CHEMISTRY OF ECOLOGICAL TOXICITY ASSOCIATED WITH NANOPARTICLES

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Abstract:

The present review encapsulates the burgeoning literature on the ecological toxicity from nanoparticles as well nanomaterials, followed by an elucidation of the underlying physico-chemistry that dictates particle behaviour within an eco-toxicological framework. Methods for quantifying nanoparticles in diverse biological and chemical matrices are also delineated. The burgeoning eco-toxicological literature indicates toxic effects on fish and invertebrates, often at low milligram per litter concentrations of nanoparticles. Currently, there is a notable deficiency of data about microbes, plants, and terrestrial species. Preliminary results indicate that some produced nanoparticles might react with other pollutants, hence affecting their environmentally harmful effects. The behaviour of particulates is affected by their dimensions, form, charge on the surface, along with their proximity to of other elements in their surroundings. Nanoparticles have a propensity to congregate in hard water as well saltwater, significantly impacted by the particular sort of organic material or other natural colloids found in clean water. The condition of dispersion will affect ecological toxicity; however, other abiotic factors influencing this, including pH, salinity, along with organic matters present, need comprehensive investigation within eco-toxicological investigations. Concentrations of engineered nanoparticles have seldom been quantified in the environment so far. Numerous methodologies exist to characterize nanoparticles for exposure and dosimetry, each presenting distinct benefits and drawbacks for the eco-toxicologist. We end by examining the consequences for the ecological safety evaluation of engineered nanoparticles.

Keywords: Nano-materials, environmental hazards, ecological toxicity, risk evaluation, nanoparticle characterisation

Introduction:

Nanotechnology as well the use of nano-scale substances represents a nascent field within science and technology. The worldwide market is valued at around $10.5 billion in 2006. Nanotechnology is the deliberate and regulated creation or alteration of materials at the nano scale (nm). Despite the utilization of nano-scale materials in contemporary research on such materials for over a decade now. Also, there has emerged now an expanded discourse about the hazards and advantages associated with the many engineered nanomaterials and consumer items emerging in the marketplace. The advantages of nanoparticles are potentially substantial and continue to be investigated. A wide array of goods and consumables are developing. Few are like optics, cosmetics, medical devices, catalysts, biosensors, etc. (Penkova et. al., 2017).

Despite the absence of routine measurements of environmental concentrations of manufactured nano particles (NPs), there are apprehensions regarding their potential release from products throughout their lifecycle (e.g., due to material erosion during use or intentional introduction during the remediation of contaminated environmental media), as well as the possibility of how the product applications may produce waste that contained nanomaterials (e.g., domestic wastewater containing nanomaterials from household products). The efficacy of sewage treatment facilities in entirely eliminating nanoparticles from final effluents remains uncertain. There is a clear worry over the potential release of these new elements into the environment, as well as possible emissions from goods now in use. Nevertheless, we are only beginning to investigate their environmental toxicology along with chemistry of the environment (Walker et. al., 2017; Germain et. al., 2020).

Characterizing nanoparticles within Eco toxicity framework

Currently, there are no universally accepted official terms for nanomaterials as well nanoparticles. However, nanomaterials are typically understood to be substances that possess at least one dimension ranging from approximately 1 nm to 100 nm. Examples of such materials include nano films, which are one-dimensional, nanowires and nanotubes, which are two-dimensional, and nanoparticles, which represent three-dimensional structures. Nevertheless, the characterization of materials with a 100 nm dimension is somewhat arbitrary, and in the context of ecotoxicology, it would be prudent to adopt a more expansive definition that encompasses materials measuring a few hundred nano meters as well. The definition does not aim to establish a specific size threshold, as the focus lies on the previously unknown harmful consequences associated with smaller sizes (Contera S, 2019). Nonetheless, a practical approach could involve examining materials with a principal dimension of 0.5 lm to distinguish between nanoscale and micro meter scale. Regardless of the pragmatic decision reached concerning size thresholds for defining NPs, it is essential to allow for some degree of flexibility. One could contend that the behaviour of a singular solid particle measuring 0.5 lm in diameter may not significantly differ from that of a marginally larger particle within the 1–2 lm range. Nonetheless, aggregates possessing an overall dimension within the lm range, yet composed of primary particles measuring \100 nm, would be classified as a nanomaterial. It is evident that for nanoparticles, one must take into account the primary dimension of the particles, such as the diameter of an individual particle. Furthermore, it is essential to take into account the dimensions of nanoparticle aggregates, which may reach several hundred nano meters or greater, as well as the spacing between the sizes of particles present within the material (Turan et. al., 2019; Trump et. al., 2018). In the realm of mammalian toxicology, particulate matter is categorized based on size: coarse particles, which range from 10 micro meters to 2.5 micro meters (PM10–2.5), fine particles measuring 2.5 micro meters or less (PM2.5), and ultrafine particles, defined as those smaller than 0.1 micro meters (PM0.1). Consequently, nanoparticles can be classified as extremely fine particles or even smaller.

Eco toxicologists and Nanomaterials

The surrounding environment encompasses a variety of natural particles at the nano meter scale, including colloids found in freshwater—defined as materials ranging from 1 micro meter to 1 nano meter, as well as volcanic dust present in the atmosphere and nano meter-scale particles resulting from the breakdown of soil (Tangaa et. al., 2016; Roberts et. al., 2018). One might contend that such elements have existed in the ecosystem for hundreds of millions of years, necessitating that organisms customize to coexist with these substances that are natural. Concerns persist regarding the inadvertent generation of nano-scale pollutants due to anthropogenic activities, including airborne particles emitted from vehicle exhausts along with nanoparticles resulting from the breakdown of materials like car tires, a phenomenon that has been occurring for an extended period. Nonetheless, there remains a considerable amount to uncover regarding the destiny and conduct of natural colloids, as well as how they interact with pollutants. It is important to acknowledge that manufactured nanoparticles may constitute a unique category, as they can be engineered to possess specific surface characteristics and chemistries that are less commonly observed in natural particles. Consequently, they may exhibit improved or unique physico-chemical or toxicological characteristics when contrasted with natural nanoparticles (Jamil et. al., 2018).

Manufactured nano particles, along with their natural counterparts, frequently demonstrate unique physical and chemical behaviours and re-activities attributable to their diminutive size and uniform composition, structure, or surface characteristics attributes that are absent at larger scales. For instance, carbon fullerene nanoparticles (C60 particles) may exhibit distinct toxicity profiles when compared to fine (lm sized) graphite particles, despite both being composed of carbon. Notably, nanoparticles exhibit a significantly greater specific surface area compared to their larger counterparts composed of the same material, as well as the ratio of surface atoms to those within the particle is considerably elevated for nanoparticles. Collectively, these elements can lead to an increased surface reactivity (for instance, in terms of adsorption and/or catalytic characteristics) for an equivalent mass of the substance. This leads to the proposition that specific surface area (e.g., square meter per gram of material) may, in certain instances, hold greater significance for the toxicity of nanoparticles than mass concentration (e.g., mg per litter). It may also serve as a more effective descriptor for the dose–effect relationship of nanomaterials, particularly when surface reactivity is a critical attribute. Undoubtedly, the overall surface area accessible will be determined by the specific surface area multiplied by the concentration of particle mass, indicating that both factors are likely to play a significant role in exposure. Furthermore, the significance of morphology and the surface area of particles in the absorption of nanoparticles through the cellular membranes of various organisms has yet to be elucidated within the realm of ecotoxicology. This represents a significant aspect of pulmonary toxicity in living things (Tang et. al., 2020; Malhotra et. al., 2020; Oberdörster et. al., 2007).

At the lower end of the nanoscale (e.g., 1 to10 nm) and at the interface with the atomic scale, one can observe distinct and intriguing physical as well as chemical characteristics. Specifically, materials within the range of a few nano meters to several tenths of a nano meter display characteristics, such as electronic states, magnetic as well optical properties, and catalytic re-activities, that diverge from those observed at the atomic or molecular level, as well as from their larger particle equivalents. For instance, quantum-confined effects have been noted in the electronic states of haematite, resulting in an increased oxidation of manganese, even when normalized to SSA. The dimensions play a crucial role in influencing various physical as well as chemical features, including zeta potential, metal binding. There exists a concern that foundational everyday assumptions regarding the chemical reactivity of molecules and atoms may require re-evaluation when examining the eco-toxicity of nano particles. Such quantum effects may also introduce previously unrecognized toxic consequences (Inoué et. al., 2019).

Furthermore, the diversity of physical structures of nano materials, such as the various crystal configurations of identical substances, along with the possibility of these structures incorporating multiple components, like Ag–Ti composites utilized as antibacterial coatings, or being produced with an array of surface ligands, presents a novel challenge for eco toxicity assessment.

Toxicity of nanoparticles confirmed from mammalians

A recent review has been conducted on the literature concerning mammalian models to presents various instances of the respiratory toxicity associated with nanoparticles and nanomaterials in small mammals. Carbon nanotubes (CNTs) have the potential to inflict considerable harm on the lungs of mammals when administered through intra-tracheal doses. In one study, mice subjected to a dosage of 0.5 mg CNT exhibited a mortality rate of 56% within a week of exposure. Additionally, the formation of macrophage granulomas was observed underneath the bronchial epithelium, accompanied by necrosis along with inflammation affecting both interstitial as well peri-bronchial tissues over a 90-day follow-up period post-exposure. Metal oxides can induce pulmonary damage when inhaled. Rats subjected to cadmium oxide nanoparticles for a duration of 6 hours exhibited a heightened presence of neutrophils and multifocal alveolar inflammation. In half of the rats subjected to 550 lm m^{-3}, a heightened blood cadmium concentration was recorded, indicating the translocation of particles within bodily systems (Felix et. al., 2016; Smith et. al., 2007).

The reports present several issues that warrant attention from an Eco toxicological standpoint. Initially, the lung serves as a quintessential example of standard mucous epithelial tissue, and it is plausible that analogous epithelia in aquatic organisms may exhibit comparable toxic effects. The epithelia of interest encompass the gills and gastrointestinal tissue of invertebrate and fish species, in addition to specialized epithelial structures such as the mantle of shellfish and the external surface of organisms like earthworms. Recent investigations have demonstrated epithelial damage to both the gill and the intestine in fish subjected to nanoparticle exposure (Correia et. al., 2019). Furthermore, the underlying consequences of acute respiratory exposure and the inflammatory responses observed in rat lung tissue provoke significant apprehension regarding the prolonged health implications for organisms following even brief encounters. Nonetheless, one might contend that the milligram doses typically employed in rodent studies are unlikely to be encountered regularly in the environment, save for instances of accidental spills involving nanomaterials. Ultimately, research involving mammals and nanoparticles like quartz, carbon black, and asbestos underscores the significance of not just particle size, but also bio-solubility with shape as critical determinants that affect uptake, toxicity, and pathology, particularly in instances of exposure through the airways and lungs (Asbach et. al., 2017).

Nano-particles Lethality over wildlife

The available literature on lethal dosage values pertaining to the Eco toxicity of nano particles is limited, despite a notable increase in the frequency of additional research being presented. Research involving fish and invertebrates indicates that C60 fullerenes exhibit toxicity within the milligram per litre range. However, the LC50 values derived are significantly influenced by the preparation methods of the material and the incorporation of dispersants. It is conceivable that dispersed C60 nano particles exhibit greater toxicity compared to their non-dispersed counterparts, or that the solvents employed may exert influence, potentially altering the toxicity profile of the dispersed nano particles themselves. These studies underscore an increasing recognition of the complexities involved in the preparation of nano particles, such as the considerations of sonication versus solvent dispersion. They also examine the methodologies employed in Eco toxicological research and the implications for environmental relevance, particularly regarding the fidelity of solvent dispersed nano particle solutions in representing their natural occurrence in the environment (Gökçe et. al., 2018; Choi et. al., 2016).

The prevailing absence of LC50 values for fish could also be attributed to technical considerations. Achieving the elevated concentrations of mg per litter required for acute lethal toxicity presents significant challenges. At concentrations exceeding 10 mg per litter, there is a notable aggregation of various types of nano particles, and despite extended sonication and the incorporation of dispersants, attaining reproducible solutions continues to pose a challenge. It is noteworthy that there exists a limited number of lethal toxicity values pertaining to in vitro assays that utilize non-mammalian cells. Consequently, it is essential to conduct research on acute toxicity concerning fish as well invertebrate cell lines.

Impact of Sub-lethal exposure on fish species

A number of authors have subjected teleost fish to nano materials. The research encompasses the impacts of C60 fullerenes on various species, including largemouth bass (Micropterus salmoides), fathead minnow (Pimephales promelas), and Japanese medaka (Oryzias latipes). Research has also been conducted on the impacts of carbon nano tubes and TiO_2 nano particles on rainbow trout (Oncorhynchus mykiss). The studies have elucidated potential target organs for nano particles (Cimbaluk et. al., 2018; Özgür et. al., 2018). Kashiwada examined the dispersion of fluorescently labelled nanoparticles within a transparent colour morph of medaka (O. latipes). This experiment employed fluorescence measurements in the organs of the transparent fish to deduce the positioning of the nanoparticles. The fish were subjected to mono-dispersed, non-ionised, fluorescent polystyrene microspheres measuring 39.4 nm in diameter, maintained at an aqueous concentration of 10 mg l-1 over a duration of 7 days (Kashiwada S, 2006).

The gills exhibited the most significant enhancement in fluorescence, closely trailed by the intestine. This indicates that nanoparticles can, at the very least, adhere to the surface of gills and may potentially penetrate the epithelial cells. The behaviour of polystyrene microspheres in comparison to other nanoparticles remains ambiguous. Nevertheless, analogous findings have been documented in experiments involving trout, wherein CNTs accumulated on the gill mucus during aquatic exposure. Nonetheless, in the medaka study, the observed increases in fluorescence within the internal structures were comparatively modest, and aside from the gall bladder, not any statistically important rises in fluorescence were noted in other tissues such as the brain, liver, kidney, or testis. It is important to note that this does not imply that the fluorescent nanoparticles were not absorbed into the bloodstream and distributed to the internal organs; rather, it may suggest that a longer exposure time was necessary or that the rate of excretion corresponded with the rate of uptake, resulting in no net accumulation. Nevertheless, one must exercise prudence when analysing the outcomes of any experiment involving labelled nano particles. For instance, definitive proof that the fluorescent label persists on the nanoparticles within the tissues is frequently lacking (Cong et. al., 2017; Smith et. al., 2007).

Both the investigation on medaka and the research on rainbow trout revealed the existence of nanoparticles in the gastrointestinal tract, notwithstanding the fact that the method of delivery was through aqueous exposure. Freshwater fish consume a small quantity of water, approximately a few millilitres per kilogram of body mass per hour. Damsgaard and his group contend that this behaviour may elucidate the presence of nanoparticles in the gastrointestinal tract. This aspect becomes particularly significant in the context of toxicity, as a drinking response triggered by stress could substantially elevate the volume of water consumed. Marine teleost fish, as a fundamental aspect of their osmo-regulatory strategy, engage in routine drinking, which consequently raises pertinent concerns regarding the exposure of the gut in marine species (Chowdhury et. al., 2016; Damsgaard et. al., 2020).

The identification of additional target organs for nanomaterials in fish is primarily based on observed toxic effects in these organs, rather than on direct evidence of nanoparticle localization within the specific organ or tissue of interest. This is in part due to the fact that the methodologies for extracting and quantifying nanoparticles within tissues have not yet become standard practice. Nevertheless, we must remain open to the notion that adverse effects may manifest at doses that are challenging to identify within specific organs, indicating a significant level of potency. In the case of carbon nano tubes, the liver seems to serve as a significant target organ. Smith and his group elucidated the pathological changes observed in the livers of trout subjected to concentrations of up to 0.5 mg per litter carbon nano tubes over a duration of 10 days. Histological alterations encompassed modifications in nuclear morphology characterized by condensed nuclear bodies resembling apoptotic bodies, alongside cells exhibiting diffuse nuclei indicative of the initial phase of cellular necrosis. Biochemical alterations are likewise noted in the liver. They observed a statistically significant decrease in thiobarbituric acid reactive substances (TBARS) in the livers of trout subjected to carbon nano tubes exposure (Smith et. al., 2007).

Conversely, Oberdo¨rster with his collegues, observed minimal impact on largemouth bass subjected to C60 for a significantly reduced duration. They conducted an investigation into the expression of mono-oxygenase, which are CYP family proteins involved in the metabolism of exogenous compounds, within the hepatic tissue of fathead minnows subjected to a concentration of 0.5 mg per litter C-60 fullerenes over a duration of 96 hours. No discernible effects were observed on hepatic CYP mRNA levels or the corresponding proteins. Nonetheless, they documented a statistically significant decrease in PMP70 protein, an iso-enzyme that plays a role in hepatic lipid metabolism. It is noteworthy that the decrease in PMP70 might vary depending on the species or the duration of exposure, as observations of PMP70 in medaka subjected to the same substance for a shorter duration (48 h) indicated no impact on protein levels (Oberdörster et. al., 2007).

Impact of Sub-lethal exposure on Invertibrate species

Daphnia magna is well recognized as a reference species in ecotoxicology testing, therefore it is unsurprising that initial research has concentrated on this organism. Numerous research has used Daphnia to determine LC50 values. Magro and his group examined chronic effects in D. magna along with other invertebrates. D. magna were subjected to concentrations of up to 5 mg per litter C-60 fullerenes for a duration of 21 days. At the maximum C-60 concentration (5.0 mg per litter), a death rate of 40% was recorded, accompanied by a reduction in progeny and a delay in molting. The research indicated that exposure of the freshwater invertebrate Hyallela azteca to 7 mg per litter C60 fullerenes for 96 hours had no impact on mobility, moulting, or eating behaviour. Recent studies have shown behavioural impacts of nanoparticles in Daphnia magna. Alterations in locomotor behaviour was observed, including hopping frequency as well appendage movement. It was also discovered that D. magna use the organic lyso-phosphatidyl-choline coating on single walled carbon nano tubes, as a nutritional resource (Magro et. al., 2018). Published studies on the Eco toxicity of engineered nanoparticles to soil and various other terrestrial organisms seem to be deficient. There are many acknowledged preliminary investigations including earthworms (Li M. et. al., 2020).

Impact of Sub-lethal exposure on aquatic floral, algal and bacterial species

In a manner akin to the circumstances surrounding aquatic invertebrates, there exists a notable scarcity of published ecological toxicity studies concerning environmentally pertinent bacteria, algae, as well aquatic plants. Iswarya and group conducted a test on growth inhibition of algae (Desmo desmus subspicatus) by exposing them to titanium nanoparticles. Their findings revealed EC50 values that varied from 44 mg l-1 to no observable effects at the maximum concentration tested (50 mg l-1), contingent upon the technique used to prepare the material. It has been observed that the surface architecture or matrix of plant cell walls can serve as a substrate for the growth of nanoparticles (Iswarya et. al., 2019). Shankar with his colleagues observed that stable nano-crystals develop on marine phytoplankton upon exposure to Cd. This suggests that the exposure of marine algae to metal nanoparticles may stem from the existence of suitable conditions for formation of crystals on the organism's surface during interactions with aqueous metal solutions (Shankar et. al., 2016). Plant viruses serve as scaffolds for the construction of nanoparticles. These observations suggest a noteworthy consideration: organisms may not require direct exposure to nanoparticles introduced into the aquatic environment, and there exists the intriguing possibility that viruses could serve as vectors facilitating the dissemination or proliferation of nanoparticles. Plant cells have served as instruments in the advancement of imaging technology for nanomaterials, yielding incidental insights regarding uptake (Zhang et. al., 2018). Venkatesha and group observed that zinc oxide nanoparticles tend to aggregate on the surfaces of plant cells (Venkatesha et. al., 2016).

The body of published research concerning the Eco toxicity of nanomaterials to bacterial species remains sparse, despite the documented bactericidal properties of these materials in the biomedical literature. For instance, it is widely recognized that TiO2 nanoparticles and silver nanoparticles exhibit bactericidal properties and have been employed in the sterilization of medical instruments. It is reasonable to anticipate that certain of these substances could exhibit toxicity towards environmental microbes. The bacterium Shewanella algae has been shown to deposit platinum nanoparticles, which is proposed as a biotechnological application for the recovery of platinum (Sano et. al. 2016). It is conceivable that bacteria could play a beneficial role in the bioremediation of nanomaterials. Berry with colleagues conducted a recent investigation into the impact of C60 nanoparticles on the diversity of bacteria present in soil environments. Through the application of DNA and fatty acid profiling techniques on the soil, the researchers observed minimal effects on the microbial community following a 30-day exposure to 1 mg C60/g of soil. Nonetheless, C60 in suspension exerts influences on bacterial cultures within a laboratory setting (Berry et. al., 2016).

Azizi-Lalabadi and group present findings indicating minimum inhibitory concentrations of C-60 at 0.5–1.0 and 1.5–3.0 mg per litter for the growth of Escherichia coli and Bacillus subtilis, respectively. It is noteworthy that C-60 exhibited a greater tendency to associate with the Gram-negative E. coli, indicating that the surface characteristics of the bacterial cell membrane could play a crucial role in toxicity. Nonetheless, in the case of C-60, it has been observed that smaller aggregates exhibit greater toxicity towards Bacillus subtilis. However, the variation in toxicity relative to particle size can only be partially attributed to surface area effects, with potential interactions involving the cell membrane being suggested (Azizi-Lalabadi et. al., 2020). ZnO nanoparticles seem to interfere with the structural integrity of the Gram-negative cell membrane in E. coli. It has been suggested that nanoparticles possessing a positive charge, such as cerium oxide, may adhere to the Gram-negative cell membrane through electrostatic attraction (Chen and Inbaraj, 2018). The intricate connection between the physico-chemistry of the medium and the membrane-based biology of the microbe is evidently becoming a crucial element in understanding NP toxicity to microorganisms.

Impact of Sub-lethal exposure on other species

The majority of the recent literature concerning wildlife has, by necessity, focused on organisms utilized in aquatic Eco toxicity assessments. Considerable deficiencies exist within the existing body of literature concerning various other organisms. For instance, there seem to be no documented findings regarding terrestrial plants, amphibians, reptiles, or birds; however, Komendova R. propose that the distant transportation of nano particulate metals in the atmosphere may play a role in the biological accumulation of metals from the platinum group in raptors. Moreover, notwithstanding the extensive information available regarding small biomedical mammals, there remains a pressing necessity to investigate pertinent small mammals in their natural habitats, including voles and shrews. It is essential to investigate the potential risks posed to livestock and the broader human food supply (Komendova R, 2020).

The majority of ecotoxicology research conducted thus far has predominantly utilized aqueous exposure methods. Additional avenues of exposure warrant examination, which includes laboratory-based exposure through diet to elucidate concerns regarding toxicity through food, alongside straightforward food web or meso-cosm methodologies to facilitate ecological comprehension of potential effects. Dietary toxicity was observed in trout, where incidental ingestion of test water (stress-induced drinking) resulted in pathological changes in the gut, accompanied by biochemical indicators of oxidative damage in the gut epithelium. The proof of direct nano particle precipitation on the mucous membrane of the gut was also observed. This finding is perhaps unsurprising, considering that particles have a propensity to aggregate even in relatively modest saline conditions, as noted by Merschel and group, which are typical of the gut lumen. For analogous reasons, the physico-chemical behaviour of nanoparticles indicates that they are likely to aggregate and adsorb onto various types of surfaces. This may involve the adherence of substances to the surfaces of aquatic sediments, algal mats, biofilms, soils, and even the outer surfaces of organisms (Merschel et. al., 2017).

Nano particles toxicity and physico-chemical properties

The essential physico-chemical characteristics of colloids and various particles are elucidated. Typically, the Eco toxicological effects of chemicals as well particles are influenced by abiotic factors, including pH, salinity, water hardness, temperature, along with the presence of dispersed organic material in the aquatic environment, among others. Thus far, there exists a limited number of systematic Eco toxicological investigations aimed at understanding the impact of alterations in abiotic factors, including pH, hardness, ionic strength, or the presence of organic ligands in aquatic environments, on Eco toxicity. A multitude of fundamental inquiries persisted, awaiting resolution. For instance, regarding metals, do the established principles concerning the protective influences of heightened water hardness or modified pH on certain organisms also pertain to metals in nano particulate form? One could contend that it is advisable for them to do so, particularly if the functional material present on the surface of the metal particle consists of a metal ion. Conversely, an increase in hardness is anticipated to enhance aggregation as a result of specific sorption with or without compression of the electrical double layer. However, the impact of these effects on toxicity remains uncertain at this time. The Eco toxicological implications of nanoparticles in marine environments, as opposed to freshwater systems, remain ambiguous.

Experimental evidence derived from colloid chemistry under saline conditions indicates that even minor elevations in salinity beyond that of freshwater (e.g., 2.5 parts per thousand) can significantly reduce colloid concentrations through aggregation and precipitation processes. For numerous estuarine organisms, a minor alteration in salinity would typically exert minimal biological impact; however, this chemical analysis forecasts the swift depletion of colloid from the freshwater immediately upon its ingress into the estuarine zone. This suggests that toxicity assessments conducted in freshwater environments may not provide relevant insights into toxicity in marine settings. Furthermore, it indicates that organisms residing in sediments and those that filter particles in estuarine and marine ecosystems are likely to play a significant role as receptors in hazard evaluations. Moreover, the mechanisms underlying toxicity may be inherently distinct, as organisms residing in freshwater and seawater encounter varying physico-chemical forms of the same nanoparticle due to the influence of salinity on aggregation (Wang et. al., 2017).

At least one investigation has incorporated certain experiments pertaining to salinity. Kashiwada subjected medaka eggs to fluorescent nanoparticles (30 mg per litters) across a range of salinities. A rise in toxicity was observed alongside an elevation in salinity, accompanied by a heightened propensity for the particles to aggregate. At a salinity of roughly 18.5 parts per thousand, the maximum fluorescence in the tissue was observed, resulting in the complete mortality of 100% of the eggs within a 24-hour period. As salinities neared those characteristic of typical seawater, there was a reduction in accumulation; however, the rate of egg mortality persisted at elevated levels (Kashiwada S, 2006).

Size and Shape of Nano Particles on its Eco toxicity

A further possibility is the fact that it is not solely the colloid chemistry of the particles that impacts toxic effects, but also their size or shape—an idea that has been demonstrated in the context of mammalian respiratory toxicity. There is a notable scarcity of Eco toxicological data that have rigorously examined the effects of particle size, despite the fact that, as previously mentioned, size influences a range of physico-chemical properties. These studies hold significant value as they elucidate the necessity for further hazard assessments of materials in their nano form relative to their bulk counterparts (Wright et. al., 2020).

Kashiwada S. also demonstrated a particle-size influence on the building up of fluorescent nanoparticles in the Japanese medaka, revealing that smaller particles accumulated at a faster rate. Conversely, research concerning mammalian cells of immunity indicates that there is no discernible difference in the toxicity of ultrafine carbon dust when compared to significantly smaller carbon nanoparticles. Reports indicate variations in the immediate toxic effects of dispersed nanoparticles in comparison to bigger masses of the same substance in invertebrates.

Surface Area of Nano Particles on its Eco toxicity

The primary issues at hand are that nanoparticles are exceedingly diminutive, resulting in a significantly large surface area in relation to their volume, or that the surfaces of engineered nanoparticles may exhibit reactivity. There exists a degree of conjecture regarding the capacity of nanoparticles to produce reactive oxygen species at their surfaces, particularly when in proximity to cellular membranes, potentially triggering inflammatory reactions or immune responses. Research indicates that oxidative stress occurs in the tissues of aquatic organisms when exposed to nanoparticles. In the case of titanium di-oxide nano particles, the catalytic characteristics of the particle surface, may indeed indicate potential toxic effects.

A notable issue regarding metal-based nanoparticles, given their diminutive size and extensive surface area, is the leaching of dissolved metal ions across the particle's surface, potentially leading to the total dissolution of the particle, leaving the metals only in the solution. Despite a solubility of merely a few percent, a 1 mg per litter solution of a metal oxide nanoparticle could yield 1 gm per litter concentrations of metal ions in the solution. This raises concerns regarding the potential of certain nanoparticles to function as delivery mechanisms for free metal ions. It is evident that monitoring free metal ion concentrations during experiments is feasible; however, possessing prior knowledge of the solubility of the nanoparticle would be advantageous. The measurement of solubility can be conducted with a commendable degree of precision through a synergistic approach that involves a size fractionation technique—such as dialysis, ultracentrifugation, ultrafiltration, or field flow fractionation—complemented by comprehensive metal analysis utilizing ICP-MS or GF-AAS, as exemplified by the work of Lyve´n and his group (Lyvén et. al., 2003). Nonetheless, these integrated methodologies are not commonplace and present significant technical challenges when the dimensions fall below 10 nm, as the precision of separation diminishes. Moreover, at low nano molar levels the contamination or loss due to sorption, of the metals, may assume significant importance (Moens et. al., 2019).

Surface Charge of Nano Particles on its Eco toxicity

The concept of surfaces engaging in the exchange or adsorption of pollutants is well-established and has been explored within the framework of colloids. Within the realm of ecotoxicology, the phenomenon of adsorption has been utilized to elucidate the mechanisms of binding of metallic substances on fish gills. This process is governed by various physical factors, including the net charge of the surface, exemplified by the presence of poly-anions on the membranes of cells, the ionic mobility of counter ions in the surrounding medium—partially determined by charge density as well the hydrated ionic radius of the ion—and the competitive interactions with other ions present in the medium, such as H+. These experiments have resulted in the development of potentially predictive equilibrium toxicological models, including the biotic ligand model, as well as bioavailability models grounded in dynamic concepts. Several of these concepts may also be relevant to nano particles.

Certain nanomaterials exhibit a net negative surface charge (for instance, fullerenes and carbon nanotubes) and consequently have the capacity to bind cationic pollutants, including metals. The charge significantly influences both the rate and the extent of aggregation, as anticipated by DLVO theory. Evidence suggests that nanoparticles engage with trace metals, and the role of surface charge may be fundamentally significant in these interactions. Cai and Zhang demonstrated that multi-walled carbon nano tubes exhibit concentrations of lead, cadmium, and copper at mg g-1 levels. While the presence of such concentrations of metals or carbon nano tubes in the environment is improbable, it demonstrates a significant potential for interactions between metals and nanomaterials. Furthermore, iron oxide particles exhibit a robust affinity for trace metals like Cu, with enhanced binding observed at reduced particle sizes (Cai and Zhang, 2016).

Consequently, the existence of nanoparticles may amplify the toxicity or bioaccumulation of additional contaminants. For instance, carp subjected to cadmium (Cd) alongside TiO2 nanoparticles exhibited significantly enhanced Cd accumulation compared to exposure to Cd in isolation. Fish subjected solely to Cd exhibited a Cd concentration of 9.07 µg g-1 dry weight, whereas the Cd + TiO2 treatment resulted in a concentration of 23.3 µg g-1. Certain interactions might not pertain to surface charge; rather, they could be influenced by the lack of charge or the hydrophobic nature of the surface. Mussels (Mytilus edulis) were also exposed to nano-sized particles of sucrose polyester in conjunction with the poly-aromatic hydrocarbon (PAH), anthracene. The presence of nanoparticles resulted in a 160% increase in anthracene uptake and a 122% rise in cellular toxicity. One possible elucidation is that the surface of the NP plays a role in the conveyance of the PAH. It is evident that the interactions between the surfaces of manufactured nanoparticles and existing chemicals merit further exploration, potentially holding significance comparable to the intrinsic toxicity of the nanoparticles themselves.

Nano material percentage in Eco space

A comprehensive review on environmental effect was conducted, regarding exposure to engineered nanoparticles, focusing on implications for human health. They recognized numerous human-induced sources, encompassing air pollution, the utilization of nanomaterials in agriculture products, which subsequently raise concerns regarding the contamination of the food chain. Additionally, applications in water treatment suggest potential exposure risks for aquatic systems. Environmental remediation represents a particular instance in which there will be a purposeful incorporation of substantial quantities of engineered nanomaterials into soils and groundwater (Patil et. al., 2016). Furthermore, there exists a potential for widespread pollution throughout the life cycle of nanomaterials, alongside apprehensions regarding their disposal through landfill and incineration. Nevertheless, while we can rationally anticipate potential origins of NP pollution, it seems that there are no recorded measurements of manufactured nano particles in samples collected from the field. It is evident that there are no standard ecological surveillance programs in place for manufactured nanoparticles. Nevertheless, straightforward models derived from estimated utilization of product along with nano particle concentration within the products may serve as an initial framework for forecasting worst-case scenarios.

Another response to concerns regarding manufactured nanoparticles is that natural nanoparticles have existed in the surroundings for millions of years due to processes of weathering along with natural geochemical cycles. However, as we elucidate in the introduction, it is the unique chemistry of manufactured nanoparticles that raises additional concerns. Natural nano particles are not inherently benign, as evidenced by instances of respiratory toxicity associated with volcanic dusts. One challenge is thus to assess both naturally occurring and synthetic nanoparticles in the environment, as well as to distinguish between their respective toxicities.

The inquiry also emerges regarding the potential for remediation of effluents and wastewaters that contain nanomaterials. The aforementioned physico-chemical analysis indicates that a significant number of nanoparticles are predisposed to aggregation, considering the elevated concentrations and varieties of organic matter and solids present in sewage treatment facilities. Consequently, the current methodologies for sewage treatment may demonstrate efficacy. Alternatively, certain engineered nanoparticles exhibit bactericidal properties, such as nano silver, yet the potential impacts on the microorganisms engaged in secondary waste treatment remain uncertain. Nevertheless, it is essential to weigh these concerns against the prospective advantages of nanotechnology. The incorporation of $TiO2$ nanoparticles in conjunction with UV light during sewage treatment has been shown to effectively eliminate 70% of total organic carbon from wastewater (Song et. al., 2016).

A final avenue of exposure arises from the inadvertent release and spillage of manufactured nanoparticles directly into the environment. This represents a potential concern associated with all synthetic materials, not exclusively nanomaterials. Information regarding the persistence of manufactured nanomaterials in environmentally relevant matrices remains scarce. Furthermore, there are concerns that the conventional octanol-water partition coefficients tests may not be applicable to nanoparticles, which raises questions about their utility in predicting bioaccumulation potential or chronic effects. As previously mentioned, nanoparticles combined with river water that contains natural organic matter persist in suspension for extended durations, although the chemical interactions between these components may alter the behaviour of both natural and synthetic materials.

Furthermore, variations in pH, ionic strength, and calcium concentration may facilitate aggregation. Considering the dynamics of a spill into a river, one might anticipate that the substance will initially remain in the aqueous phase, yet it is likely to aggregate and eventually settle as it progresses downstream. Regardless of the circumstances, the substance remains in the environment and will endure over time. It is likely that the sole mechanisms for the removal of these nano materials from the environment involve solubilisation or diagenetic processes. Consequently, both of these processes hold significant relevance in our comprehension of environmental concentrations. Nevertheless, in the case of persistent nano materials, it is reasonable to anticipate that sludges, sediments, and soils will serve as repositories for these substances, thus warranting a concentrated examination of soil and benthic organisms within the realm of ecotoxicology research.

Obstacles in quantifying nanoparticles in surroundings

The identification of nanomaterials in the environment is rendered complex by three primary challenges (Lai et. al. 2018).

(i) The presence of low concentrations of nanomaterials in the environment appears probable (ng per litter or low µg per litter),
(ii) a somewhat elevated concentration of natural nanoparticles (e.g., colloids) or organic carbon (mg per litter) could complicate the detection of engineered carbon-based nanoparticles significantly,
(iii) analogous considerations pertain to metal-based nanoparticles and the background concentrations of trace metals in the surrounding atmosphere, whether in dissolved or colloidal states.

The afore mentioned consideration precludes the direct bulk measurement of total metal nanoparticles in environmental samples through methods such as ICP-MS for the purpose of quantification; it necessitates fractionation prior to the application of ICP-MS. Nonetheless, a multitude of methodologies exists for quantifying nanoparticles in laboratory settings. The challenge lies in employing these techniques to isolate nanoparticles from environmental matrices, followed by the application of established size-separation methods to segregate the nanoparticles within the extract. Consequently, a critical area of investigation is the extraction of nanomaterials from soil as well sediments, or other intricate matrices.

Nevertheless, these challenges are not more formidable than the extraction of other intricate contaminants, such as organic pollutants from soil matrices. It is our conviction that one can devise methodologies for physical and chemical measurements of samples gathered in the field, subsequently validate these methods, and ultimately implement them within monitoring programs. It is probable that these methodologies will encompass size fractionation, comprehensive element or isotope analysis, in conjunction with appropriate labelling (whether fluorescent or isotopic) and supplementary measurements.

Assessing concentration & chemical composition nano particles

Concentrations may be determined by mass, specific surface area, or numerical count. Eco toxicologists routinely engage with mass concentration measurements (e.g., mg per litter) and employ various methodologies to ascertain particle concentration. The straightforward techniques, including gravimetric methods, turbidity assessments, and spectrophotometric analyses of samples, are capable of detecting concentrations in the mg per litter range. Furthermore, the requisite equipment is commonly known and accessible in the majority of laboratories. These methodologies could prove advantageous for conducting a lethal dose assessment involving elevated concentrations. Nevertheless, these methodologies typically fail to identify concentrations of 1 gm per litter or lower, which may restrict their applicability in chronic studies or in certain field-collected samples where nanoparticle concentrations could be minimal. Moreover, the selection of standards to correlate instrument signals with concentration presents challenges within these intricate systems.

More refined methodologies, such as laser induced breakdown detection (LIBD), may be utilized for the latter; however, this technique is more specialized, and the requisite equipment is not commonly accessible in the majority of laboratories. LIBD, akin to all laser methodologies, presents greater challenges when applied to non-spherical particles or porous organic materials that could influence the interaction of laser light with the material's surface. However, it demonstrates efficacy with hard metal oxide spheres, for instance. In the realm of metal-based manufactured nanoparticles, one can utilize established techniques for trace element detection, including ICP-MS, ICP-OES, and GFAAS, which have been integral to metal toxicity research for numerous years (Depledge M. H., 2020). Nevertheless, a degree of prudence is also warranted. It is essential to validate routine procedures for trace metals with the specific metal nanoparticle of interest. For instance, there exists evidence suggesting that ICP-MS for TiO2 nanoparticles exhibits distinct behaviour compared to titanium metal solutions, raising concerns that nanoparticles may not completely atomize within the furnace of the instruments. Certainly, ICP-MS and comparable conventional metal analysis methodologies can be employed to examine the elemental chemical makeup of a liquid sample. Nonetheless, in the case of natural waters or samples collected from the field, this will also encompass the inherent metal levels, making it challenging to distinguish the metallic makeup of the manufactured nanoparticles from the existing background.

An alternative methodology involves examining the elemental composition of individual nanoparticles through the application of electron microscopy techniques. These can be integrated with techniques for analysing element concentrations and speciation within an individual particle, including X-ray diffraction and reflection methods, such as energy dispersive X-ray transmission electron microscopy. Geochemists as well biologists have employed these methods to examine naturally occurring metal granules and nanoparticles. These methodologies provide spatial resolution at the nano meter scale, and in the case of metals, it is feasible to identify the primary constituents within a particle, such as heavy metals and significant anions like phosphorus. The primary constraint for the Eco toxicologist lies in the necessity of possessing some proficiency in electron microscopy; however, such facilities are accessible at numerous universities.

The quantity of particles per unit volume, potentially indicative of the aggregate toxicological impact linked to the morphology or surface area of individual particles, could be as significant as the assessed mass concentration in determining particle toxicity. The quantification of particle number can be achieved through visual counting techniques, including light microscopy and electron microscopy (EM). Light microscopy possesses a limited resolution, enabling the detection of substantial aggregates or polymerized strands of nanomaterials, yet it falls short in identifying individual nanoparticles. Electron microscopy techniques provide nano meter scale resolution, enabling the quantification of individual particles and the discernment of their shapes (Ema et. al., 2017).

Regardless of whether one employs scanning, transmission, or atomic force microscopy, each of these methodologies presents certain limitations. Initially, it is essential to transition the nanoparticles from their dispersed condition to a dried or vacuum state on a support grid, facilitating their subsequent placement within the microscope. The drying process will undoubtedly modify the colloidal behaviour of the material, and one cannot be entirely confident that the aggregates observed on an EM grid accurately reflect the sample, or if they merely represent a by-product of the preparation method. Furthermore, EM techniques utilize minuscule volumes, and considerable number of grids derived from repeated sub-samples of the dispersion must be analysed to provide a statistically sound estimate of the particle count per litter of dispersion. Consequently, alternative methodologies that quantify particle numbers throughout the entire suspension may prove to be more feasible. Microscopy techniques are indeed invaluable for visualizing and determining the shape of particles; however, one must remain cognizant of the inherent limitations mentioned above, and it is advisable that characterization not rely exclusively on microscopy.

Evaluation of nano particles risks-hazards

The foremost aspect to consider in hazard and risk assessment is the necessity to comprehend both the characteristics of the initial nanomaterial along with the physico-chemical attributes of the testing and potential receptor systems prior to initiating an Eco toxicological investigation. While the allure of initiating an Eco toxicological test is considerable, the preceding review illustrates that a comprehensive grasp of the fundamental properties of the starting material (such as particle size as well ligand chemistry) and an awareness of its behaviour in the study medium (for instance, by evaluating zeta potential in relation to media pH to determine potential colloid stability; titrating humid substances in the media, etc.) are essential for elucidating the probable fate, behaviour, uptake, and Eco toxicity of the material in environmental contexts. The insights gained should be utilized to guide the study's design. The assessment of intrinsic properties is indeed acknowledged as a crucial element in the environmental risk assessment for chemicals.

Conclusion

The existing body of scientific research on the ecotoxicology of nanoparticles and nanomaterials is still in its nascent stages. However, there is evidence of toxic effects observed in various fish as well invertebrate species, which raises significant concerns regarding the potential adverse impacts of nanoparticles on wildlife, particularly when present in elevated concentrations in the environment. There exist numerous notable deficiencies in our understanding of ecotoxicology. For instance, there is a notable deficiency of information regarding bacteria, plants, and higher vertebrate species. We consequently advocate for research on these taxa, provided that credible source-pathway-receptor relationships can be established, which would result in exposure concentrations of nanoparticles that are likely to induce harm. Moreover, the studies conducted to date are predominantly observational in nature and frequently employ elevated mg per litter doses to guarantee a biological effect, serving as proof of principle experiments. This is likely to be expected, and prior to formulating credible hypotheses regarding the mechanisms of Eco toxicity, a period of observation and data collection is essential. It is evident that we remain in the phase of gathering data concerning biological effects, and further insights into effects at significantly lower concentrations and extended timescales will be essential as knowledge concerning ambient exposure becomes available.

The Eco toxicity of nanomaterials and nanoparticles necessitates a comprehensive approach, and Eco toxicologists must grasp the fundamental concepts of particle chemistry to accurately interpret Eco toxicological data. This encompasses the implications of particle dimensions, morphology, and surface characteristics, as well as the interactions between the particles and other substances within the aqueous or environmental context. The understanding of how abiotic factors influence the Eco toxicity of nanoparticles remains limited, necessitating further investigation into variables such as pH, salinity, water hardness, in addition the presence of natural organic matter or other colloidal substances. It is essential to meticulously observe all the aforementioned parameters in ecotoxicology experiments involving nanoparticles. There exist additional considerations that may not be immediately apparent. Nano particles and nanomaterials possess the potential to adsorb various chemicals, raising concerns about the possibility of nanomaterials acting as conduits for other toxic substances. Additionally, there exists the potential for synergistic toxic effects when nanoparticles coexist with mixtures of other chemicals.

Ultimately, the circumstances surrounding environmental monitoring present significant challenges. It is essential to advance physico-chemical methodologies for the detection of engineered nanoparticles in the environment to enhance the efficacy of chemical monitoring. Furthermore, there exists a lack of biomarkers for NPs that could be integrated into a biological monitoring program. While current regulatory toxicity tests may be applicable (with adjustments) for nanoparticles, the risk assessment would be fundamentally lacking without the quantification of actual nanoparticle concentrations in the environment.

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