harmful if they exceed the permissible limits set by environmental experts. In general, the conventionally known hazardous HMs in the environment are cadmium (Cd), arsenic (As), mercury (Hg), lead (Pb), and chromium (Cr). HMs are chemicals that can pollute the environment. According to many scientific articles, the lower limits of a hazardous metal density range from 3.5 to 7 g/cm [103,104].

The synergistic impact of NPs and HMs in the environment may endanger human health, microorganisms and plants. However, the data on each and every single NPs and HMs are still to be investigated in realistic and

descriptive conditions. According to the experts, humans could be exposed to NPs and HMs' toxicity in three ways: inhalation into the pulmonary system, absorption through the dermal system and ingestion through the gastrointestinal system. In recent years, various investigations have been performed on the ecotoxicological effects of terrestrial and aquatic microorganisms, including bacteria, algae, zooplankton, fish, and other vertebrates, as indicated in Table 4. NPs can activate significant co-contaminants, including trace metal elements and organic compounds. NPs have exhibited strong reactions to organic pollutants and trace metals such as arsenic, lead, copper and rare earth metals. These reactions to contaminants may increase their bioavailability and allow them to bioaccumulate more easily through cell membranes, causing biomagnification in the human body. According to the Thesaurus Dictionary, bioaccumulation and biomagnification are, respectively, the accumulation of a substance over time, especially a contaminant in a living organism and the process by which that substance increases its concentration in the tissues of organisms as it travels up the food chain. Under UV and polychromatic light, NPs have been shown to produce reactive oxygen species in water. Some researchers studied the physicochemical interaction between TiO<sub>2</sub> NPs and HMs to understand the fundamental mechanisms of synergistic toxicity effect in the environment. They discovered that it increases the speciation distributions in sediments, which improves bioavailability and, finally, the biomagnification process, causing cell reproduction issues [3,8]. An investigation held by Yuan and her colleagues on

the conjugated effects of NPs and HMs on microbial activity has indicated that it reduced microbial biomass and diversity of the species.

TiO<sub>2</sub> NPs have been shown to increase the toxic effects of Cd in aquatic organisms. Research performed by Balbi et al. confirmed that after 25 days of exposure, the toxic metal concentration in carp increased by 146% [105]. Zhao et al. examined the impact of ZnO NPs at concentrations of 10, 30, 60, 90, or 120 mg/L on the zebrafish (*Danio rerio*) embryo for 5760 minutes. They found that the ZnO NPs increased zebrafish heartbeat and embryo dysfunction [106]. Sharma and his colleagues conducted a 168-hour

study on the effects of Ag NPs on river fish (*Labeo rohita*) at concentrations of 100, 200, 400, and 800 g/L. They discovered toxicity in terms of cellular response and DNA damage at 400 and 800 g/L. A time and dose-dependent relationship between hepatocytes and vacuolar degeneration was observed on liver examination [107]. Boran and Ulutas exposed larval zebrafish (*Danio rerio*) to Zn NPs (0.2-6 mg/L) and ZnCl<sub>2</sub> (0.1-3 mg/L) for 4 days and discovered that ZnCl<sub>2</sub> caused more DNA damage. The toxicity of diverse stress-related genes (p53, rad51, mt2) was investigated, and significant induction of mt2 was observed at high concentrations (3 and 6 mg/L) due to Zn(II) release [108]

**Table 4. Conjugated effects of nanoparticles and heavy metals on human and organism**

NPs and HMs	Organisms	Conjugated effects	References
TiO <sub>2</sub> +Hg/Cd	Daphnia Magna	Affects reproduction, cellular pathways, and Acute morbidity and accumulation in the digestive system.	[109,110]
CuO+As	Human organs (kidneys, cells, lungs and livers)	Changes cellular pathways	[111]
ZnO+As/Cd	Rat	Changes in albumin, cholesterol, triglyceride, total protein, urea, high-density lipoprotein, low-density lipoprotein and aspartate aminotransferase activity	[60]
Fe+Pb/Hg	Bacillus subtilis	Damage to the cell membrane and disruption of cellular function	[47]
Ag+Pb	Fish	Mortality by oxidative stress and inhibition of acetylcholine. Mucous cell loss and damage to gill epithelium were observed after 15 days, whereas substantial.	[106]
Fe <sub>2</sub> O <sub>3</sub> +Cd	Bacteria	Generation of ROS, disruption of the membrane integrity, interacts with proteins and nucleic acid and affects replication	[9]
CeO <sub>2</sub> +Hg	Danio rerio	Decreased body length, bent tail and cardiac oedema	[13]

Acronyms: Ag: Silver, Cd: Cadmium, As: Arsenic, Pb: Lead, Hg: Mercury, TiO<sub>2</sub>: Titanium oxide, ZnO: Zinc oxide, CuO: Copper oxide, ROS: Reactive Oxygen Species, SiO<sub>2</sub>: Silicon dioxide.

## 6. Conclusion

Previously, the toxicity of NPs and HMs was mainly studied separately in aquatic organisms. To our understanding, only a few existing scientific investigations focused on the synergistic effects of NPs and HMs in soil. As a result, this chapter investigated the relations between NPs and HMs and their impacts on HMs in soil. The conjugated toxicity of NPs and HMs on soil organisms was investigated. Many studies stipulated that high contamination of NPs and HMs in the environment may harm humans and organisms. These co-contaminants promote Reactive Oxygen Species (ROS) production, harming the organism in the environment. It was discovered that soil properties are critical in the interaction of NPs and HMs. Motoring the synergistic effect of NPs and HMs in the soil would be a significant step forward in terms of environmental protection and pollution reduction.

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## Author Contributions

Djibril Sekou Keita Conceptualized and designed the review paper. Carried out literature search and review, compiled findings, and drafted the manuscript.

Hannah Akasi Abbey participated in the search and review of the literature. Contributed to synthesizing data from various sources and significantly revised the manuscript.

Bachir Yaou Balarabe Reviewed and selected relevant articles for inclusion in the review. He contributed to the analysis and interpretation of the literature.

Irédon Adjama Assisted in data synthesis and interpretation and provided critical feedback on the manuscript.

Manka Marycleopha helped with the interpretation and provided critical feedback on the manuscript.

Harshad Patel Oversaw the entire review process, provided guidance, and ensured the accuracy and quality of the manuscript. Made significant revisions and final edits and gave final approval for submission.

## Data Availability Statement

The raw data used in this review paper are available from the corresponding author and can be accessed through the following source: [Corresponding author: kd70405936@gmail.com].

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