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MINI-REVIEW

Toxicological Effect of Metal Oxide Nanoparticles on Soil and Aquatic Habitats

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Abstract
Metal oxide nanoparticles (MO-NPs) with multifunctional properties are used extensively in various industries and released into the environment as industrial effluents and waste nano-products. These non-degradable, toxic MO-NPs are accumulating in the environment, debilitating the ecosystem and their biological communities. In this review article, a real-time scenario of MO-NP toxicity towards the soil and aquatic ecosystem and their mode of toxicity have been addressed in detail. The up-to-date information presented here suggests serious consideration of the consequences before random utilization of MO-NPs.

The advent and the worldwide growth of nanoparticle (NP)-based industries have been referred as the next industrial revolution by Lux Research 2008. In past 2 decades, successful synthesis of engineered nanoparticles (ENPs), especially metal oxide nanoparticles (MO-NPs) with fascinating physico-chemical properties, such as transparency to visible light, semi-conductivity, intrinsic UV-absorbing capacity, etc., has facilitated the golden age of these industries (Bondarenko et al. 2013). NP-rich industrial effluents are continuously disposed to the environment, resulting in alteration of soil and aquatic equilibrium, thus challenging to their living population (Ciacci et al. 2012). These risks are growing in tandem with increasing demand of nano-products in the global market (Morales-Diaz et al. 2017). A schematic presentation of eco-toxicological aspects of MO-NPs is shown in Fig. 1.

In recent years, many of studies have reported MO-NP induced toxicity in mammalian cells, specifically humans (Yamamoto et al. 2004; Bondarenko et al. 2013), and plants (Morales-Diaz et al. 2017; Siddiqi and Husen 2017). Although a few scientific reports are available focusing the eco-toxicity of individual MO-NP on a specific biological species, complete information comprising the MO-NP toxicity as a whole towards the entire soil and aquatic habitats is yet to be explored extensively.

This review article is a compact attempt to understand the real-time MO-NP induced eco-toxicity and its threshold level towards the entire soil and aquatic habitats. The most abundantly used MO-NPs, such as TiO_2, ZnO, CuO, etc., have been studied with special consideration. This review strongly demonstrates the necessity of monitoring the random use of toxic MO-NPs to avoid the irreversible environmental impairment in the near future.

Global Production, Production Strategy and Application of MO-NPs

Global Production

In the year 2000, the very first national nanotechnology programme was launched in the United States, and in 2010 itself, the worldwide funding for NT was 1.78 billion dollars (Sargent 2012). Effectively, mammoth quantity of SiO_2, TiO_2, and other MO-NPs were produced (Piccinno et al. 2012). Projections indicate this exponentially increasing market value of NT to reach as high as $1 trillion by 2020 (Chakraborty et al. 2016).

Production Strategy

NPs are traditionally synthesized by a number of physical, chemical, and biological routes. The physical methods in practice include gas condensation technique, spray pyrolysis, laser pyrolysis, vapour deposition (Dhand et al. 2015), etc. Highly pure NPs with desired shape and size can be

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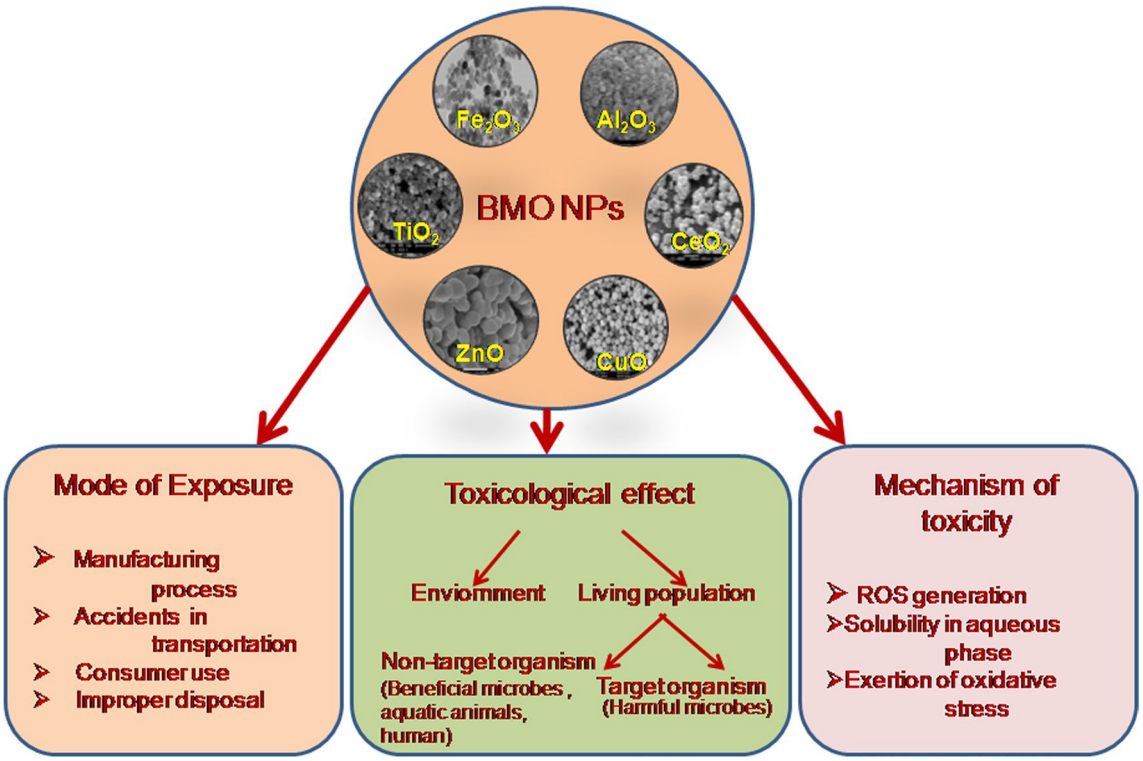

Fig. 1 Schematic presentation of eco-toxicity of MO-NPs

achieved this way, but complicated instrumentation and high-power consumption make these processes inconvenient and expensive. Chemical methods include sol–gel, microemulsion, hydrothermal, chemical vapour synthesis, etc. (Dhand et al. 2015), but employment of highly toxic and non-biodegradable chemicals causes environmental hazard and limits its biomedical applications (Boxi et al. 2016). Recently, biological synthesis of NPs has come to the fore where biomolecules secreted by plants or microorganisms being used as reducing agents for the material salts (Dhand et al. 2015).

Applications

The MO-NPs are critically used in manufacturing industries to reinforce the physical properties of bulk materials or to achieve enhanced surface features like scratch resistance, water repellence, reflectivity, photo-activity, etc. (Bondarenko et al. 2013). These are most commonly used in sensor and sensing devices, catalyst designing, sunscreens, cosmetics, electronic devices, textiles, agriculture, diagnostic imaging, potential cancer treatment, antimicrobial applications, etc. (Exbrayat et al. 2015; Dhand et al. 2015). Conclusively, MO-NPs have become an integral part of our daily life.

Eco-toxicology

NPs as Contaminant

NPs existed in the environment from the beginning of the earth's history as volcanic dust, soil-particles, rock erosion, etc. With time, living systems had learnt to withstand the ill effects and interference of these natural NPs (Exbrayat et al. 2015). In the past 2 decades, synthesis of ENPs has introduced multipurpose industries but imposed new challenges to the living population. Even though some researchers deny the size-dependent mechanical toxicity of MO-NPs (Yamamoto et al. 2004; Warheit et al. 2006), manipulating the surface area, surface chemistry, and ionic characters of these ENPs for achieving desired properties has increased their toxicity and bioavailability to much higher level than their bulk form (http://europa.eu.int/comm/health/ph_risk/committees/04_scenihr/04_scenihr_en.htm). These toxic NPs are continuously disposed and accumulated in the environment resulting consequent ecological imbalance (Hu et al. 2010). The major sources of the NP contaminants in environment are summarized in Fig. 2.

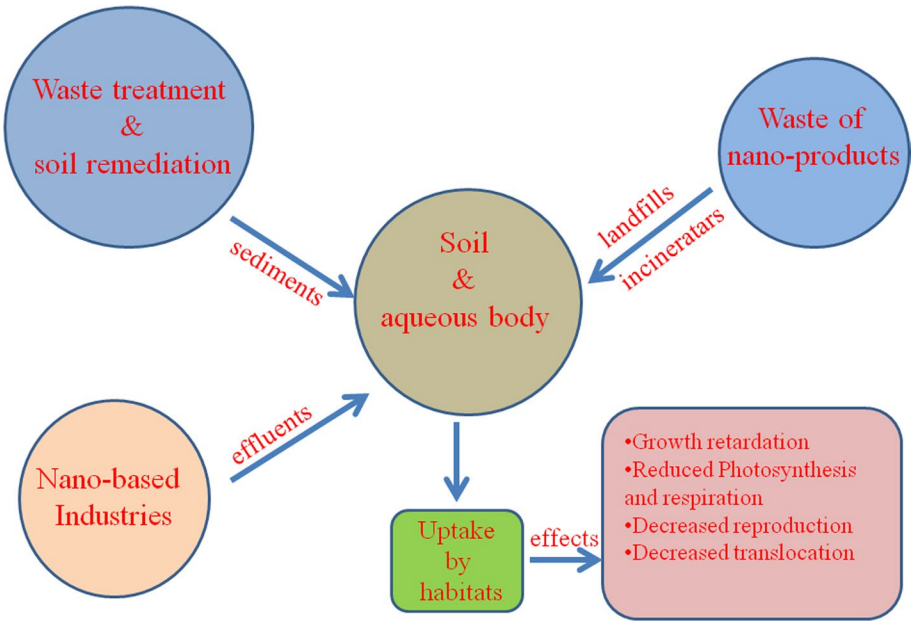

Fig. 2 Major sources of NP contaminant to soil and aquatic environment

MO-NPs in Aquatic Eco-system

Aquatic ecosystem consists of many organisms ranging from producers to decomposers (Bondarenko et al. 2013). The MO-NP toxicity on growth and survival of the producers causes depletion of dissolved oxygen in the water bodies. Again, lethal effects on decomposers limit biodegradation process resulting accumulation of waste materials that contribute to the pollution in aquatic environment (Navarro et al. 2008; Siddiqi and Husen 2017). Consumers at different levels, such as Zebrafish (Chakraborty et al. 2016), Daphnids and other crustaceans (Heinlaan et al. 2008), sea urchin (Fairbairn et al. 2011), rainbow trout (Federici et al. 2007), some amphibians, and molluscs (Exbrayat et al. 2015), are the most reported aquatic habitats to suffer from MO-NP toxicity (Table 1).

Toxicity of the MO-NPs are relative to their solubility in aqueous medium. TiO_2 and CeO_2-NPs aggregate and sediment fast (~30–60 min) and are completely insoluble in seawater (Keller et al. 2010) that limits their toxicity and bioavailability, too. In contrast, ZnO and CuO-NPs are readily soluble and release metal ions (Zn^{++} and Cu^{++}) in aqueous solution, making them more toxic and bioavailable (Chang et al. 2012). In some cases, bulk $ZnSO_4$ releases more metal ions in aqueous medium exerting higher toxicity than nano-ZnO, which supports the size independent toxicity of MO-NPs (Yamamoto et al. 2004; Warheit et al. 2006; Heinlaan et al. 2008). Similarly, influence of Cu^{++} ions in CuO-NP toxicity has been reported by Bondarenko et al. (2013).

Hence, without even entering the cell, MO-NP may exert toxicity by altering the ionic character of the micro-environment in close vicinity of cell-particle contact area. However, each metal ion is unique in its mode of toxicity and the toxicity is highly species-specific (Bondarenko et al. 2013; Exbrayat et al. 2015).

MO-NPs in Soil Environment and Its Impact on Soil Habitats

Nanoparticles are introduced into the soil environment during transportation, consumer's use, and improper disposal (Navarro et al. 2008). The NP toxicity becomes more complex when it combines with the organic and inorganic substances present in the soil matrix. Dissolved or particulate organic matters present in the soil environment may get adsorbed onto the NP surface and influence its ionic character in a number of ways. In humus-rich soil, negatively charged substances are adsorbed onto the MO-NP surface and forms a negative charge bearing complex. The resulting complex increases MO-NP stability by reducing the chances of agglomeration (Ben-Moshe et al. 2010; Fang et al. 2009). Nature of humus, such as hydrophobicity and the capacity to change ionic character of MO-NPs, improves the stability of NPs in soil (Ghosh et al. 2008). Stability of the MO-NPs also influences the NP transportation through the soil matrix (Fig. 3). Aggregation of the MO-NPs make them deposit heavily on the soil surface (Dunphy et al. 2006). Likewise, oppositely charged soil surface and NPs form a conjugate and immobilize the NPs onto the soil surface (Cornelis et al. 2011). As an example, positively charged Al_2O_3-NPs are relatively less mobile but in phosphate rich soil (negatively charged) mobility increases due to phosphate sorption onto the surface (repulsive force) (Darlington et al. 2009). On the contrary, the electrostatic interaction between the soil surface and the MO-NPs determines the NP mobility through

Table 1 MO-NP toxicity towards aquatic habitats

Organism tested	NPs	Size (nm)	Concentration range	Duration	End point	Outcome	References
Bacteria (*E. coli*)	ZnO	13.1	10^{-2}–3×10^{-3} M	12 h	100% growth inhibition	MIC = 3×10^{-3} M	Brayner et al. (2006)
	CeO_2	7	1.2–37 mg L^{-1}	1 h	Aggregation and sedimentation of bacteria	N.D.	Thill et al. (2006)
(*Vibrio fischeri*)	ZnO	50–70	1.1–1.9 mg L^{-1}	30 min	Complete growth inhibition	EC_{50} = 1.8 mg L^{-1}	Heinlaan et al. (2008)
	CuO	30	1.6–3811 mg L^{-1}	30 min	Complete growth inhibition	EC_{50} = 79 mg L^{-1}	Heinlaan et al. (2008)
Protozoa (*Tetrahymena thermophila*)	ZnO	70	0.001–10 mg L^{-1}	24 h	Inhibition of growth	EC_{50} = 9.4 mg L^{-1}	Blinova et al. (2010)
	CuO	30	0.006–20 mg L^{-1}	24 h	Accumulation of CuO in food vacuoles, inhibition of growth	N.D.	Blinova et al. (2010)
	ZnO	50–70	1.85–25 mg L^{-1}	24 h	Metal accumulation in food vacuoles, 70–90% decrease in ATP content, retarded cell viability	EC_{50} = 5 mg L^{-1}	Mortimer et al. (2010)
	CuO	30	31.25–500 mg L^{-1}	24 h	Decreased ATP content, metal accumulation in food vacuoles resulting reduced cell viability	EC_{50} = 128 mg L^{-1}	Mortimer et al. (2010)
Microalgae (*Pseudokirchneriella Subcapitata*)	ZnO	50–70	0–0.5 mg Zn L^{-1}	72 h	Algal growth inhibition	EC_{50} = 0.042 mg Zn L^{-1}	Aruoja et al. (2009)
	CuO	30	0–7 mg Cu L^{-1}	72 h	Complete growth inhibition	EC_{50} = 0.71 mg Cu L^{-1}	Aruoja et al. (2009)
	TiO_2	25–70	0–100 mg Ti L^{-1}	72 h	The nanoparticle aggregates entrap the algal cells and reduces the light availability resulting growth inhibition	EC_{50} = 5.83 mg Ti L^{-1}	Aruoja et al. (2009)
Green algae (*Desmodesmus subspicatus*)	TiO_2	25	3.1–50 mg L^{-1}	72 h	Death of algae under illumination	EC_{50} = 44 mg L^{-1}	Hund-Rinke and Simon (2006)
Amphibian (*Xenopus laevis*)	CuO	6	143–200 µM	48 h	Significant retardation in cell proliferation and increase in apoptosis	N.D.	Thit et al. (2013)
Amphibian *(Rana catesbeiana*)	TiO_2	20	8–800 ng L^{-1}	48 h	Significant effect on stress related transcript is observed but chance of adverse tissue damage is low	N.D.	Hammond et al. (2013)
Blue mussel (*Mytilus edulis*)	CuO	100	400–1000 ppb	1 h	Decreased protein thiols and increased carbonylation in gill tissue	N.D.	Hu et al. (2014)
	TiO_2	7.4	4.5 mg L^{-1}	2 h	No accumulation of nanoparticles	N.D.	Doyle et al. (2016)

Table 1 (continued)

Organism tested	NPs	Size (nm)	Concentration range	Duration	End point	Outcome	References
Marine mussels (*Mytilus galloprovincialis*)	ZnO	20–30	0.1–2 mg L^{-1}	12 weeks	Increase in respiration and retardation in growth and survival rate	N.D.	Hanna et al. (2013)
	ZnO	10–2000	1–10 µg mL^{-1}	30–60 min	Lysosomal destabilization, increased phagocytosis	N.D.	Ciacci et al. (2012)
	TiO_2	15–60	1–10 µg mL^{-1}	30–60 min	Lysosomal destabilization, increased phagocytosis	N.D.	Ciacci et al. (2012)
	SiO_2	5–30	1–10 µg mL^{-1}	30–60 min	Decreased cellular lysozyme activity	N.D.	Ciacci et al. (2012)
	CeO_2	5–20	1–10 µg mL^{-1}	30–60 min	Complete inhibition of phagocytosis	N.D.	Ciacci et al. (2012)
Eastern oyster (*Crassostrea virginica*)	TiO_2	7.4	4.5 mg L^{-1}	2 h	No accumulation of nanoparticles	N.D.	Doyle et al. (2016)
Crustacean (*Daphnia magna*)	ZnO	50–70	6.1–8.8 mg L^{-1}	48 h	Absolute immobilization	EC_{50} = 3.2 mg L^{-1}	Heinlaan et al. (2008)
	ZnO	48	0.01–10 mg L^{-1}	48 h	Accumulation of NP in GI track and interfere in food intake resulting acute and chronic toxicity	EC_{50} = 0.76 mg L^{-1}	Hai-zhou et al. (2012)
	CuO	51	0.01–10 mg L^{-1}	48 h	Retardation in food intake results in growth and reproduction inhibition	EC_{50} = 0.46 mg L^{-1}	Hai-zhou et al. (2012)
	CuO	30	3.2–165 mg L^{-1}	48 h	Absolute immobilization	EC_{50} = 3.2 mg L^{-1}	Heinlaan et al. (2008)
	TiO_2	25	1–3 mg L^{-1}	48 h	Immobilization of Daphnids in pre-illuminated media	N.D.	Hund-Rinke and Simon (2006)
	TiO_2	10–20	0.2–10 mg L^{-1}	48 h	100% mortality	MIC = 10 mg L^{-1}	Lovern and Klaper (2006)
Crustacean (*Thamnocephalus platyurus*)	ZnO	50–70	0.18–0.98 mg L^{-1}	24 h	100% mortality	EC_{50} = 0.18 mg L^{-1}	Heinlaan et al. (2008)
	CuO	30	0.11–95 mg L^{-1}	24 h	100% mortality	EC_{50} = 2.1 mg L^{-1}	Heinlaan et al. (2008)
Zebrafish (*Danio rerio*)	ZnO	20	0.1–50 mg L^{-1}	96 h	Retardation in embryo and larvae development, decrease in survival and hatching rate, serious tissue ulceration on larvae	EC_{50} = 1.79 mg L^{-1}	Zhu et al. (2008)
	ZnO	10–12	0.5–3.51 mg L^{-1}	5 days	Mortality combined with malformation	N.D.	Wehmas et al. (2015)
	ZnO	20–30	0.01–10 mg L^{-1}	96 h	Pericardial and yolk-sac edema	LC_{25} = 2.64 mg L^{-1}	Choi et al. (2016)
	TiO_2	50–100	1–100 mg L^{-1}	96 h	Malformation and retardation in embryo hatching. DNA damage, alteration in defence enzyme activity and increased MDA concentration in larvae	N.D.	Zhao et al. (2013)

Table 1 (continued)

Organism tested	NPs	Size (nm)	Concentration range	Duration	End point	Outcome	References
Sea urchin (*Lytechinus pictus*)	ZnO	300–350	0–200 µg L^{-1}	96 h	Delayed/arrested development (gastrula stage), exogastrulation, skeletal abnormalities and radialized plutei	EC_{50} = 99.5 µg L^{-1}	Fairbairn et al. (2011)
Rainbow trout (*Oncorhynchus mykiss*)	TiO_2	24	0–1 mg L^{-1}	14 days	Alteration in tissue Na^+K^+-ATPase, TBARS and total glutathione are observed. Pathologies are reported in the gill and other internal organs	N.D.	Federici et al. (2007)
Fresh water fish (*Cyprinus carpio*)	ZnO	< 100	0–16 mg L^{-1}	96 h	100% mortality observed. At 21 days exposure, pathological lessons on damaged gill structure is noted	LC_{50} = 4.89 mg L^{-1}	Subhaskumar and Selvanayagam (2014)

N.D. not determined

the soil gradient. The identical charge on the NP and soil surfaces create repulsive force that favours NP mobility towards deeper level causing ground water contamination.

Hence, accumulation of MO-NP and their consequent toxicity in soil environment is highly associated with the soil chemistry, composition, and its biological community. Again, the toxicological implications of MO-NPs affect the soil habitats significantly, and thus it has been specially considered (Table 2).

Toxicity of MO-NPs on Living Population

Toxicity of MO-NPs is highly species-specific and depends on its environmental chemistry. Among all industrially used MO-NPs, ZnO and CuO are reported to be most toxic in recent studies. Toxicity of the abundantly used MO-NPs is discussed individually with special focus to the microbial community and plant kingdom.

ZnO-NP

ZnO is one of the most studied and most toxic MO-NPs in the present age. According to Jiang et al. (2009), among ZnO, Al_2O_3, TiO_2, and SiO_2-NPs, ZnO is the most toxic causing 100% mortality to *E. coli*, *B. subtilis*, and *P. fluorescens*. Effect of ZnO-NP on soil bacterial community also has been studied by Ge et al. (2014). Another study stated that nano-ZnO affects the bacterial taxa associated with nitrogen fixation (order *Rhizobiales*), methane oxidation (family *Methylobacteriaceae*), and recalcitrant organic compound decomposition (family *Sphingomonadaceae* and *Streptomycetaceae*) (Ge et al. 2012). Arakha et al. (2015) reported the higher inhibition of tested group of bacteria by negatively charged ZnO-NP compared with the positively charged one, which reveals the influence of surface charge on the antimicrobial propensity of the MO-NP.

ZnO induces seed germination inhibition in *Zea mays* plant and collapses the epidermis and cortex cells in the plant root of *Lolium perenne* was reported by Lin and Xing (2007, 2008). In aquatic environment, ZnO-NP delays embryo and larvae development in Zebrafish and decreases their hatching rate and survival significantly (Zhu et al. 2008).

CuO-NP

Toxicity-based categorising of the MO-NPs is a difficult task because of their species-specific reactivity. However, according to literature, CuO-NP can be ranked alongside ZnO-NP. In some instances, CuO-NP was reported to be more toxic to beneficial rhizosphere soil isolate *P. chlororaphis* 06, than ZnO-NP (Dimkpa et al. 2011). Similarly, Baek and An (2011) observed toxicity of CuO-NP to be higher

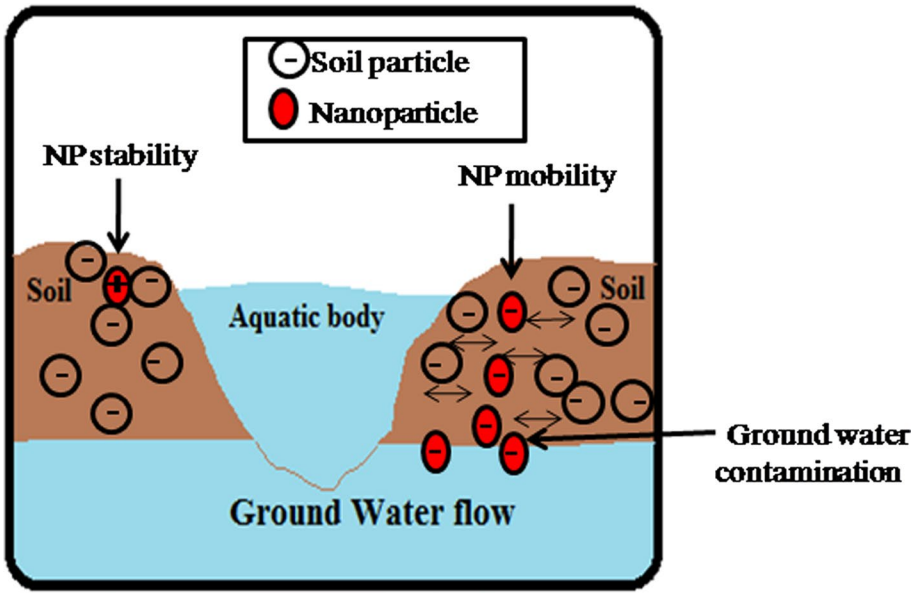

Fig. 3 Schematic presentation of stability and mobility of NP through soil gradient

on *E. coli*, *B. subtilis*, and *S. aureus* compared with NiO, ZnO, and Sb_2O_3-NPs. Kim et al. (2013) studied the soil enzyme activities in CuO-NP treated and untreated soil. A considerable reduction in dehydrogenase, phosphatase and β-glucosidase (62, 80, and ~ 60%, respectively) activity were observed in NP treated soil. However, the toxicity of NPs is highly influenced by plant species and soil characteristics. Frenk et al. (2013) studied the toxicity of CuO-NP on soil bacterial community, which is highly influenced by soil composition. The NP was found to be less toxic in soil samples containing larger clay and organic matter. A similar study has been reported by Ben-Moshe et al. (2013), which states the negative impact of CuO-NP on soil bacterial community. CuO-NP-induced morphological and genetic alterations in leaf litter decomposing fungus have been studied by Pradhan et al. (2011).

TiO_2-NP

TiO_2 is the most abundant, industrially used NP, reported to be less toxic to a living population compared with ZnO and CuO-NPs. In the presence of ultraviolet irradiation, it releases reactive oxygen species (ROS), which scavenges biomolecules, resulting in cell damage. Generation of ROS is restricted or limited in absence of UV light. Adams et al. (2006) studied the higher toxicity of TiO_2-NP on Gram-positive *Bacillus subtilis* compared with the Gram-negative *E. coli.* The growth inhibitory effect of TiO_2-NP under darkness reveals the involvement of alternative mode of toxicity other than ROS generation. The toxic effect of TiO_2-NP on *Zea mays* plants has been reported by Asli and Neumann (2009). The NP accumulation around the root cell wall resulted in hindrance of hydraulic conductivity of the primary root and induction of water stress in shoot of the young seedlings. However, no intracellular accumulation of NP has been observed.

Other MO-NPs

Other MO-NPs, such as Fe_3O_4, CeO_2, Al_2O_3, etc., are much less toxic (Fairbairn et al. 2011; Zhu et al. 2008) compared with those already discussed. He et al. (2011) reported the Fe_3O_4 induced alteration in anthrosol soil bacterial community that consequently influences the soil chemistry and property. Non-toxicity of CeO_2-NP has been studied on the sea urchin (*Lytechinus pictus*) at concentrations up to 10 mg L^{-1} (Fairbairn et al. 2011). Similarly, non-toxicity of alumina-NP (Al_2O_3) against Zebrafish embryo has been reported by Zhu et al. (2008).

Mechanism of Toxicity

Three main mechanisms have been implicated for MO-NP-induced toxicity: *generation of reactive oxygen species (ROS), dissolution property in aqueous phase,* and *exertion of oxidative stress*.

Generation of ROS is the most common mode of MO-NP toxicity (Boxi et al. 2016; Chakraborty et al. 2016), which reacts with biomolecules, and inhibits the biological system's ability to detoxify the reactive intermediates or to repair cellular damage. The MO-NP induced extracellular ROS causes oxidative damage to the cell membrane, resulting in severe cellular impairment while the intracellular ROS breaks DNA strands or alters gene expression (Chang et al. 2012).

Table 2 Effect of MO-NP on soil habitats

Organism tested	NPs	Size (nm)	Concentration range	Duration	End point	References
Soil bacterial community	ZnO	20–30	0.05–0.5 mg g^{-1}	60 days	Exponential reduction in soil DNA pool but no significant effect on soil basal respiration	Ge et al. (2011)
	TiO_2	15–20	0–2 mg g^{-1}	60 days	Linear decrease in soil DNA content but soil basal respiration remains unchanged	Ge et al. (2011)
Rhizobiales	CuO	< 50	0.1–1%	48 h	Significant negative impact on bacterial hydrolytic activity, oxidative potential, community size and composition	Frenk et al. (2013)
	Fe_3O_4	< 50	0.1–1%	48 h	Alters the hydrolytic activity and bacterial community composition	Frenk et al. (2013)
	CuO	15–20	500 mg L^{-1}	160 days	Lower susceptibility	Collins et al. (2012)
Sphingobacteriaceae	CuO	< 50	0.1–1%	48 h	Significant negative impact on bacterial hydrolytic activity, oxidative potential, community size and composition	Frenk et al. (2013)
	Fe_3O_4	< 50	0.1–1%	48 h	Alters the hydrolytic activity and bacterial community composition	Frenk et al. (2013)
Sphingomonadales	CuO	15–20	500 mg L^{-1}	160 days	Complete elimination of the bacteria from deeper horizons of contaminated soil	Collins et al. (2012)
Flavobacteriales	CuO	15–20	500 mg L^{-1}	162 days	Absence of the bacteria in 3rd horizon of the contaminated soil	Collins et al. (2012)
Soybean plant	ZnO	10	0–0.5 g kg^{-1}	48 days	Significant amount of metal is accumulated in leaves and beans affect the food quality	Priester et al. (2012)
	CeO_2	8	0–1 g kg^{-1}	48 days	Inhibits N_2 fixation potential and retards plant growth	Priester et al. (2012)
Cucumis sativus	CuO	50	1000 mg kg^{-1}	15 days	Yellowing of shoots, shortening and damage of root	Kim et al. (2013)
	ZnO	50	1000 mg kg^{-1}	15 days	Reduction in root growth and yellowing of shoot	Kim et al. (2013)
Zea mays	CuO	50	1000 mg kg^{-1}	15 days	Yellowing of shoots, shortening and damage of root	Kim et al. (2013)
	ZnO	50	1000 mg kg^{-1}	15 days	Reduction in root growth and yellowing of shoot	Kim et al. (2013)
Terrestrial isopod (*Porcellio scaber*)	TiO_2	15	0.5–3000 mg g^{-1}	3 days	Decrease in catalase and glutathione-S-transferase activity but weight change and survival were not affected	Jemec et al. (2008)
	TiO_2	25–75	10–1000 µg g^{-1}	14 days	Alteration in feeding parameters	Drobne et al. (2009)
	ZnO	84.9	2000–5000 µg g^{-1}	4 weeks	Accumulation of 16% Zn into the animal body	Pipan-Tkalec et al. (2010)

Table 2 (continued)

Organism tested	NPs	Size (nm)	Concentration range	Duration	End point	References
Nematods (*Caenorhabditis elegans*)	CeO_2	15	1 mg L^{-1}	24 h	Decreased worm fertility but no significant alteration in growth	Roh et al. (2010)
	TiO_2	7	1 mg L^{-1}	24 h	Decreased growth and fertility	Roh et al. (2010)
	ZnO	1.5	325–1625 mg Zn L^{-1}	24 h	Significant reduction in worm mobility, survival and reproduction	Ma et al. (2009)
	ZnO	20	0.8–1.6 mg L^{-1}	96 h	Significant retardation in reproduction	Wang et al. (2009)
Arthropod (*Folsomia candida*)	ZnO	< 200	100–6400 mg Zn kg^{-1}	4 weeks	Retardation in reproduction but survival not affected	Kool et al. (2011)
Earth worm (*Eisenia fetida*)	Al_2O_3	11	100–10,000 mg kg^{-1}	28 days	Significant decrease in reproduction and cocoon production but no effect on survival	Coleman et al. (2010)
	ZnO	10–20	0.1–5 g kg^{-1}	7 days	Significant inhibition in cellulose activity, DNA damage, abnormalities and damage in mitochondria, decreased antioxidant enzymes activity	Hu et al. (2010)
	TiO_2	10–20	0.1–5 g kg^{-1}	7 days	Significant inhibition in cellulose activity, DNA damage, abnormalities and damage in mitochondria, decreased antioxidant enzymes activity	Hu et al. (2010)
	ZnO	40–100	0.1–10,000 mg L^{-1}	4 weeks	Complete inhibition in cocoon production	Canas et al. (2011)
	TiO_2	32	0.1–10,000 mg L^{-1}		Decreased cocoon production	Canas et al. (2011)
	TiO_2	5, 10, 21	200–10,000 mg kg^{-1}	28 days	No negative effect on survival, growth and reproduction of the worm	McShane et al. (2012)
Earth worm (*Eisenia andrei*)	TiO_2	5, 10, 21	200–10,000 mg kg^{-1}	28 days	No negative effect on survival, growth and reproduction of the worm	McShane et al. (2012)
Earth worm (*Eisenia veneta*)	ZnO	< 100	750 mg kg^{-1}	21 days	Accumulation of Zn in worm tissue and gut, significant reduction in cocoon production but survival rate is not affected	Hooper et al. (2011)
Earth worm (*Lumbricus terrestris*)	TiO_2	50	0–100 mg kg^{-1}	2–8 weeks	Induced apoptosis and adverse damage in cuticle and gut tissue	Lapied et al. (2011)

Dissolution property of MO-NPs play significant role in their individual toxicity, which has already been discussed in section "MO-NPs in aquatic eco-system". Released metal ions in aqueous medium enter the cell by ion/voltage-gated channels (Colvin et al. 2003) and exert toxicity in different ways, such as: (1) inducing intracellular ROS generation by various chemical reactions, (2) chelating with essential biomolecules, (3) dislodging metal ions in specific metallo-proteins resulting in functional protein inactivation, and (4) increasing metal ion concentration, thus disrupting the cellular metal cation homeostasis (Chang et al. 2012).

Exertion of oxidative stress is another common mechanism of toxicity, especially for the MO-NPs insoluble in aqueous phase (Gurr et al. 2005; Xiong et al. 2011). In the absence of light, when ROS generation is arrested, NP-induced intracellular oxidative stress modifies cellular

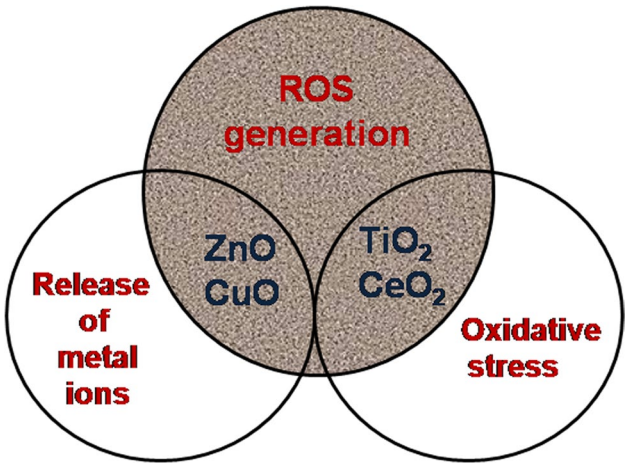

Fig. 4 Mechanistic outline of MO-NP toxicity

proteins, lipids, and nucleic acids, stimulating the antioxidant defence system and leading to cell death (Adams et al. 2006; Handy et al. 2008). The mechanistic details of MO-NP toxicity have been schematically presented in Fig. 4.

Conclusions

The attractive physico-chemical properties of the MO-NPs are extensively exploited in multipurpose industries and released to the environment as industrial effluents and consumed nano-products. Discovery and use of some MO-NPs induced massive eco-toxicological and bio-cellular damages have alarmed the scientific community to consciousness. Although some studies have been performed on MO-NP toxicity in recent times, a broad research focusing on eco-toxicological threats remains untouched to date. Much extensive research and critical analysis is needed at a molecular level for better understanding the mechanistic details and species-specific toxicity of MO-NPs. An interdisciplinary approach for developing standard techniques and methodologies for NP toxicity assessment has become mandatory and have to be followed strictly before the utilization of any NP at an industrial scale. The random consumption of these NPs in different industries has to be restricted to protect the environment for our own well-being and future generations.

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Compliance with Ethical Standards

Conflict of interest All authors declare that they have no conflict of interest.

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