

Accumulation of Engineered Nanomaterials in Soil, Water, and Air



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1 Introduction

In the early 2000s, the beginning of “Nano-era” has led to the initiation of various research programs in nanotechnology field which increased the engineered nanomaterials (ENMs) production steadily (Roco 2003). ENMs possessed unique characteristics such as high reactivity and surface area-to-volume ratio when compared with bulk materials, where it allows utilization of various technologies. The production and incorporation of ENMs have been elevated subsequently with increase of consumers that lead to the release of ENMs to the environment. The commercially available ENMs are zinc oxide (ZnO), titanium dioxide (nano-TiO₂), carbon nanotubes (CNTs), silver (nano-Ag), gold (nano-Au), graphite, C60 fullerenes, and silica (nano-SiO₂) and the products included are inkjet printer ink, plastics, cosmetics, sunscreens, sporting goods cleaning materials, and textiles (Shah et al. 2010).

ENMs are considered to be one of the newly formed non-biodegradable pollutants. The usage of ENMs intensively has led to the raise of concerns related to the possible build up in ecosystems and food supply. In addition, the concerns related to agriculture are greater, where the soils are exposed to products that contain ENMs intentionally. The nanomaterials form and state determines its fate, which influences its properties, such as particle density, aggregation behavior, and solubility. Due to

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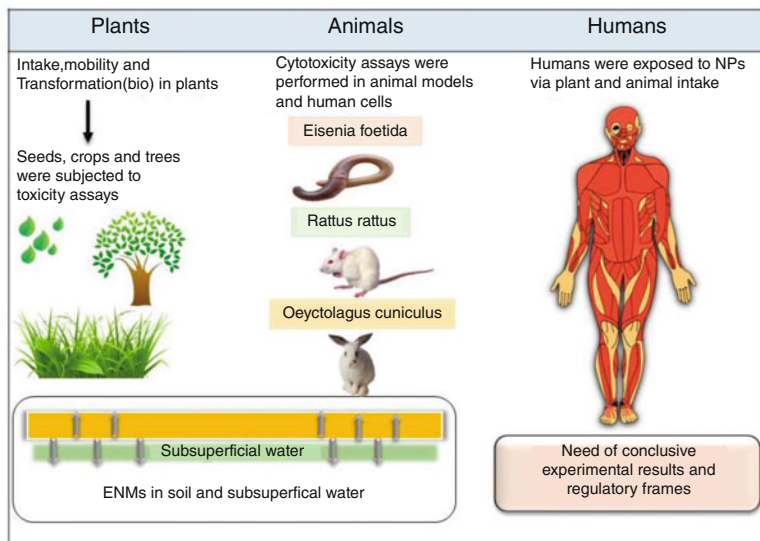


Fig. 1 Exposure of ENMs during the lifecycle

the special characteristics, the ENM usage has increased rapidly in industrial and agricultural products, as well as in environmental systems. Also, the rapid usage and expansion lead to the release of ENMs in environment particularly in the aquatic ecosystems, where it is ultimate sink. ENMs present in the environment may interact with human through direct or indirect way. Thus, there is a vital need to understand the fate, transformation, mobility, and behavior of ENMs in air, water, and soil. Figure 1 shows the exposure to ENMs during their lifecycle.

1.1 Fate of ENMs in Soil

Soil acts as major sink for ENMs. Several factors determine the transportation and fate of ENMs entering into the soil, such as the composition, pH, morphology, and the cation exchange capacity, size, chemical composition, zeta potential, and surface coating of ENMs. It is essential to understand the ENM dynamics in soil. Figure 2 shows that the factors influencing the fate, transportation, and retention of ENMs in soil.

1.2 Soil Type

In last few decades, irreversible changes occurred in the soil due to its contact with chemical contaminants originated because of anthropogenic actions. These irreversible changes are long termed, stable, and the physical and chemical properties of soil

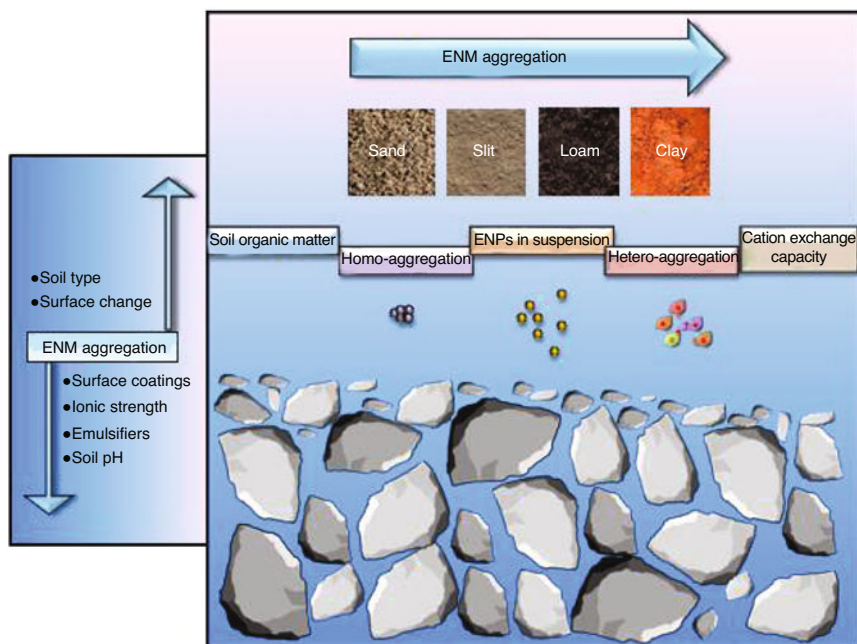


Fig. 2 Factors influencing the fate, transportation, and retention of ENMs in soil

transforms persistently, where it is resistant to remediation procedures and natural attenuation.

The characteristics of the soil are important for determining the fate of ENMs such as the silt, clay, porosity, loam, organic matter, and grain size. ENM's retention and transport have been influenced greatly by soil. ENMs get coated with organic matter such as humic acids or fulvic acids present in the soil environment, and it leads to the increase in particle size. Due to soil-derived coating, the particle undergoes a change in its zeta potential from positive charge to negative charge. Some of the clay particles or natural organic matter in the native form dissolves in ionic state resulting in heteroaggregation. Hence, the available surface area for the chemical interaction is reduced.

It is estimated by Keller et al. (2014) that the total ENM's waste ending up in landfill is 63–91%, in which 8–28% are deposited in soil. It is clear that the exposure of ENM to soil is more vulnerable (Keller et al. 2014). From the previous studies, it is well-understood that the behavior of ENMs differs based on the physical and chemical properties (Keller et al. 2014). The ENM transforms into different forms in plants and soil. Servin et al. (2013) reported the interaction of ENM with components of soil and other co-contaminants. The multiple factors associated may be the reason for the contradictory findings in the literature such as the species used, region, and the measurement of endpoints. The ENM toxicity or direct uptake is not only the factor impacting the growth of plant. In general, plants form complex symbiotic

relationship with microbes present in the Rhizophore (nitrogen fixing bacteria). The plant gets affected indirectly due to the ENM impact on these species (Gardea-Torresdey et al. 2014). The microbial population disturbances could lead to nitrogen starvation resulting in stunted growth.

1.3 Accumulation of NPs in Soil and Plant Tissues

Agriculture makes more profit by developing very effective and less contaminant agrochemicals by nanoformulation. Also, the nanosensors help in detecting biotic or abiotic stress before it affects the output (Giraldo et al. 2019). Nanotechnology has facilitated the development of intelligent nanotools and high tech agriculture fields (Kumar and Arora 2020; Giraldo et al. 2019). The development of these technologies can transform the changes in the agriculture fields, which can create a significant impact on the modern agriculture (Arora 2018; Kwak et al. 2017). Currently, the research in the agriculture fields focuses on developing nanoagrochemicals including nanofertilizer and nanopesticide (Kah 2015). These materials offer the release of agrochemicals in a controlled manner and the selective delivery of macromolecules. The fertilizers and pesticides can integrate efficiently with the carriers which are in nanoscale and the applied compounds can lead to reduction in its amount without the impairment in application (Parisi et al. 2015). The nanoagrochemical application seems to be important for the promotion of modern agriculture. In the food chain, plants are the important factor as it is the producer in the primary trophic level in the ecosystem. The bioaccumulation and the NP impact on long term to the plants can affect the food chain with unknown consequences to humans (Rajput et al. 2018b). The studies were reported that NP's uptake can lead to its accumulation in edible tissue of crop plants (Da Costa and Sharma 2016). The accumulation of original metal ions or NPs can cause changes in the physiochemical properties of the plant (Cota-Ruiz et al. 2018; Patel et al. 2018). The NP accumulation can alter the physiological process of plants, and it can affect the cell integrity, nucleic acids, lipids, and sub-cellular organelle organizations and modify the proteins content (Rajput et al. 2018a, 2018b, c). The wide range of applications of NPs can increase the issues concerned with the health, ecology, and safety point of view (Garner et al. 2017). Till now, the negative impact of these NPs on human health is uncorroborated and speculative (Baranowska-Wojcik et al. 2020). The massive disposal of NPs in several hundred tons every year that made the experts and researchers worried. These released NPs can be detected according to the normative documents recommended recently in soil, air, objects, fungi, algae, and water objects (Gupta and Xie 2018; Keller et al. 2017). The NPs reached into the soil system undergo a transformation in its biogeochemical cycles (Chen et al. 2018; Servin et al. 2017).

1.3.1 Soil as Sink for NPs

The pathway followed by the NP's entry in the soil can be characterized through its entry, content of accumulation and migration. The entry of NPs in the soil via the precipitation in the atmosphere, sedimentation in dust and aerosol form, leaves abscission and direct absorption of gases (Gladkova and Terekhova 2013). In general, NPs released from the anthropogenic sources can be categorized into point and non-point sources. The NPs disperse freely into the environment by outleting it directly to the environment or NP degradation. The remediation of contaminants using NMs causes the discharge of NPs significantly into the environment (Attia and Elsheery 2020). The landfills and waste water discharge plants are also responsible for the release of NPs in the form of discharged effluents or concentrated sludge. The other ways of exposure in the environment are leakages or spill out during the transport and production steps of NPs (Gottschalk et al. 2013).

Nanopesticides, nanofertilizers, hydroponic solutions, and seed treatment are the wide applications which concern the soil and agro-environment expecting to open a new way for the NP's release into the cultivated soils. According to this, the speculation says that 95% of the copper used are ended up eventually into the aquatic sediments and soils with the concentrations of 500 $\mu\text{g}/\text{kg}$ (Keller et al. 2017). In case of ZnO, the concentration estimated was 16 $\mu\text{g}/\text{kg}$ (Feng et al. 2016), whereas the concentration of CeO₂ NPs varied from 0.01 to 4.3 mg/kg (Boxall et al. 2007). The information provided above only tells us about the necessary to study the route which can alter the NP property and facilitate the release into the nature. During its release into the agro-environment, NPs undergo immediate transformations facilitating its accumulation in the soil. The transformation speed differs depending on the state of its aggregation. The soil constituents and its properties such as water content, pH, or organic matter can mediate the dissolution process of the NPs (Benoit et al. 2013). The bioavailability of NPs is depended mainly on its transformations into the soil. The NPs in its dissolved form show higher risk and bioavailability in the environment. The environmental risk can be associated and depends on the chemical species and bioavailability of NPs in the soil (Lead et al. 2018). Hence, it is a critical issue to evaluate the bioavailability of NPs rapidly and accurately in the soil.

1.3.2 Influence of ENMs in Germination, Growth, and Yield of Plant

The accumulation of NPs in the edible plant tissue can affect the health of the human through the food chain considered to be one of the important critical issues. The interaction of NPs with the plant roots can cause translocation in the aerial parts and also cause accumulation in subcellular or cellular organelles. The first step of bioaccumulation is the adsorption of NPs by plant roots (Nair and Chung 2015). During this competition between the ions, the adsorbed CuO NPs cannot be desorbed (Rajput et al. 2018a). The evaluation of different NPs by researchers

suggests that the accumulation of NPs in plants occurs by adsorption through roots and is distributed through the plant tissue with some modifications, including the crystal phase dissolution, bioaccumulation, and biotransformation (Peng et al. 2015). The studies were also reported that NPs can be taken up and tend to accumulate in the plant cells (Peng et al. 2015; Da Costa and Sharma 2016). These discussions suggest that the NPs entered via root and shoot tissues.

The presence of ZnO NPs in the shoots and roots has also been confirmed in *M. sativa* (Bandyopadhyay et al. 2015) and *B. juncea* (Rao and Shekhawat 2016). The accumulation of NPs in plant tissue can adversely affect the physiological process in plants and also alter the cellular and subcellular organizations (Fedorenko et al. 2020). It modifies the lipids, nucleic acids, and proteins contents by generation of reactive oxygen species (Halliwell and Gutteridge 1985).

The accumulation rate of NPs in the plants root can influence the NPs property and also the environmental conditions (Chen 2018). Ag uptake through biosolids-amended soil has increased the Ag NPs concentration in *L. sativa* plant roots and shoots (Doolette et al. 2015). In *Z. mays*, the accumulation of CeO₂ NPs is found to be low in roots (Zhao et al. 2012a, b). The NP's bioavailability in the rhizosphere has increased because of the microbial siderophores occurrence and root exudates. Also, it has been known that microorganisms and plants produce ligands for solubilizing minerals from the inadequately available sources. Microbial siderophores are formed from various organisms, where it is low molecular weight organic compounds for chelation of iron under restraining conditions of iron. Recently, the studies have shown that the siderophores provides high affinity toward other NPs such as Cu, Ag, and Zn (Patel et al. 2018). Consequently, the chelation between the siderophores, augmentation, and dissolution of NPs is expected and promoted. Also, the uptakes of nutrients are exudated often from the insoluble sources of plants (Jones and Darrah 1994). The study conducted by Huang et al. (2017) indicates that the exudation of synthetic roots can promote the Cu²⁺ dissolution rate in the soil system (Huang et al. 2017). The organic matter composition in the rhizosphere differs for each plant. Thus, the effects are different in each plant. Judy et al. (2012) conducted experiment on bioavailability of Au NPs in plants and he concluded that the aggregation of Au NPs occurred in *Nicotiana tabacum* and *T. aestivum* and the variation in root exudates affects the plants bioavailability.

The plant tissue and shoots got accumulated by NPs including the newly developed seeds (Rico et al. 2011). The characteristics of plants and NPs play an important role in the translocation of NPs. Au NPs accumulate in the shoots of *O. sativa*, whereas in *Raphanus raphanistrum* and *Cucurbita pepo*, it is not accumulated in shoots (Zhu et al. 2012). In addition, Au NPs with positive charge can be readily taken up by the plant roots. Contrastingly, Au NPs with negative charge are resourcefully translocated into the plant shoots from the roots (Zhu et al. 2012). Among the most commonly studied NPs, TiO₂ and SiO₂ NPs are found in plant tissue of their immaculate speciation (Larue et al. 2011; Servin et al. 2012). The accumulated speciation in plants changes as a result of transformation of NPs such as CuO, La₂O₃, and CeO₂ by disparity. Castillo-Michel et al. (2017) reported the transformation of ZnO NPs during the exposure to plants which are determined by

X-ray absorption spectroscopy (XAS). Zn majorly accumulates in *Z. mays* roots and shoots, where it found in different forms like Zn-phosphate under the hydroponic exposure of ZnO NPs. The translocation of Zn in ionic form has improved the dissolution in rhizosphere. The accumulation of Zn leads to its speciation in the wheat crop (Dimkpa et al. 2012). Although different Zn speciation occurred, there was no ZnO found in shoots when ZnO NPs were exposed to roots. Thus, the transportation and uptake of Zn in the form of Zn^{2+} ions released from ZnO NPs have caused the higher exposure (Lv et al. 2015). The CuO NPs exposure can lead to accumulation of Cu^{2+} ions in *T. aestivum*. It has been reported that CuO in the form of Cu(II) ions formed by reduction of Cu(I) within the plants caused Cu(I)–S complex formation (Dimkpa et al. 2012). Similarly, Cu(II) was reduced to Cu(I) in plants and its observed in the soil cultivated with *Z. mays* and *O. sativa* (Peng et al. 2017). The CuO NPs of 40 nm were transported to shoots and roots in *O. sativa*. The Cu(II) ion was combined mostly with cysteine, phosphate ligands, and citrate, and few are reduced from Cu(I) to Cu_2O .

The CeO_2 and ZnO NPs were translocated from soil in *G. max*. The translocated CeO_2 reveals the form of NPs and Zn biotransformed into Zn–citrus inside the tissue of plant (Hernandez-Viezcas et al. 2013). Table 1 gives the summary of NP's accumulation in crop plants.

1.3.3 Oxidative Stress Responses

1.3.3.1 Enzyme Assays

Several responses are included against environmental stress in the defensive systems of plants at biomolecular level. The oxidative stress enzymes were synthesized, such as peroxidases, catalase (CAT), malondialdehyde (MDA), SOD, and a range of glycoproteins in response to the environmental stress (de la Rosa et al. 2017). MDA is produced when peroxidation of polyunsaturated fatty acids occurs with free radical which is a biomarker of oxidative stress (Placer et al. 1966). In Cilantro plants, CAT increases when exposed to 0–500 $mg\ kg^{-1}$ of $nCeO_2$ in soil and $nCeO_2$ of 62.5 and 125 mg/kg , the accumulation caused increase of ascorbate peroxidase activity. The increase of CAT activity causes elongation in plants which is correlated with cellular activity increase and production of H_2O_2 (Morales et al. 2013). The impact of exposure of nano-Fe (5 ng –50 mg) in *Physcomitrella patens* was investigated for 7 days and no impact was observed on reactive nitrogen species, and reactive oxidative species. The production of MDA and regulation of glutathione were determined through the negative effects (Canivet et al. 2015). The catalytic interaction between plants and NPs is confirmed by the enzyme activity which demonstrates the hermetic effect in plants. The dose response activity is defined in plants by hormesis effect in which the lower doses induce beneficial effect and higher doses cause inhibitory effect (Calabrese and Blain 2009). The membrane leakage, MDA (lipid peroxidation), and H_2O_2 measurements prove to be a successful indicator of oxidative stress assessment in plants.

Table 1 Accumulation of different NPs in the root part of various crops

NPs	Concentration (mg/L × mg/kg)	Crops	Accumulation in root (mg/kg)	References
ZnO	1000	<i>Z. mays</i>	10	Lv et al. (2015)
	100	<i>S. lycopersicum</i>	—	Raliya et al. (2015)
TiO ₂	100	<i>T. aestivum</i>	110	Larue et al. (2012)
	1000	<i>S. lycopersicum</i>	—	Raliya et al. (2015)
Mg (OH) ₂	1000	<i>Z. mays</i>	1000	Shinde et al. (2020)
Ag based	250	<i>Solanum lycopersicum</i>	—	Adisa et al. (2020)
	1000	<i>O. sativa</i>	20	Thuesombat et al. (2014)
	4000	<i>Glycine max</i>	2102	Hernandez-Viezcas et al. (2013)
	418.4	<i>L. sativa</i>	—	Doolette et al. (2015)
Cu based	100	<i>Oryza sativa</i>	9000	Peng et al. (2015)
	500	<i>B. juncea</i>	>500	Nair and Chung (2015)
	20	<i>Lactuca sativa</i>	9941.3	Hong et al. (2015)
	1000	<i>Ipt-cotton</i>	7000	Le Van et al. (2016)
	125	<i>Vigna radiata</i>	—	Dimkpa et al. (2012)
	100	<i>Phaseolus vulgaris</i>	800	Apodaca et al. (2017)
	20	<i>Cajanus cajan</i>	5.82	Shende et al. (2017)
	1000	<i>Cucumis sativus</i>	500	Kim et al. (2013)

1.3.3.2 Omics

The metabolomics (metabolite profiles of a unit), genomics (structure and function of DNA), transcriptomics (mRNA study), and proteomics (structure and study of proteins) are the omics-based approaches in biology which are well-known (Espín-Pérez et al. 2014).

The literature suggests that these analytical methods are good oxidative stress indicators in ENMs–plant exposure studies (Ruotolo et al. 2018). Majumdar et al. (2015) performed proteomic analysis in *P. vulgaris* seeds where the plants cultivated by embedding CeO₂ NPs. There is an up-regulation of stress-related to proteins in plants and seeds which are exposed to 125 and 62 mg/kg. The exposure of CeO₂ NPs showed similar results when applied via foliar route (Salehi et al. 2018). The effects of ENMs in plants were explored using proteomics and genomics. Rice plants exposed to TiO₂ NPs were analyzed using gas chromatography and mass spectroscopy which revealed that the amino acids level and palmitic acids in grains have increased due to its exposure (Zahra et al. 2017). The results observed were similar when *Cucumis sativus* plants exposed with CuO NPs. The metabolomics approaches

based on NMR and GC–MS have reported an alteration in fatty acid metabolites, sugars, and amino acids (Zhao et al. 2012a, b). The results suggest that ENM's exposure affected the fatty acids and amino acids. Few studies have used omics techniques, where the prematuration can be concluded only through the effects of specific ENM in several plant species. The complexities in omics-based approach is the data handling, instrumentation, and sample handling.

2 NPs Toxic Effects on Human Health

The extensive usage and production of NMs have raised many concerns to human's health based on their potential toxicity, life cycle, and fate (Khan et al. 2010). The indispensable research are the soil contaminants and their sources were identified which are in close association with human health (Khan et al. 2010; Rai et al. 2018). The applications of nanotechnology in various sectors are environment, agriculture, energy, and medicine (Rai et al. 2018; Xiong et al. 2017). The nano-toxicity of the food crops should be considered because of its adverse and harmful effects on human health and physiology of crops (Xiong et al. 2017). The interaction of NPs with the human is a critical subject which necessitates its determinations. The stress reactions are activated by ingestion and destruction of foreign matters by the phagocytes. These can lead to weakness as well as inflammation against the other pathogens in the body defense. In addition, the exposure of NPs to fluids and tissues can take up more macromolecules on the surface which will affect the regulation of enzymes and proteins. The NP toxicity is highly complicated to simplify apropos the health risk associated with the exposure of NPs. The human body has developed tolerance against naturally occurring molecules and elements. Figure 3 shows the natural pathways of NP exposure with affected organs and its associated diseases.

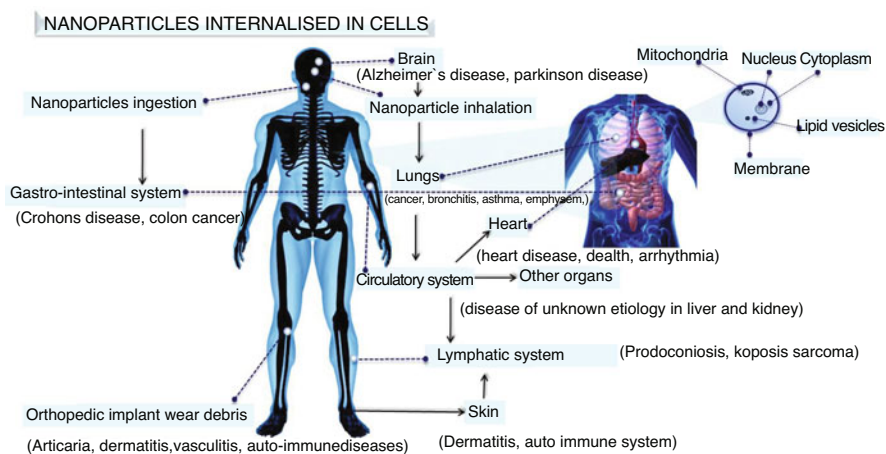


Fig. 3 Natural pathways of exposure of NPs with affected organs and associated diseases

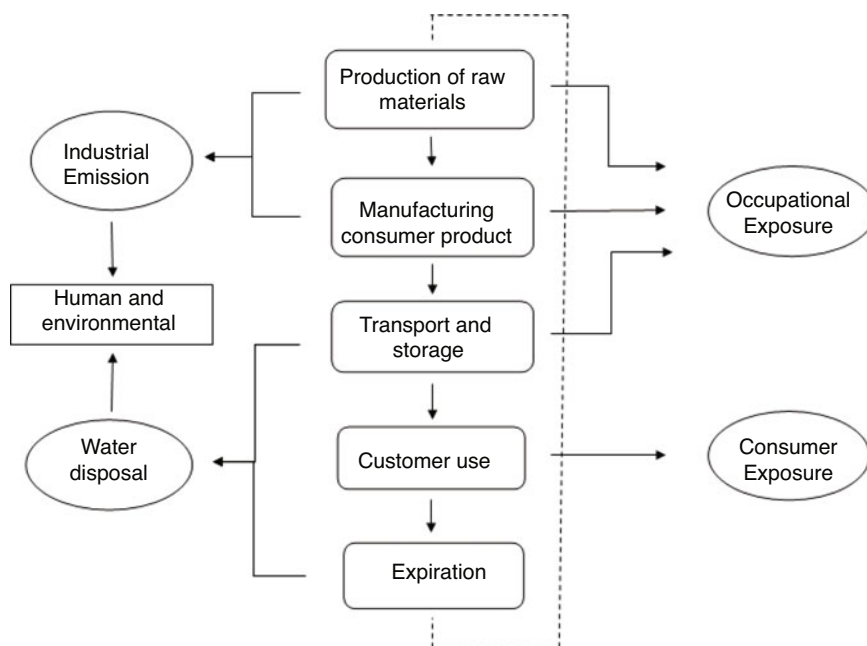


Fig. 4 Flow chart of sources of occupational and consumer exposure

The exposure of NPs to human can be categorized as (1) inhalation from workplaces, (2) dermal route through usage of cosmetics, (3) ingestion which includes food products containing the NPs, and (4) injection such as medical nanotechnology. The NPs can enter into the body through skin, lungs, and digestion systems, where it facilitates free radicals generation that damages the cell. When NPs are in blood stream, NPs become competent for traverse into the blood–brain barrier (Thomas et al. 2013). The toxicological effects of NPs were investigated during the products life cycle which includes usage, disposal, and production. Hence, the hazardous impacts on human health and the food chain can be restricted. The possible pathway of occupational, environmental, and human exposure to ENMs is shown in Fig. 4.

The three most significant causes of toxicity of NPs on living cells are (1) the chemical toxicity occurred from the material and it is made such as the release of Cd^{2+} from CdSe NPs. (2) The small size of NPs can make it stick to the cell membrane and enters into the cell. The attachment of NPs to the membrane and NPs storage can damage function of cells even if the NPs are inert, where it will not react and decompose with the matrix of the components. (3) Depends on the NP's shape.

The NPs entering into the body through various routes possess severe toxicity. The NPs passage into the soil, air, and aquatic systems are reported by Gupta and Xie (2018).

The NPs contact with the environment and human beings can be dangerous. Few research have shown that consumption of TiO₂ NPs of size 20 nm and Fe NPs causes lung damage to rats (Fraser et al. 2011; Gonzalez et al. 2008). Also, fullerene and TiO₂ can cause brain damage in dogs and fish (Shaw and Handy 2011). Ag and TiO₂ NPs have demonstrated genotoxic and cytotoxic effects to mice cells and human cells because of the generation of reactive oxidative species which causes DNA damage and cell proliferations (Mohamed and Hussien 2016; Wan et al. 2012). The toxicological effects of ZnO and CuO NPs through the plant system on human health were demonstrated by Rajput et al. (2018a).

3 Toxic Impacts in Aquatic Systems

The rapid increase in the usage of ENMs in industrial, agriculture, and consumer products elevates the ENM's production globally. The quick increase in the use of the ENMs can lead to its release into the environment, particularly in the aquatic environment. The discharge of ENMs directly from sewages, river influx, and effluents or indirectly from aerial deposition, run-off, and dumping discharges leads to the movement of ENMs into different ecosystems, such as in water, biota, and sediments (Rocha et al. 2015). In the aquatic systems, the behavior and fate of ENMs are dependent on the property, such as size, shape, charge, particle size, chemical composition, shape, and solubility which are the important characteristics for explaining the stability, bioavailability, reactivity, and homogeneity in different media of ENMs (Kahru and Dubourguier 2010). The transport of ENMs in the water can help to interact with the organisms easily. When the size increased by the process of agglomeration, they become less mobile and tend to deposit to the sediments which becomes less available to the aquatic organism in water column, but it is available more for benthic organisms and deposit feeders (Freixa et al. 2018). Due to the particulates settling behavior, the benthic organisms are exposed more likely (Selck et al. 2016). A review reported by Minetto et al. (2016) points out an important asymmetry that is almost 76% of the papers published are related to ENM's behavior in freshwater animal species, whereas 24% are marine species making it to be highly difficult to understand the possible interactions with inhabiting organism of marine environments. Table 2 shows the predicted environmental concentrations (PECs) of highly produced and used nanoparticles in different major pathways in the environment.

Therefore, the toxic effects toward the microorganisms by ENMs depend mainly on the NM behavior and also the physical and chemical characteristics in the aquatic systems. Also, the toxicological effects are depended mainly on the uptake of ENMs by the aquatic organisms. The different behaviors of the NPs were observed by Ward and Kach (2009) when fluorescent polystyrene NPs of 100 nm delivered to *C. virginica* and *Mytilus edulis*, where the long retention time was induced in the aggregates which indicates the NP transfer from gut to digestive gland and the crucial role of suspended matter. The following sections deal with the knowledge

Table 2 Predicted environmental concentrations (PECs) of highly produced and used nanoparticles in different major pathways in the environment

Nanoparticles	Predicted environmental Conc.	Pathway into the environment	References
Ag-NPs	0.088–10,000 ng L ⁻¹	Surface water	Kim et al. (2013)
	0.0164–17 ng L ⁻¹	Waste water treatment effluent	Kim et al. (2013)
	0–0.6 pg/L	Sea water	Garner et al. (2017)
CNTs	3.69–32.6 ng L ⁻¹	Waste water treatment effluent	Kim et al. (2013)
	0.02–0.2 pg L ⁻¹	Seawater	Garner et al. (2017)
	0.003 ng L ⁻¹	Surface water	Kim et al. (2013)
Au NPs	100,000 ng L ⁻¹	Surface water	Kim et al. (2013)
CeO ₂ -NP	0.00–0.001 ng/L	Sea water	Gottschalk et al. (2015)
	10 ⁻¹² , 10 ⁻¹¹ kg/m ³	Surface water	Maurer-Johnes et al. (2013)
	0.03 pg/L		Garner et al. (2017)
Fullerene	0.003 ng/L		Kim et al. (2013)

of ENMs that are hazards, selected based on the published list of ENMs by OECD WPMN (OECD 2010). The ENMs selected are: (1) silver, (2) gold, (3) cerium dioxide, (4) titanium dioxide, (5) carbon nanotubes, and (6) fullerene. Table 3 shows the effects of different NPs on bivalve species.

3.1 Metal-Based Nanomaterials

3.1.1 Ag NPs

3.1.1.1 Characteristics

Ag NPs hold small-to-numerous number of metal atoms which are stabilized by surfactant, polymers or dendrimers and ligands (Beyene et al. 2017). The size of Ag NPs ranges from 1 to 100 nm in diameter (Behra et al. 2013). The spherical Ag NPs are used most commonly and the well-known form of Ag NPs is thin sheets, diamond, and octagonal. The distinct physiochemical properties of Ag NPs are thermal conductivity and high electrical property, catalytic activity, SERS, and chemical stability (Tran and Le 2013).

Table 3 Effects of different NPs on bivalves species

NPs	Concentration	Bivalves time	Species	Tissues	Effects
Ag	10 mg L ⁻¹	7 days	Mussels <i>Mytilus</i>	G, DG	Increased DNA damage
				LPO	Increased SOD, CAT and
	0.7 mg L ⁻¹	3 h	Mussels <i>Mytilus</i>	O, DG	Increased accumulation of Ag
	10 µg L ⁻¹	14 days	Clams <i>Scrobicularia</i>	O	Increased accumulation
	0.2 mg L ⁻¹			H ₂ , O	Decreased phagocytosis in hemolymph
Au	2 mg L ⁻¹	180 h	Clams <i>Corbicula</i>	O	Subsurface transfer of NPs via Bio deposition
	100 µg L ⁻¹	16 days	Clams <i>Scrobicularia</i>	O, DG	Increased DNA strand breaks and genetic damage
	6–30 mg L ⁻¹	28 days	Clams <i>Ruditapes philippinarum</i>	O, DG, G, F	Increase SOD; CAT; GSTs accumulation of Au-NPs increases
	0.1, 1 mg L ⁻¹	14 days	Clams <i>Ruditapes decussatus</i>	O	Increase SOD; CAT; GST; MDA
TiO ₂	0.1, 1 and 10 mg L ⁻¹	96 h	Clams <i>Tegillarca granosa</i>	G	Increase neurotransmitters; decrease AChE
	0, 2.5 and 10 mg L ⁻¹	14 days	Mussels <i>Mytilus coruscus</i>	H	Increase hemocyte count; increased hemocyte mortality
	1, 10 µg L ⁻¹	30 min	Clams <i>Ruditapes philippinarum</i>	H	Phagocytic activity
	1, 10 and 100 µg L ⁻¹	14 days	Mussels <i>Mytilus galloprovincialis</i>	DG, H	Increase CAT; decrease lysosome membrane stability
ZnO	0.1–2 mg/L	12 weeks	<i>Mytilus galloprovincialis</i>	O	Increase respiration rate; increase ZnO accumulation
	1, 5, 10 µg L ⁻¹	4 h	Mussels <i>Mytilus</i>	H ⁺	Increase ROS production Decrease lysosome membrane stability
	3 mg kg ⁻¹	2 weeks	<i>Scrobicularia plana</i>	O	Increase oxidative stress
	4 mg L ⁻¹	48 h	Oysters <i>Crassostrea gigas</i>	G, DG	Increase ZnO accumulation Increase LPO; GPs
CeO ₂	100 µg L ⁻¹	6 days	Clams <i>Corbicula fluminea</i>	O	Increase DNA damage Increase LDH
				O, G	Increase concentration of CeO ₂ NPs resulted
	1 and 10 mg L ⁻¹	96 h	Mussels <i>Mytilus galloprovincialis</i>	O, G	Increase concentration of CeO ₂ NPs resulted
	3–30 mg L ⁻¹	8 days	Mussels <i>Mytilus galloprovincialis</i>	O	Increase concentration of CeO ₂ NPs resulted
	1, 10, 50 mg L ⁻¹	30 min	Mussels <i>Mytilus galloprovincialis</i>	H	Decrease lysosome membrane stability; decrease phagocytic activity

3.1.1.2 Applications

Ag NPs utilize 313 products according to PEN (project on emerging nanotechnologies) which corresponds to 24% of the listed product by Tran and Le (2013). Various applications of Ag NPs are industrial, cosmetics, healthcare-related and household products, antimicrobial agents, and optical sensors, and also as anti-cancer drugs (Balasurya et al. 2020; Janani et al. 2020; Kokilavani et al. 2020; Korani et al. 2015). It is also used frequently in keyboards, biomedical devices, textiles, wound dressings, and water purification systems (Li et al. 2014; Sondi and Salopek-Sondi 2004; Broglie et al. 2015).

3.1.1.3 Toxic Effects of ENMs

Ag NPs change the permeability of cell membrane to K^+ and Na^+ ions which affects the ATP, or mitochondrial activity (Kone et al. 1988). The reported literatures have proven that the toxic effects on cytokine expression by human peripheral blood mononuclear cells and proliferations are induced by Ag NPs (Shin et al. 2007). Severe toxic effects on reproductive systems are shown by Ag NP's exposure (Auffan et al. 2009). The sperm cells were affected adversely, where the materials deposited by crossing the blood–testes barrier. The release of Ag^+ ions and ROS generation is a more relevant factor which strongly indicates the Ag NPs toxicity (Molleman and Hiemstra 2015). The toxicity of Ag NPs increased under UV radiation when compared to dark, where it can accelerate the release of Ag^+ ions and generation of ROS (Zhang et al. 2018). In aquatic environments, the interaction of Ag NPs with invertebrates is through different numbers of biological surfaces such as skin, gut tissues or gills, and cell wall (Zhang et al. 2018).

In bivalves, Ag NPs of 10 mg/L concentration shows damage in hemocyte and accumulation in the mussels *M. galloprovincialis* (Gomes et al. 2013). The same authors have performed another study by exposing Ag NPs to mussel species for the measurement of metal accumulation and as a biomarker for oxidative stress (Gomes et al. 2013). In digestive glands and gills, Ag^+ ions and Ag NPs were accumulated. Ag NPs and Ag^+ ions activate the anti-oxidant enzymes, such as catalase, glutathione peroxidase, and superoxide dismutase. The direct accumulation of Ag has induced metallothionein in gills, but in the digestive glands, it is found that only small Ag fraction is associated with protein. The gills exposed to Ag NPs have caused higher lipid peroxidation, where Ag^+ ions caused lipid peroxidation in digestive glands. Zuykov et al. (2011) provided new information that Ag NPs circulate internally in bivalves. Ag NPs penetrate the hemolymph demonstrated by the authors specifically by radiolabeled Ag NPs of size more than 40 nm and 0.7 mg/L, where the accumulation in the soft tissues is 60% in mussels *M. edulis* with higher concentration in the digestive organs and 7% of accumulation was found in extrapallial fluids. In *M. edulis*, the shell nacre micromorphology of juveniles and adults was examined by Zuykov et al. (2011). However, Ag exposed after depuration to the nacreous layer of adults and young, where there is no evidence found for

alteration processes and carbonate particles in grain forms on the nacre tablets. The toxic effect was not always found in bivalves exposed to Ag NPs. In deposit-feeder clam case, Ag NPs in different forms such as aqueous ions, micrometer-sized, and nanoparticles at a concentration of 150–200 microgram per gram were tested. In the tested concentrations, there were no effects on burrowing behavior, mortality, and condition index in all the experiments performed (Dai et al. 2013). The effect and uptake of Ag NPs (40 nm size of 10 µg/L) on clam species *Scrobicularia plana* were examined by Buffet et al. (2013) which were exposed directly to water contaminants or through diet to microalgae. To assess the effect on behavioral changes and reproductive system in animals, the effect on anti-oxidants activity such as glutathione peroxidase, superoxide dismutase, glutathione-S-transferase, and catalase, and effects on intracellular levels of ROS were examined when Ag NPs of 0–500 µg/L were exposed to animals. Furthermore, the activity of sodium–potassium triphosphate was explored. Moreover, the ATPase activity was inhibited to 82.6% at concentration of 500 µg/L. The toxicity on oysters embryonic development was characterized by Ringwood et al. (2009) and relative sensitivity was compared for embryos and adults of oysters *C. virginica* on exposure of 16–0.0016 µg/L. The adverse effects on development of embryo were observed at Ag NPs' concentration of 0.16 µg/L and also the lysosome of adults was destabilized. In both adult and embryo oysters, there is a significant increase on the metallothionein mRNA levels and particularly in embryo, the metallothionein levels were elevated. However, authors cannot identify whether the cause for gene expression and toxicity is Ag⁺ ions dissociated from the NPs or Ag NPs (Ringwood et al. 2009). The citrate-capped Ag NPs of 20–30 nm have increased the level of proteins in the same species and further it causes greater oxidative damage to hepatopancreas (McCarthy et al. 2013). The result reveals the Ag NP's uptake and transport to the hepatopancreas in situ. Ag NPs of 26 nm from 1 to 400 mg/L concentration were exposed in which the phagocytosis was significantly decreased in the *C. virginica* when comparing it with the control and it differed very little in Ag NPs and Ag⁺ ions (Chalew et al. 2012).

3.1.2 Au NPs

3.1.2.1 Characteristics

Au NPs are studied extensively as it is the key materials in nanotechnology and nanoscience (Zhou et al. 2009). The range of its applications is extended widely because of its versatile surface chemistry and spherical morphology allowing them to be coated with polymers, biological recognition molecules, and smaller molecules (Li et al. 2013). Au NPs of spherical shaped possess optical property which differs in its aggregated states due to electron oscillation at its surface and the properties are fine-tuned by controlling its size, sharpness, chemistry, and composition (Chen et al. 2018). Au NPs serve to be an excellent scaffold for immobilizing specific functional groups in large quantities which lead to high sensitivity and rapid responses for

targeting the analyte because of its high surface area-to-volume ratio (Yeh et al. 2012). They also exhibit good compatibility with almost biologically and chemically active molecules (Chen 2018).

3.1.2.2 Applications

Au NPs are of great interest in various fields due to its unique properties. Their wide range of applications are drug delivery, therapeutic agents, sensory probes, electronic conductors, organic photovoltaics, and catalysis. Also, it is used widely as anti-fungal, anti-microbial, and anti-biotic agents and it is used in coatings, plastics, textile, nanofibers, therapeutic drug delivery, sensor devices, electronic chips, and catalytic applications (Yeh et al. 2012).

3.1.2.3 Toxic Effects of ENMs

Au NPs attribute to the interaction of cell membrane that causes oxidative stress leading to cytotoxicity, and metabolomic activity inhibition which leads to mitochondrial and nuclear condensed DNA damage (Goodman et al. 2004). The toxicity of Au NPs is associated with ROS generation which is connected to the catalytic property of Au NPs. The Au NP's ecotoxicity in bivalves shows that NP's uptake and accumulation cause unexpected biological responses (Canesi et al. 2014). The exposure of Au-citrate NPs of 5.3 nm to *M. edulis* causes oxidative stress condition and the accumulation of Au NPs was found to be much higher in both gills and digestive glands. It shows that Au could specifically cause induction of higher ubiquitination in both gills and digestive glands (Tedesco et al. 2010). Also, Au NPs of 95% were accumulated in digestive glands which cause lipid peroxidation and decrease in thiol containing proteins and the exposure causes decrease in LMS in the hemocytes (Tedesco et al. 2010). In *M. galloprovincialis*, the four metal NPs were selected by the different physiochemical characteristics for screening its cytotoxicity in hemocytes and gills with different Au NP's concentrations (0.1, 1, 10, 25, 50, and 100 mg/L). The toxicity was low in mussel hemocytes by bulk Au and Au NPs. The most toxic form of Au was in ionic form which causes decreased hemocyte viability from 25 mg/L. From 50 mg/L, Au NPs of three sizes decreased the hemocyte viability. (5, 15, and 40 nm) (Katsumi et al. 2016). At 50 mg/L, Au³⁺ ion concentration and Au NPs of 6 mg/L and 30 mg/L accumulated in both gills and digestive glands (Garcia-Negrete et al. 2013) of clam species *R. philippinarum*. Au NPs internalization was also studied and investigated thoroughly in the early stages of oyster *C. gigas*.

3.1.3 TiO₂ NPs

3.1.3.1 Characteristics

TiO₂ exists in different polymorphs, such as brookite, anatase, and rutile. The most stable form of it is rutile. The common oxidation states of Ti are +2, +3, +4, and +6. Due to the oxygen deficiency in TiO₂, it is said to be an n-type semiconductor (Wisitsoraat et al. 2009; Asahi et al. 2000). TiO₂ investigated widely as a photocatalyst because of its high photo-activity, thermal stability, low toxicity, low cost, and good chemical stability (Hoffmann et al. 1995). Many undesired compounds are mineralized using TiO₂. Also, TiO₂ absorbs UV radiation for the generation of reactive oxidative species which can damage the DNA substantially (Dunford et al. 1997; Hidaka et al. 1997).

3.1.3.2 Applications

Various applications of TiO₂ NPs include electronics, medicine, cosmetics, environmental remediation, and innovative food products. TiO₂ used in food products, coatings, pharmaceuticals, papers, toothpaste, medicines, paints, cosmetics, inks, and plastics (Kaida et al. 2004; Wang et al. 2007). It is also used as a pigment for whitening the skim milk. TiO₂ used extensively in sunscreen, because it is considered to be a safe physical sunscreen agent, where it reflects and scatters UVB and UVA which causes skin cancer (Trouiller et al. 2009). In addition, in articulating prosthetic implants, TiO₂ is used for a long time (Jacobs et al. 1991). TiO₂ as a semiconductor photocatalyst can be used for the treatment of contaminated water which is by-products of hazardous industry (Wigginton et al. 2007). The photocatalytic effects of TiO₂ NPs are utilized in industries for several applications mainly for anti-fogging and self-cleaning purposes, such as anti-fogging car mirrors, self-cleaning windows, self-cleaning textiles, and self-cleaning tiles (Robichaud et al. 2009). TiO₂ NPs in nanomedicine fields have been investigated and are said as useful tools for nanotherapeutics and advanced medicines. In addition, TiO₂ NPs possess unique physical properties and it is used ideally in anti-microbial applications and many skin care products (Kaegi et al. 2008).

3.1.3.3 Toxic Effects of ENMs

The physiochemical properties that affect the parameters of the particles are shape, surface characteristics, inner structure, and size. The increase in surface area decreases the TiO₂ NP's size and it increases the harmful effects on human health which are of great concern by the researchers (Andersson et al. 2011). TiO₂ NP's activity is influenced by modification of its surface by coating (Tedja et al. 2012). The cytotoxicity was diminished due to the surface-modified TiO₂ NPs by a

polymer-grafting technique in combination with catalytic chain process (Saber et al. 2012).

The effects of TiO₂ NPs on marine bivalves have become issues of major concern (Wang et al. 2014). Doyle et al. (2015) ingested bivalves with TiO₂ NPs and they observed the TiO₂ NPs accumulation and toxicity targets to the gills and digestive glands on *M. galloprovincialis* (Canesi et al. 2012). The NMs reach higher trophic levels from marine bivalves through biomagnification (Wang et al. 2014). Furthermore, the studies have reported that TiO₂ NPs cause oxidative damages in mussels with confirmed increase in catalase activity (Barmo et al. 2013). The toxicity of TiO₂ NPs is not known fully as though there are evident that ROS is generated under UV or visible light exposure (Dalai et al. 2013; Konaka et al. 2001). Sureda et al. (2018) exposed TiO₂ NPs on *M. galloprovincialis* for 24 h in the form of sunscreen. The results showed the increase of metallothionein content. At low sunscreen concentration, the antioxidant and activity of the enzyme glutathione S-transferases were detoxified which showed an increased activity possessing a bell-shaped profile. It was not induced in higher sunscreen concentration. According to the enzyme activity, the malondialdehyde levels are lipid peroxidation marker, where the enzyme level elevates at high concentration of TiO₂ NP. The acetylcholinesterase activity was found to decrease at a higher sunscreen concentration containing TiO₂. D'Agata et al. (2014) exposed TiO₂ NPs (10 mg/L) for 7 days on *M. galloprovincialis*. The mussel tissue was analyzed by ICPES analysis and the results shows that Ti accumulation is tenfold higher in the digestive gland when comparing it with the gills. The accumulation of nano-sized TiO₂ is much greater than bulk mostly in digestive gland that is higher by sixfold. The histology, metallothionein gene expression, and the histochemical analysis reveal that more toxicity caused due to the bulk material. The DNA damage increased significantly in the hemocytes which was determined by the comet assay. Also, the mussels exposed with different TiO₂ NP concentrations of 1, 10, and 100 µg/L caused severe damages (Barmo et al. 2013).

3.1.4 ZnO NPs

3.1.4.1 Characteristics

ZnO NPs possess hexagonal structure and the structure has alternating planes which are composed of O²⁻ and Zn²⁺ ions coordinated tetrahedrally. ZnO NPs possess high surface area-to-volume ratio, long life span, polar surfaces, and high UV absorption (Nolan et al. 2009).

ZnO heterostructure properties were investigated which are essential for the development of nanoscale devices based on the physical properties which includes the chemical sensing, optical, mechanical, electrical, magnetic, and piezoelectric properties (Applerot et al. 2009; Emamifar and Mohammadzadeh 2015). The effects of ZnO on the anti-microbial and mechanical property were studied by Li and Wu (2003) on polyurethane (PU) films. The low-density polyethylene (LDPE) film's

anti-microbial activity was tested by incorporating the LDPE along with ZnO NPs in orange juice (Emamifar and Mohammadzadeh 2015).

3.1.4.2 Applications

On large scale, ZnO NPs are used in cosmetic, pigments, anti-virus agent in coatings and in sunscreens (Chen and Lia 2003; Hu et al. 2003; Li et al. 2013) and in tires or polymers were used as stabilizers. The surface-coated ZnO are used in MRI (magnetic resonance imaging) (Xue et al. 2010) and specific delivery of desired drug by magnetic NPs (Fujishima and Honda 1972; Frank and Bard 1977). Ceramic nanoparticulates such as ZnO NPs grow rapidly with wide range of applications, such as polishing, polymer additives, and gas sensor (Lin et al. 1998), catalysis, and medical materials (Nolan et al. 2009).

3.1.4.3 Toxic Effects of ENMs

The relationship between oxyradical production and concentration of ZnO NPs has been studied and ZnO interaction with subcellular compartments can induce the production of n-oxidase which are found to be dose dependent (Miller et al. 2015; Manzo et al. 2013). The study on clam *R. philippinarum* and mussels *M. galloprovincialis* showed toxic effects when exposed with ZnO in calm and mussels on hemocytes and gill cells (Katsumiti et al. 2016). The study performed on *S. plana* reveals that the quantity of Zn of 5.4 µg was accumulated with the exposure of 3 mg of Zn (Buffet et al. 2013). The anti-oxidants were activated which indeed reduced the feeding and burrowing activities. The bivalve *S. plana* shows an increase in oxidative stress when 3 mg of ZnO was sedimented (Devin et al. 2017). The ZnO NPs of 4 mg/L were exposed to *C. gasas* for 24 and 48 h, and the accumulation was 49% and 80%, respectively, which indicates that the accumulation is time dependent (Trevisan et al. 2014). Due to the exposure of both Zn ions and ZnO NPs, the morphology of gills become irregular which led to mitochondrial cristae loss and the digestive glands were damaged as revealed by histopathological analysis. ZnO NPs of concentration of 1–10 mg/L were exposed for 96 h and the uptake of Zn was investigated by Montes et al. (2012). The accumulated amount of Zn is 21% in mussels and pseudo-feces with concentration of 63 µg/L, where the threshold for Zn has saturated.

3.2 Carbon-Based Nanomaterials

3.2.1 Fullerenes

3.2.1.1 Characteristics

Fullerenes are also known as geodesic dome in which the C molecules are arranged in the shape of sphere. Based on the C atoms number, fullerenes exists in multiple configurations, that is, C₆₀, C₇₀, and C₈₀. The buckminsterfullerene with a molecular formula of C₆₀, which is more prevalent in scientific interest terms, production, and aquatic organisms are engaged in research (Petersen and Henry 2012; Britto et al. 2015). The buckminsterfullerene composed of 60 carbon atoms which are in polyhedral form in the hexagon and pentagon configurations. The unique properties exhibited by C₆₀ molecule which includes the specific morphology, small size, high electrochemical stability, and well-ordered structure because of the structural characteristics of C₆₀. The specific morphology of fullerene makes it unique when compared with the traditionally used carbon ENMs and such properties include good mechanical properties, special electroconductivity, and good thermal conductivity (Coro et al. 2016).

3.2.1.2 Applications

The various applications of C₆₀ are adsorption electrodes (Noked et al. 2011), printing technologies (Dzwilewski et al. 2009), solar cells (Brabec et al. 1999), biosensors (Gavalas and Chaniotakis 2000) and electronic applications such as in microwave, and mobile telephones (Coro et al. 2016) and many number of products are exploited.

3.2.1.3 Toxic Effects of ENMs

Fullerene C₆₀ caused toxic impacts in the organisms by inducing oxidative stress (Usenko et al. 2008). Fullerene generates ROS particularly superoxide and singlet oxygen in the presence of UV and visible light (Kamat et al. 2000) which induces oxidative stress leading to various detrimental downstream effects, including cell death, protein adduction, DNA repair, and lipid peroxidation (Pickering and Wiesner 2005). The shape, size, surface structure, aggregation, and chemical composition of Fullerene C₆₀ can modify the binding site of protein, cellular uptake, and cause injury to tissues (Nel et al. 2006). The studies demonstrated that fullerene causes toxic effects on bivalve through biochemical and physiological responses. The exposure of fullerene (1, 5, and 10 µg/L) to *Mytilus galloprovincialis* hemocytes in the form of suspension induces the release of lysozyme, production of extracellular nitric oxide and oxyradicals. The other concentrations of fullerene

(0.05–0.2–1–5 mg/L) were investigated by the same authors which demonstrates that the NMs caused destabilization of digestive gland and hemocytes. Fullerene induced the accumulation of lysosomal lipofuscin at higher concentrations of C₆₀ which increases the anti-oxidant enzyme catalase activity and stimulated glutathione S transferases (Canesi et al. 2014). The exposure of fullerene C₆₀ (1.5 and 10 µg/L) was reported to cause cytotoxicity generated through the circulation (Moore et al. 2009). Sanchis et al. (2018) evaluated the metabolic responses when *M. galloprovincialis* exposed to fullerene (10 mg/L). The bioaccumulation was confirmed by these authors when metabolomic of the organism caused a significant difference in free amino acid concentrations when compared with control groups. The glutamine concentrations decreased significantly which suggest that the metabolism of facultative anaerobic energy has been activated. Also, the lipid content has differed significantly which concludes that these results confirm the oxidative stress and hypoxia. The other model species, oyster *Crassostrea virginica* exposed to fullerene, have caused destabilization of lysosomes and embryonal development and the effects of fullerene were dosage depended (1–500 µg/L) (Ringwood et al. 2009). The accumulation of C₆₀ fullerene was also found in hepatopancreas cells and lysosomes which conclude that the targeted pathway of fullerene is lysosomal and endocytotic cells.

3.2.2 Carbon Nanotube (CNTs)

3.2.2.1 Characteristics

Nanotubes belong to fullerene structural family including buckyballs. CNTs are cylindrical shaped, and buckyballs are spherical shaped, and it is single walled with <1 nm of diameter or multi-walled carbon nanotubes (MWCNTs) of diameter more than 100 nm which consists of several nanotubes linked concentrically (McEnaney 1999). The length can reach from millimeters to micrometers. The chemical bonding in CNT with sp² and it allows stronger interaction between the molecules (Baughman et al. 2002).

Various properties of CNTs include that they are highly flexible, high thermal conductivity, high aspect ratio, electrical conductivity, and tensile strength, very high elasticity, which can be considerably bent without damage and low thermal expansion co-efficient (Ajayan and Zhou 2001).

3.2.2.2 Applications

CNT materials are incorporated by the commercial applications. The commercial applications of CNTs at present and future are the most promising one possessing excellent thermal conductivity, conductive properties, energy storage, field emission for molecular electronics, structural applications, air and water filtration, and biomedical applications (De Volder et al. 2013).

3.2.2.3 Toxic effects of ENMs

According to the data available regarding the toxicity of CNT, harmful effects are induced by CNTs, where it can cross the membrane barriers and it can cause inflammatory and fibrotic reactions. The interaction between CNT and cells includes the cellular uptake and the CNTs entered by different routes cause cytokines production, reactive oxidative species, membrane perturbations, and cell apoptosis (Zhao et al. 2012a, b). The CNTs accumulate in various subcellular compartments which include mitochondria (Neves et al. 2010), cell cytosol (Al-Jamal et al. 2011), perinuclear region (Lacerda et al. 2007), endosomes (Antonelli et al. 2010), and nucleus (Shi Kam et al. 2004) in accordance with the functionalization and physiochemical properties. The indirect toxic effects of CNTs which are non-specific include the surface tissue occlusions and physical irritations and it is observed in aquatic organisms (Oberdorster et al. 2006).

At larval stages, the ecotoxicity by CNT was observed in *Xenopus laevis* with physical blockage in the digestive tract and gills and it bioaccumulates in the intestine (Mouchet et al. 2008). Various studies on exposure of CNTs on bivalves have provided the biochemical and physiological responses on bivalves. Also, the toxicity of different CNTs was evaluated by Mwangi et al. (2012), where he noticed the reduction of its growth and survival of mussel *Villosa iris*, but there is no evidence for supporting the CNTs penetration inside the cell membranes.

4 Exposure of ENMs in Atmosphere

ENMs interact with the naturally occurring NPs present in the atmosphere. Airborne viruses and bacteria are nano-organism which interacts by attaching itself to ENMs and making them as disease spreading particles. The atmospheric properties of nanoparticles need to be studied in detail which help us in understanding the residing time in the atmosphere, penetration of the NPs inside the respiratory system, and probability of them being inhaled. ENMs in smaller size behave like vapor, dominate the dispersion, and it diffuses rapidly in the air for longer period.

The Ag, TiO₂, and carbon nanotubes concentrations were estimated by modeling study of exposure of Ag and TiO₂ ENMs in the atmosphere (Mueller and Nowack 2008). Sanchis et al. (2012) studied the effect of fullerene and the results show that the concentration of fullerene bound aerosol was more than the concentration of modeled, which attributes to natural fullerene. The formation of naturally occurring fullerene has been observed in the studies of Heymann et al. (2003).

Several studies have reported the involvement of ENMs that is nano-sized aerosols which cause global radiative forcing in the atmosphere (IPCC 2007). The release of ENMs in the air has also led to the accumulations of ENMs in other environments, such as water and soil. The ecological effects caused by ENMs are an important link for quantitative establishment of ENM release (Aschberger et al.

2011). The applications of ENMs to soil and water exposure is high even if the ENMs are directly deposited on soil or washed out of the atmosphere (Zhang 2003).

The chemical reactions are triggered due to the deposition of NPs in soil which interferes with the ecological process. The plant physiology is affected by the accumulation or deposition of airborne NPs on the surface of plant, where it can penetrate through stomata to enter into the cell (Da Silva et al. 2006). The photosynthesis process is affected due to the reduction in availability of sunlight causing shedding effect. The deposition of nanoparticles which are highly toxic and reactive on crops, where it can enter to the high trophic levels via food chain. Similarly, the paddy yield has been reduced by carbon black, where it particularly makes the wheat crop prone to other pollutants (Wild and Jones 2009).

In the atmosphere, ENM's capping can lead to the addition of various contaminants such as zinc oxide and iron oxide in the atmosphere. Algal growth is promoted due to iron oxide deposition. It is a major problem in sea water which has been reported previously. In the presence of light, the generation of ROS by titanium dioxide affects the microorganisms. Reijnders (2008) observed inflammatory injury and respiratory distress, where it have caused oxidative stress in aquatic organism by TiO_2 . Also, carbon nanotubes have caused oxidative injury and act as respiratory toxicant to organisms in water (Smith et al. 2007).

5 Conclusions

The specific properties of ENMs make it undergo various levels of environmental degradation when released into the atmosphere possessing different toxicologically and physiological properties. The results are of different degree causing different or similar health effects. The ENMs released in the atmosphere have been altered, where it is important for assessing the human exposure by understanding the knowledge related to inhalation of toxicity of specific ENM. The fate and behavior of ENMs released into the atmosphere are important for studying the effects on atmospheric environment. The overall exposure has been influenced by various abiotic, soil, and plants. A significant progress has been made in understanding the fate, effects, and sources of ENMs in the environment. According to the data available on the volume of production of ENMs, TiO_2 NPs are considered worldwide as most relevant materials in terms of production more than 10,000 t/a, followed by CNTs, CeO_2 NPs, and ZnO NPs, from the range of 100–1000 t/a and Ag NPs of more than 55 t/a. In aquatic environment, these transformations affects the fate, transport, and toxicity of NPs. The fate of ENMs in environment must be understood for assessing the ecosystem exposure and toxicity in biota. Nanotoxicity in water, soil, and air resources is little difficult for locating due to its nanosize compared with bigger pollutant particulates. The concentration of ENMs at nanomolar level is proven to be toxic for the organisms in aquatic environment. The major findings in the literature are based on the predicted number of realistic exposure scenarios which cause potential hazard to agricultural ecosystems. The

toxicity, fate, and transport were affected due to the dynamic transformation in the aquatic environments. Only limited studies are made to understand the fate of ENMs in the environment, even though there is same degree of adverse effects are observed in most of the toxicity studies and large number of the behavior is still unexplored.

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