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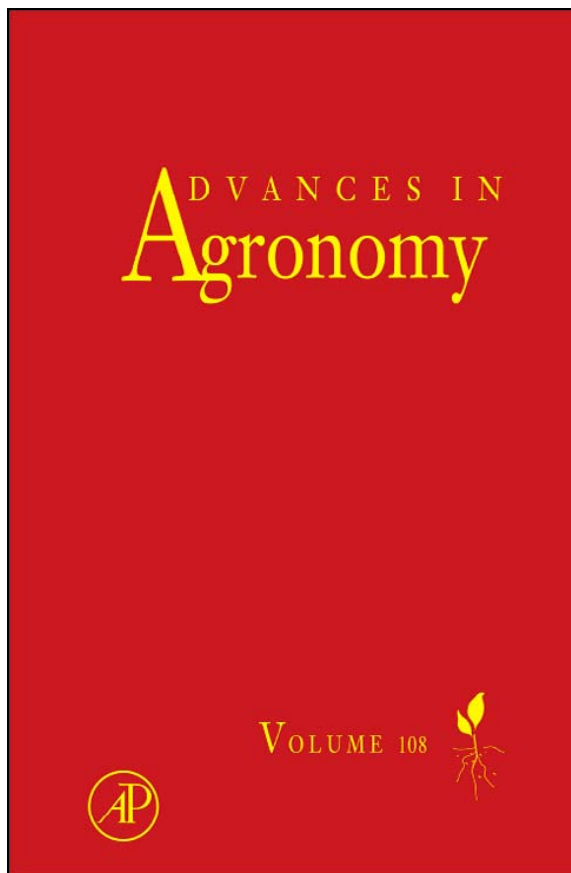
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## CHAPTER THREE

# MANUFACTURED NANOPARTICLES AND THEIR SORPTION OF ORGANIC CHEMICALS

Bo Pan<sup>\*,†</sup> and Baoshan Xing<sup>†</sup>

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## Abstract

With the rapid development and application of nanotechnology, increasing concern has been raised on the environmental risks of manufactured nanoparticles (MNPs) because they will find their way into the environment during their production, purification, application, and disposal. The interactions between organic chemicals and MNPs will alter the environmental behavior of both organic chemicals and MNPs. Therefore, understanding organic chemical–MNP adsorption mechanisms as well as the consequent influences on organic chemical and MNP environmental behavior is fundamental to assessing their environmental exposure and risks. Thus, current research progress and knowledge gaps regarding adsorption mechanisms of organic chemicals on MNPs are the main focus of this review. In addition, MNP application, general properties, occurrence, and entry pathways to the environment are summarized. MNP colloidal behaviors, which are their unique properties in comparison to other adsorbents, are discussed. The mobility and toxicity of both organic chemicals and MNPs after adsorption are also addressed. Finally, future research directions are presented.

## 1. INTRODUCTION

Nanoparticles (NPs) are fine particles with one dimension smaller than 100 nm. In comparison to bulk particles, the atoms in NPs have the following two features: (1) less coordination number and (2) more exposed reactive species in the surrounding circumstances ([Jones and Grainger, 2009](#)). Surface atom percentage increases with decreasing particle size

(Auffan *et al.*, 2009). For microparticles, less than 1% of the atoms locate on particle surface (Nel *et al.*, 2006). But 10% of atoms occupy the surfaces for particles with a diameter of 10 nm. If the particle size is further decreased to 2 nm, 60% of the atoms are located on the surface and are in contact with the environment. Thus, as particle size decreases, the reactivity of the surface atoms could increase dramatically. These unique properties make nano-sized particles valuable engineering materials because of their extraordinary strength, chemical reactivity, electrical conductivity, or other characteristics that the same material does not possess at the micro- or macroscales. The novel technologies developed based on these unique properties of NPs are called nanotechnologies (EPA, 2007). The application of nanotechnology could greatly improve the efficiency of industrial processes and facilitate human daily life. Therefore, human started to synthesize NPs since 1970s. Nanotechnology has become one of the most promising new technologies of the twenty-first century and will have dramatic impacts across the fields of physics, chemistry, biology, medicine, material science, engineering, and environmental sciences. Up to November 2009, the Project on Emerging Nanotechnologies (<http://www.nanotechproject.org>) listed over 1000 nanotechnology products closely related with our daily life, covering the categories of automotive, electronics, food/beverage, household tools, toys, clothing, and personal care products. The potential market value for nanotechnology-related products in 2011–2015 will be up to \$ 1 trillion per annum (NSF, 2001; Wiesner *et al.*, 2006).

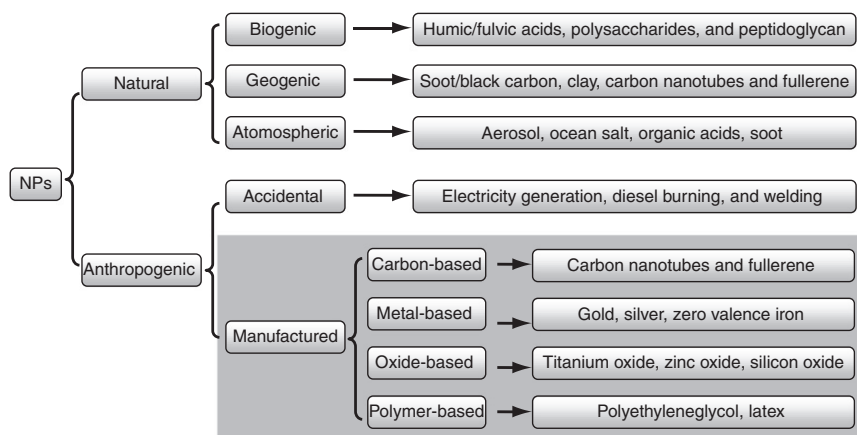
Although reliable detection and analytical techniques are still lacking, the presence of natural NPs (NNPs) in the environment is believed to be very high. However, because these particles are naturally derived and they have been in the environment with the evolution of organisms, their environmental risk has been lessened and showed very good compatibility with the environment. Therefore, their environmental risks are not the main concern of current studies. On the other hand, manufactured NPs (MNPs) are emerging materials and the ecological system has not developed adaptive mechanisms. During the synthesis, purification, application, and disposal, MNPs will inevitably enter the environment. Because of the recent appearance of MNPs, the organisms have not developed the resistance to these new materials. Especially, because the properties of MNPs are intentionally strengthened during synthesis for their applications, their environmental risks are much higher than NNPs. Therefore, the environmental risks of MNPs are attracting increasing attention from both the public and scientific communities.

The toxicity of MNPs has been widely reported (Nel *et al.*, 2006). Therefore, the vast production and application of MNPs surely bring along the public concern of their health risk. To ensure the safe application and sustainable development of nanotechnology, we need to systematically investigate the environmental risks of MNPs (Maynard *et al.*, 2006). Because of their large surface area, MNPs are reported to strongly interact

with heavy metals (Rao *et al.*, 2007) and organic contaminants (Pan and Xing, 2008). Specifically, the interaction between MNPs and organic chemicals would control the environmental behavior and toxicity of both MNPs and organic chemicals. In addition, this interaction could show distinct effect on ecological systems. Therefore, this review will give emphasis on the interaction mechanisms between MNPs and organic chemicals. The particle sizes of MNPs are in the range of colloids and thus the concepts in colloidal chemistry could be applied to study MNPs. MNP colloidal behavior will alter their adsorption properties with organic chemicals. Therefore, this review will summarize MNP colloidal behavior in a separate section. The toxicity and environmental behavior of MNPs and organic chemicals as affected by their interaction will also be discussed and summarized. Several important types of NNPs, such as soot and humin, which have very strong interactions with organic chemicals, will also be presented for comparison with MNPs.

### 1.1. Nanoparticles and their sources

NPs could be classified according to different criteria, such as sources, bulk materials, and sizes. Because this chapter focuses on MNPs, the first level of NP classification will be based on their sources. To facilitate the detailed discussion on adsorption mechanisms, the bulk material will be a second level of NP classification (Fig. 1). Depending on their sources, NPs could be



**Figure 1** Classification of nanoparticles (NPs). Natural NPs are classified as biogenic, geogenic (including burning of geogenic sources), and atmospheric NPs which present in the environment for a long period of time. Anthropogenic NPs contains two categories, namely accidental NPs and manufactured NPs. Manufactured NPs are of the major concern of this study (gray background).

divided into NNPs and anthropogenic NPs (ANPs). MNPs are the major constituent of ANPs. According to their matrix materials, MNPs could be divided into the following groups: carbon-based NPs (such as carbon nanotubes (CNTs) and fullerene), metal-based NPs (such as nanogold and nano-zero-valent iron), oxide-based NPs (such as nano silver oxide, nano titanium oxide, nano zinc oxide, and silicon oxide), and polymer-based NPs (such as polyethyleneglycol). During manufacturing and human daily activities, such as cooking, electricity generation, industrial boiling, diesel burning, and welding, NPs may be accidentally produced and discharged into the environment ([Murr et al., 2004](#)). This type of NPs is known as accidental NPs.

#### 1.1.1. Natural nanoparticles

NNPs have been present in the environment for millions of years, such as organic colloids (including dissolved organic matter, polysaccharides, humic materials, and peptidoglycan), soot/black carbon, and inorganic particles (including clay and ocean salt) ([Nowack and Bucheli, 2007](#)). Black carbon is produced during incomplete combustion of fossil fuels, biofuel, and biomass and could exist in soils/sediments in NP size range ([Maurice and Hochella, 2008](#)). Black carbon derived from biomass burning was estimated to be 0.05–0.27 Gt/year ([Kuhlbusch and Crutzen, 1995](#)), and that produced from fossil fuel combustion was 0.012–0.024 Gt/year ([Penner et al., 1993](#)). The increased biomass burning and fossil fuel consumption in recent years have drastically increased the input of black carbon to the environment. Soot is a production of incomplete combustion of fossil fuels and vegetation. Soot belongs to black carbon and has the dimension in the range of NPs. Black carbon/soot is also viewed as accidental ANPs because they are also by-products from human activities, such as diesel burning and cooking.

Biogenically derived NPs are mostly organic colloids, such as polysaccharides, proteins, organisms of nano-size (e.g., viruses), and humic/fulvic acids. These particles are actively involved in biological processes. Researchers even detected CNTs and fullerene in ice core formed 10,000 years ago ([Murr et al., 2004](#)). The formation of fullerene and CNTs in the environment was attributed to metamorphosis of PAHs at 300–500 °C in the presence of sulfur ([Heymann et al., 2003](#)) or natural combustion.

#### 1.1.2. Manufactured nanoparticles

MNPs could be easily classified according to their bulk materials. The easily controlled size, surface charge, morphology, and composition of polymers enable the synthesis of polymeric NPs. Polymeric NPs attracted many applications in drug delivery because this type of NPs could pass through cell membranes and cross the blood–brain barrier ([Koziara et al., 2003](#)).

Carbon-based NPs are mostly synthesized using the following methods:

(1) *Arc-discharge* – Carbon-based NPs were initially found in soot produced

in arc-discharge with catalytic metals such as Fe, Ni, and Co. This method was then modified and reacted in a controlled condition to produce CNTs and fullerene. (2) *Laser ablation* – Carbon-based NPs are produced by pulsed YAG laser ablation of graphite target in a furnace at 1200 °C. (3) *Chemical vapor deposition* – Using this method, carbon-based NPs are grown from nucleation sites of a catalyst in carbon-based gas environments (such as ethylene, methane, and propane) at elevated temperatures (600–1000 °C). The production and type of carbon-based NPs are dependent on catalyst material, gas, temperature, flow rate, and reaction time.

Inorganic NPs include a wide range of NPs. Up to now, the most widely used MNPs is elemental silver NPs which accounted for more than 25% of nanoproducts (<http://www.nanotechproject.org>). Silver has been used for medical application for over 100 years because of its antibacterial and antifungal properties ([Morones et al., 2005](#)). Nano-sized silver particles have an extremely large specific surface area and thus their contact with and effectiveness to target organisms are maximized. The most important benefit of nano-sized silver particles is that they can be embedded in/with or coated on other materials. Thus, the antibacterial activities could be applied in various products, such as cooking tools, cloth, personal care products, and sports instruments.

Because of their inert properties, TiO<sub>2</sub> NPs are used in paints, paper, plastics, sunscreens, and even food (e.g., confectioneries, white-colored sauces and dressings, nondairy creamers, and mozzarella and cottage cheeses) ([Nohynek et al., 2007](#)). The estimated human daily intake of TiO<sub>2</sub> NPs exceeds 5.4 mg/day ([Lomer et al., 2000](#)). TiO<sub>2</sub> NPs are highly efficient catalyst and are used in photocatalytic processes such as water treatment. They are commercially available in the form of dry powder, cream, or aqueous suspension. Current TiO<sub>2</sub> NP production is estimated be 40,000 MT/year in the United States alone and predicted to reach more than 2,000,000 MT/year at 2025 ([Robichaud et al., 2009](#)).

Aluminum NPs are currently used in a number of applications, such as energetics, alloys, coatings, incendiary devices, and sensors. Reduced Al particle size could greatly reduce the ignition time and enhance the burn rate because of the increased surface area ([Meda et al., 2006](#)). This property suggests promising applications in aerosolization of Al NPs. Thus, the deposition of Al NPs in a large area is expected.

The physical properties of gold are changed distinctively when its particle size is reduced. In bulk scale, gold, known as a shiny, yellow metal that does not tarnish, is nonmagnetic and melts at 1336 K. However, gold NPs could be used as a very efficient catalyst and exhibit strong magnetism. The melting temperature decreases dramatically as size goes down, reaching around 400 K. In nanoscale, gold is not even golden any more. It appears green, red, blue, yellow, and other colors.

The most widely accepted application of nanotechnology in environmental remediation is zero-valent iron (ZVI) NPs used in groundwater



remediation ([Zhang, 2003](#)). ZVI particles are a powerful reductant and ZVI NPs are much more reactive than granular ZVI. Thus, ZVI NPs have the potential to quickly react with many environmental contaminants. In addition, nano-sized particles make the injection in the soil pores much easier than coarse particles. Therefore, ZVI NPs could be readily delivered and are used as a permeable reactive barrier.

## 1.2. Toxicity of nanoparticles

Strong evidence has been reported to show the toxicity of NPs to plants, fish, rats, and cells. The toxicity of MNPs is quite different from larger particles. They could enter different types of cells by nonendocytic and actin-independent mechanisms ([Mayhew \*et al.\*, 2009](#)). The mechanisms of the toxic effect of MNPs on organisms could be summarized as follows: (1) NPs could generate reactive oxygen species because of their redox activity and thus pose oxidative stress to organism. (2) NPs could be adsorbed on cell membrane, disturbing its permeation properties, puncturing cell membrane, and interfering with physiological activities. (3) NPs could retain electrons and thus disturb electron transfer in organisms, such as phosphorylation and energy transfer. (4) NPs could interact with proteins and thus disturb the transfer of biosignals or even gene information ([Chen and von Mikecz, 2005](#); [Linse \*et al.\*, 2007](#); [Oberdorster, 2004](#)). All the aforementioned mechanisms are based on the studies on plants and animals, thus may not be applicable to humans. However, on August 19, 2009, Reuters reported a disease or even death case because of longtime contact with NPs ([Reuters, 2009](#)).

The toxicity and the mechanisms of NP toxic effect are all dependent on their properties. This viewpoint could be firstly understood from the bulk materials. However, for a same material, different types of NPs may manifest different toxic effects. For example, single-walled CNTs could be accumulated on the surface of fish gills, and thus disorder fish respiration system ([Smith \*et al.\*, 2007](#)). This mechanism belongs to the second toxic mechanism. On the other hand, because of their small size and lipophilicity, fullerene could pass through the external cellular membrane and be localized to the mitochondria, the cytoplasm, lysosomes, and cell nuclei ([Porter \*et al.\*, 2007](#)). Fullerene thus poses peroxide stress to fish ([Zhu \*et al.\*, 2006](#)), which belongs to the first mechanism.

Up to date, various toxic effects have been reported, sometimes with controversial results. The results from different studies could be hardly compared. For example, nano-TiO<sub>2</sub> was reported to stimulate the growth of spinach when applied to the seeds or sprayed onto the leaves ([Gao \*et al.\*, 2006](#); [Hong \*et al.\*, 2005](#); [Yang \*et al.\*, 2006a](#); [Zheng \*et al.\*, 2005](#)). The benefited spinach growth was attributed to the increased activity of several enzymes, promoted nitrate adsorption, and enhanced efficiency of transforming inorganic nitrogen to organic nitrogen. However, the toxicity of nano-TiO<sub>2</sub> was

reported to algae and daphnids (Hund-Rinke and Simon, 2006). One of the main reasons for these various or even controversial results is lack of a general standard procedure of toxicity experiments for NPs. Thus, the comparison between the results from different toxicity experiments is not quite appropriate. The factors to be considered for procedure standardization include the preparation of NPs, the selection of organism species, the endpoints of toxicity experiments, and the environmental conditions in the experimental system. The readers are suggested to refer to the review by (Handy *et al.*, 2008) for a more complete presentation on MNP ecotoxicity.

### 1.3. Environmental behavior of organic chemicals regulated by nanopariticsles

The environmental fate of organic chemicals has been a hot topic for several decades. The basic framework of this line of research is to study the interactions between organic chemicals and environmental components, and then summarize all the processes in a complex model to provide a general view on organic chemical environmental behavior. This work is essential in understanding the environmental risks of organic chemicals and will provide fundamental information of their risk assessment. The presence of emerging material in the environment will inevitably raise new environmental concerns. How to understand the environmental risk of MNPs is a new challenge to environmentalists. CNTs possess a strong hydrophobic surface, and thus their interaction with organic chemicals attracted the greatest attention in comparison with other MNPs. In addition to the aforementioned influence on organic chemical fate, the importance of understanding organic chemical–CNT interactions could be further viewed from the following two points: (1) the strong interaction showed potential application of CNTs as effective adsorbents for organic chemicals in environmental analysis and water treatment and (2) the structures of CNTs are well defined and their surfaces are relatively uniform in contrast with activated carbons (ACs). Therefore, CNTs are considered to be a good choice to study adsorption mechanisms. For these reasons, understanding of organic chemical–CNT interactions will provide important information on assessing the environmental risks of both organic chemicals and CNTs and exploring CNT applications.

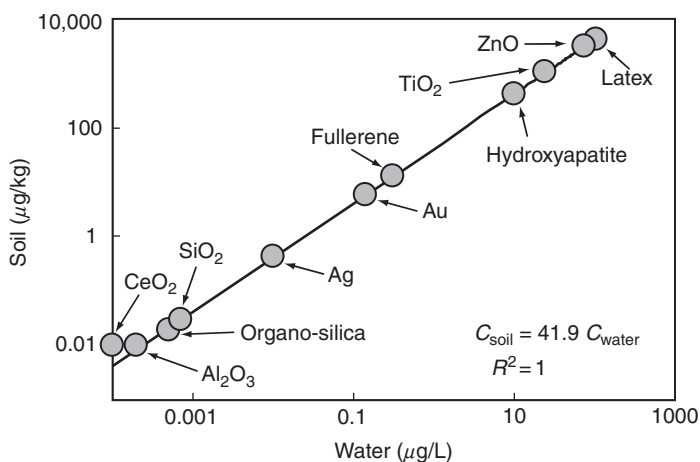
## 2. OCCURRENCE, CHARACTERIZATIONS, STRUCTURES, PROPERTIES OF MANUFACTURED NANOPARTICLES

To understand the effects of MNPs on organic chemical environmental behavior, it is fundamental to know MNP properties and their occurrence in the environment. A summary on this research area will provide a

basis for environmental relevance of MNP research. In addition, it is important to learn the disadvantages of current technologies used in MNP characterization and quantification. Thus, their limitations will also be summarized in this section.

## 2.1. Occurrence of manufactured nanoparticles in the environment

Lack of identification and quantification techniques of MNPs hinder our knowledge on the occurrence of MNPs in the environment. Currently, investigators applied simple algorithms to predict the discharge of MNPs to the environment. Very high concentrations of Latex, ZnO, and TiO<sub>2</sub> are expected in soil and water (Boxall *et al.*, 2008; Fig. 2). It seems that a distribution parameter (i.e., 41.9 L/kg as indicated in Fig. 2) was applied to describe the distribution of MNPs between soil and water, which is only an estimation. Gottschalk *et al.* (2009) also calculated environmental concentrations of MNPs in different environmental media based on a probabilistic material flow analysis. The most frequent values for fullerenes, CNTs, TiO<sub>2</sub> NPs, ZnO NPs, and Ag NPs are two to four orders of magnitude higher in sewage treatment effluents than in surface water, indicating current MNP risks to aquatic organisms are mostly in the region affected by sewage treatment effluents. Kiser *et al.* (2009) investigated the behavior of TiO<sub>2</sub> NPs and larger-sized TiO<sub>2</sub>. They observed that TiO<sub>2</sub> particles



**Figure 2** Predicted MNP concentrations in water and soil (modified from Boxall *et al.*, 2008). The expected MNP concentrations in soil are 40 times higher than those in water. The highest concentrations for MNP are Latex, ZnO, and TiO<sub>2</sub>, because of their wide applications.

larger than  $0.7\ \mu\text{m}$  were well removed by wastewater treatment plant processes. The detected Ti in the effluents was mostly in the particles  $<0.7\ \mu\text{m}$  with the concentration of  $5\text{--}15\ \mu\text{g/L}$ . Most of Ti accumulated in the settled solid with concentrations of  $1000\text{--}6000\ \text{mg/g}$ . The  $\text{TiO}_2$  NPs discharged with the effluent and field-applied sludge will bring  $\text{TiO}_2$  NPs to the environment and lead to environmental exposure and risk. More accurate estimation is still unavailable because of the absence of proper quantitative methods.

## 2.2. Manufactured nanoparticle characterization and quantification

In order to understand the environmental risks of MNPs, characterization and quantification are of the fundamental importance. Methods traditionally used in organic colloid analysis could be borrowed in MNP characterization and quantification. For example, microscopic methods (TEM, SEM, and AFM), size fractionation (ultrafiltration, ultracentrifuge, cross-flow filtration, and field-flow fractionation), chromatography (size-exclusive chromatography, gel permeation chromatography), and size distribution analysis (zetasizer) could all be applied to characterize MNPs (Tiede *et al.*, 2009). Microscopic methods are often used in characterizing MNPs. However, only a very small fraction of the sample was used to obtain the image and thus the result may be sometimes subjective and incomplete. To get a representative sample is very difficult. In addition, during the procedure of preparing the samples for microscopic analysis, the structure of the NPs can be altered (Burleson *et al.*, 2003).

Field-flow fractionation (FFF) is successfully used to determine the particle size distribution of MNPs (Carpino *et al.*, 2005). In comparison to common liquid chromatography containing mobile and stationary phases, FFF achieves the separation within the mobile phase alone. Particles interacting less strongly with the field are eluted more quickly than those interacting more strongly. The application of this method could be extended by connecting inline with other quantification devices, such as UV-vis and HPLC-MS.

Size-exclusion chromatography (SEC) is an effective, nondestructive method for purification and size separation using a stationary phase with defined pore sizes. This method is known as gel filtration chromatography if the particular samples are transported by aqueous phase, or gel permeation chromatography if the aqueous phase is organic solvent. SEC is widely used to purify and analyze synthetic and biological polymers, such as proteins, polysaccharides, and nucleic acids. This method was successfully used to characterize CdSe quantum dots (Krueger *et al.*, 2005) and CNTs (Duesberg *et al.*, 1998).

In the framework of MNP characterization, MNPs should be distinguished from NNPs. There is no discussion on distinguishing these two classes of NPs. The aforementioned methods are mostly dependent on the physical shape and size of MNPs, and thus could not identify the chemical composition of MNPs. Therefore, only nano-sized particles are observed without recognizing their origin and chemical properties. Energy dispersive X-ray (EDX) is applied in association with imaging techniques and the chemical composition in a specific small region could be identified. Therefore, it is a very powerful way for MNP environmental behavior analysis. However, this method is relatively expensive and could not be widely applied in research. In addition, as other imaging techniques, EDX provide information only about a very limited area or amount, and the overall information may not be provided.

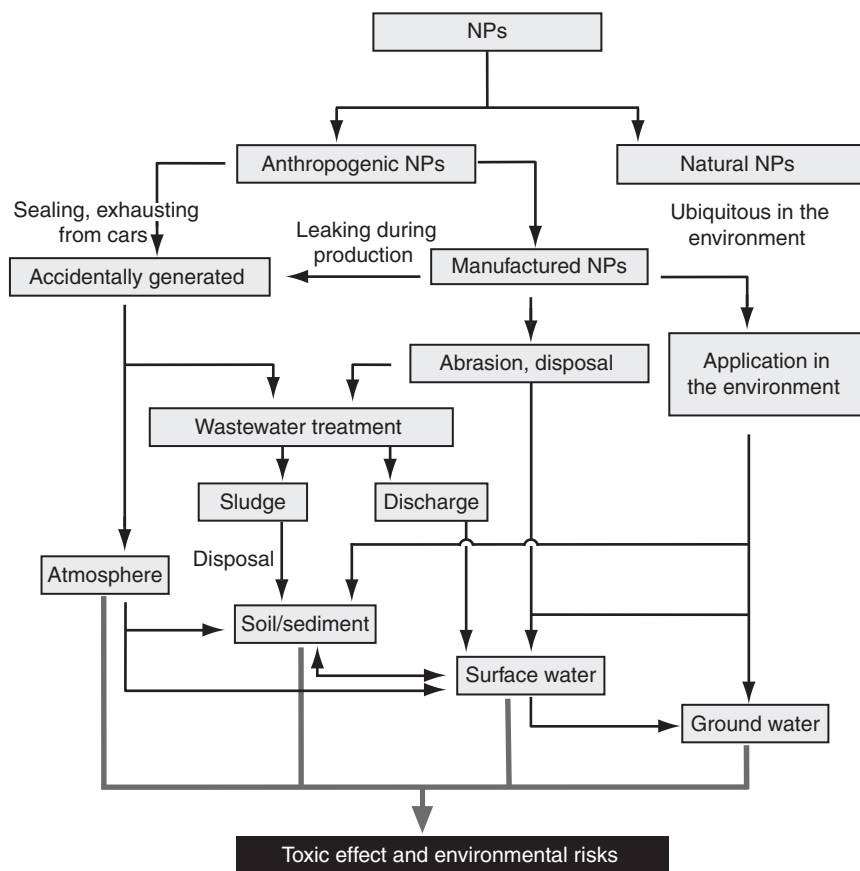
The methodology applied in black carbon studies may provide valuable ideas in developing new method for MNP characterization, especially for carbon-based NPs. Systematic evaluation of black carbon/soot quantification methods in environmental samples is summarized in the paper by [Cornelissen \*et al.\* \(2005\)](#). Two quantification methods are widely used in the analysis of black carbon, namely thermal and chemical methods. Both methods could be viewed as two steps. Non-black carbon organic matter is selectively removed using thermal or chemical method, then the remaining carbonaceous materials are BC. These residue particles are then characterized using different methods, such as microscopic methods, titration, coulometry, NMR, or elemental analysis ([Nowack and Bucheli, 2007](#)).

Explicit quantification method is available only for fullerene. Fullerene is usually quantified using UV-vis spectrometer at 336, 407, 540, and 595 nm. But the method is only applicable for high concentrations, mostly in laboratory systems. HPLC is more reliable method of quantifying fullerene at low concentrations ([Fortner \*et al.\*, 2005](#)). HPLC method is also reported to be efficient in analyzing fullerene from environmental samples ([Chijiwa \*et al.\*, 1999](#)).

UV-vis spectrometer is also used to quantify CNTs at very high concentrations at 253, 266, 350 nm or 800 nm. However, this method is only applicable in simple systems, for example laboratory simulated systems. For the samples from the environment, pretreatment of the samples, such as extraction from the environmental matrices, separation from interfering materials, and concentrating to a higher concentration, is needed. However, these pretreatment methods are not available for CNTs, yet.

### 2.3. Pathways of manufactured nanoparticles to enter the environment

MNPs could enter the environment in various forms through different pathways ([Fig. 3](#)). During their synthesis, application, and disposal, MNPs may enter the environment directly. For example,  $\text{TiO}_2$  NPs were detected in soil and water around the place where  $\text{TiO}_2$  NP-containing paints were applied



**Figure 3** Environmental fate of NPs. Both accidentally generated and manufactured NPs may enter wastewater treatment system or directly discharged into the environment. All types of NPs will eventually find their way into the environment, and pose toxic effect to organisms and ecosystems.

(Kaegi *et al.*, 2008). During environmental remediation, MNPs were directly applied in open environments, and inevitably, these particles will transport in environmental media. MNPs related with daily activities were discharged into sewage system. If MNPs were removed during water treatment procedure, these particles will mostly be precipitated into sewage sludge. During sludge burial or application of sewage sludge on land, MNPs enter the environment and may be transported and spread out by water and wind. If MNPs were not removed during water treatment, these particles will be discharged with the effluent into surface water and groundwater, or even drinking water system. Therefore, during their life cycle, MNPs could find their way into the environment and transport in air, water, and soil systems.

Understanding the pattern that MNPs enter the environment is a fundamental requirement to study MNP environmental fate and consequently their risks. For traditional chemicals, the physiochemical parameters are applied as inputs in multimedia modeling, such as octane–water distribution coefficient, saturation vapor pressure, and adsorption coefficient. These parameters are readily available from literature or through simple experiment measurements. However, this modeling concept is not applicable to MNPs because all these parameters are not applicable to MNPs. The first attempt to quantitatively describe MNP environmental fate was provided by [Mueller and Nowack \(2008\)](#). They developed a conceptual model and compared the environmental transport and exposure of silver,  $\text{TiO}_2$ , and carbon NPs. In this model, the authors systematically incorporated global production, application, recycling, and disposal of MNPs. In all the procedures, the pathways and amount that MNPs could enter the environment are estimated. The possible concentrations that MNPs may be present in environmental media were compared with the concentrations that pose no toxic effect. Thus, MNP environmental risks were evaluated. Their results showed that the environmental behavior and risks were distinctly different for different MNPs. In addition, the current modeling results and predicted risks will be changed soon with more development and application of nanotechnology ([Nowack, 2009](#)). However, because the environmental concentration of MNPs could not be detected properly up to now, the accuracy and reliability of the model could not be tested. Further, explicit quantification of MNP behavior instead of the conceptual mass calculation is needed.

Most of the NPs are embedded in nanotechnology products. The release of NPs from these final products is dependent on the technology that these products are synthesized, the surface coating as well as the application and disposal of these products. The only available information is on silver NPs releasing from socks ([Benn and Westerhoff, 2008](#)). Systematic examination of NP release from different final products is still not available.

### 3. COLLOIDAL BEHAVIORS OF MANUFACTURED NANOPARTICLES

The adsorption of organic chemicals on MNPs is dependent on their properties, such as particle size, size distribution, shape, surface and core chemistry, agglomeration state, crystallinity, purity, surface charge, and porosity. These properties could also control and/or are affected by MNP colloidal behaviors, namely aggregation and dispersion. For example, MNPs tend to form big aggregates in water because of the attractive interaction (mostly London–Van der Waals force) between particles of nanoscale ([Nowack and Bucheli, 2007](#)). These interactions could be well described using DLVO (Derjaguin, Landau, Verwey and Overbeek) theory. It is easy to understand

that aggregated MNPs could precipitate and hardly be transported by water. Consequently, the ability of MNPs to adsorb and carry organic chemicals will be decreased. Higher degree of MNP oxidation ([Templeton et al., 2006](#)) and lower ionic strength of the aqueous system ([Li et al., 2009](#); [Saleh et al., 2008](#); [Wiesner et al., 2008](#)) usually result in better suspension.

### 3.1. Colloidal behavior of manufactured nanoparticles and their mobility

The mobility of iron NPs is discussed by several studies because of their application in underground water remediation. The stability and transport of iron NPs were influenced by their electrostatic and magnetic interactions. Iron NPs with less magnetism could elute more easily from soil column and more stable in water than highly magnetic particles ([Hong et al., 2009](#)). In addition, hydrophilic carbon and poly(acrylic acid)-supported iron NPs form very stable colloidal suspensions and settle very slowly in comparison to unsupported iron NPs ([Schrick et al., 2004](#)). Thus, the anionic surface of the supported NPs facilitated their transport and consequently enabled these particles to reach polluted underground water.

The deposition of MNPs in porous media could be viewed as two processes: (1) If the pores are too small for the colloids to pass through, straining occurs. This process plays an important role when the ratio of particle to collector grain diameters is greater than 0.05 ([Sakthivadivel, 1969](#)), or even as low as 0.003 ([Braddord et al., 2007](#)). The shape of MNPs, for example, the large aspect ratio, the variability of their length, and bundled state also play a significant role in straining ([Jaisi et al., 2008](#)). (2) Physico-chemical filtration. [Jaisi et al. \(2008\)](#) observed significant increase of CNT deposition with ionic strength higher than 3 mM and this observation is consistent with conventional colloid deposition theory. The authors stated that physicochemical filtration is the dominant mechanism for the column to retain CNTs. They also connected three columns and the eluted solution was used as an influent of the subsequent column. They observed decreased deposition as the colloidal solution successively pass through the three columns. This result indicated that the column selectively retained long and more bundled Single-walled CNTs (SWCNTs) in the first column and more mobile SWCNT fractions were leached out. Consequently, the extent of SWCNT deposition decreased in the subsequent runs.

The properties of the stationary matrix are also important. For example, the transport of Al NPs through soil column was much slower than that through sand column ([Darlington et al., 2009](#)). Various factors should be combined to understand this difference, for example, the electrostatic interactions between the particles and the matrix, the dynamic pore size of the matrix over time, and the specific surface area. At the very beginning stage of MNP environmental transport study, all these parameters are still under investigation.



### 3.2. Colloidal behavior as affected by ionic strength and pH

Ionic strength and pH control MNP surface charge and thus determine their colloidal behavior. One of the most important properties of colloids is their point of zero charge (pHzpc). This parameter is a pH value at which the colloid surface exhibits zero net charge. Generally, colloids at this pH show minimum stability or maximum coagulation/aggregation rate. For example, the stability of TiO<sub>2</sub> colloids is mainly governed by solution pH ([Guzman et al., 2006](#); [Kallay and Zalac, 2002](#)). At pH around pHzpc (6.2 for TiO<sub>2</sub>), TiO<sub>2</sub> NPs were highly aggregated. But at other pHs (either higher or lower), over 80% of TiO<sub>2</sub> NPs were mobile ([Guzman et al., 2006](#)). pHzpc for iron NPs is lower than 6, which is why iron NPs are more negatively charged at pH 9 than at pH 6, and thus iron NPs eluted to a greater extent at pH 9 ([Hong et al., 2009](#)).

At neutral pH, the zeta potential of nC60 (fullerene suspension) is about  $-50$  mV. Therefore, once C60 are dispersed in water, they could be stable for months. In the aqueous condition with cations of Ca and Mg in the range of 0.01–10 mM, nC60 remain negatively charged ([Brant et al., 2005](#)). The increased Ca or Mg concentration could neutralize the surface charges of nC60. As the ionic strength increased to 100 mM, the zeta potential reached zero and thus the electrostatic repulsion is minimized, which consequently result in larger aggregates. Investigators observed that MNP dispersion decreased with increased ionic strength ([Wiesner et al., 2006](#)). Divalent cations are more effective in reducing the stability of colloidal particles than monovalent cations, even at a same total ionic strength ([Jaisi et al., 2008](#); [Lin et al., 2009](#)). However, [Li et al. \(2009\)](#) observed higher solubility of C60 in 1 mM Ca<sup>2+</sup> (13.9 mg/L) than that in 0.1 mM NaCl (5.9 mg/L). But the authors did not discuss about the reason that Ca<sup>2+</sup> could increase the stability of C60 in their study.

It is well known that the presence of natural organic matter (NOM) could enhance the dispersion of MNPs. The presence of ions could neutralize and shrink NOM molecules adsorbed on MNP surface and thus the electrostatic repulsion between NOM molecules, then steric hindrance of the adsorbed NOM molecules are decreased ([Li et al., 2009](#)). As a result, the suspension of MNPs by NOM could be decreased because of the presence of ions. More discussion regarding MNP dispersion by NOM could be found in [Section 5](#).

### 3.3. Colloidal behavior as affected by surface functional groups

Surface functional groups may alter the surface charge or the steric interactions between NPs. Untreated CNTs usually have pHzpc around pH 7. The acid treatment introduced oxygen-containing functional groups on CNT surface and thus CNTs are negatively charged at pH 7 with a zeta potential from  $-30$  to  $-70$  mV ([Hu et al., 2005](#)), which is one of the

reasons that surface modified CNTs could be easily dispersed in comparison to the original ones. In addition, the surface functional groups on CNTs made them more polar than their original counterparts ([Zhang \*et al.\*, 2009](#)). Therefore, these functional groups have a positive effect on CNT dispersibility in water.

The solubility of C60 in water is reported to be very low. For example, after mixing with 10 mM  $\text{NaN}_3$  for 2 weeks, the concentration of C60 in ultrapure water was 0.23 mg/L. When the mixing time extended to 11 months, C60 solubility increased slightly to 0.26 mg/L ([Dhawan \*et al.\*, 2006](#)). However, fullerene could be easily dispersed after derivatized with ionizable or hydrophilic groups ([Wudl, 2002](#)). C60 could be chemically modified in ozone ([Fortner \*et al.\*, 2007](#)), in organic amines ([Li and Liang, 2007](#)), and by sunlight and thus the dispersion was increased. C60 dispersion was observed to be further accelerated by sunlight in the presence of NOM. The reason is that NOM could act as photosensitizers under sunlight. In addition, NOM could produce highly reactive species, such as singlet oxygen, hydroxyl radicals, organic peroxy radicals, and triplet state of NOM ([Schwarzenbach \*et al.\*, 2003](#); [Stumm and Morgan, 1996](#)).

Al NPs are often positively charged. Thus, these particles could be retained by the negatively charged soil particles ([Darlington \*et al.\*, 2009](#)). However, phosphate could be tightly bound with aluminum surface. When phosphate is coated on Al NP surface, the surface charge is reversed. After this surface modification, Al NPs and soil particles may repel each other because of electrostatic repulsion, and then the phosphate-coated Al NPs could be easily transported. This result indicated that electrostatic interactions are important in the transport of MNPs and surface properties should also be incorporated in the consideration of MNP environmental behavior. The authors ([Darlington \*et al.\*, 2009](#)) also observed that the uncoated NPs were increasingly retained in the column during the leaching. This result could not be explained by the electrostatic interactions because the retained positively charged NPs may pose repulsion to the particle in the flow through the column and consequently increased transport of Al NPs should be observed. The authors hypothesized that uncoated Al NPs may form aggregates with time and the larger particles could be more easily settled.

#### 4. ADSORPTION MECHANISM OF ORGANIC CHEMICALS ON MANUFACTURED NANOPARTICLES

Studying the interactions between organic chemicals and MNPs not only provide important information to understand their environmental behavior and risks, but also promote the application of MNPs in various fields, such as in water treatment, environmental analysis, as well as drug

delivery. This section summarizes our current understanding on the adsorption mechanisms of organic chemicals on MNPs. To facilitate the discussion, subsections will be entitled with different types of MNPs.

#### 4.1. Carbon-based nanoparticles

Carbon-based NPs could be viewed as graphite sheet(s) rolling up into different shapes, such as CNTs and fullerene. Their surfaces form systematic benzene ring structures and have very high hydrophobicity. Thus, the adsorption of organic chemicals on CNTs is expected to be very high. However, if compared from adsorption capacity, CNTs did not show significant higher adsorption than AC. It should be noted that the specific surface areas of AC (around  $1000 \text{ m}^2/\text{g}$ ) are several times higher than those of CNTs (generally in the range of  $100\text{--}300 \text{ m}^2/\text{g}$ ). If the adsorption capacity is normalized by specific surface area, the resulted adsorption capacity of a unit surface area ( $Q^{\text{SSA}}$ ) is much higher for CNTs than that of ACs. Because CNTs normally exist as aggregates, the higher  $Q^{\text{SSA}}$  for CNTs indicates that CNTs have very high adsorption potential. If technologies to disperse CNTs are applied, CNT surface area will increase, and possibly their adsorption capacities increase as well.

Studies have indicated that CNTs with a higher degree of oxidation could be easily suspended by ultrasonic ([Templeton et al., 2006](#)). More adsorption sites will be available after CNT dispersion and the adsorption capacity may be increased. On the other hand, CNT aggregation will remarkably decrease their surface area and their adsorption ([Zhang et al., 2009](#)). Up to now, various techniques have been proposed to disperse CNTs, such as ultrasonic ([Templeton et al., 2006](#)), surfactants coating ([Moore et al., 2003](#); [Tan and Resasco, 2005](#)), and NOM adsorption ([Chen and Elimelech, 2007](#); [Hyung et al., 2007](#); [Yang et al., 2009](#)). However, these methods usually alter the surface properties of CNTs and these changes may not always enhance their adsorption capacity. For example, ultrasonic could disperse CNT aggregates and at the same time may oxidize CNT surface ([Templeton et al., 2006](#)). The enhanced surface oxidation was reported to decrease the adsorption for organic chemicals ([Cho et al., 2008](#)). The reasons could be understood from the following two aspects: (1) The hydration shell of oxygen-containing functional groups is much thicker than that of the plain CNT surface, and thus the adsorption of organic chemicals is inhibited. [Zhang et al. \(2009\)](#) observed decreased adsorption of phenanthrene, biphenyl, and 2-phenylphenol on CNTs after surface oxidation. The authors also reported that the surface oxygen contents measured by XPS were higher than those measured using elemental analyzer. Similar data were also reported by [Lin and Xing \(2008a\)](#). This phenomenon indicated that the oxidation mostly occurs on the outer surface of CNT aggregates. Water clusters formed at the outer surface and thus the adsorption of the hydrophobic organic chemicals decreased.

(2) The oxidation of CNTs could increase the polarity of CNT surface. Hence, for some polar compounds, CNT oxidation may increase their adsorption capacity, such as organic chemicals whose adsorption processes are controlled by hydrogen bond or electron-donor-acceptor (EDA) systems ([Lu et al., 2006](#); [Piao et al., 2008](#)). Obviously, the effects of CNT oxidation on their adsorption capacities are highly dependent on the properties of organic chemicals. Therefore, proper classification is needed in order to accurately interpret the interaction mechanisms between organic chemicals and CNTs.

Regarding to desorption hysteresis, different investigators have different points of view. Some of the results showed no obvious desorption hysteresis, such as the data for polyaromatic hydrocarbons ([Yang and Xing, 2007](#)), butane ([Hilding et al., 2001](#)), and atrazine ([Yan et al., 2008](#)). But another group of researchers observed significant desorption hysteresis from small organic molecules (such as methane, ethylene, and benzene) to polymers ([Chen et al., 2002](#); [Pan et al., 2008b](#)). The strongly adsorbed organic chemicals could not be released as washed by organic solvents ([Wang et al., 2002](#)), buffering solution ([Chen et al., 2003](#)), or water ([Shim et al., 2002](#)). This strong interaction was also confirmed using SEM and AFM ([Shim et al., 2002](#); [Wang et al., 2002](#)). The resistant desorption was attributed to the following two reasons: (1) CNT aggregates were rearranged after the adsorption and thus the desorption pathway is different from the adsorption one. For example, fullerene aggregates were reorganized after adsorption of PAHs, and significant desorption resistance was observed ([Yang and Xing, 2007](#)). (2) The strong and exothermic interaction between CNT surface and organic chemicals results in retarded desorption. The desorption is not possible without energy input. For example, the adsorption of bisphenol A and 17 $\alpha$ -ethinyl estradiol on CNTs is through EDA system and significant desorption resistance was observed ([Pan et al., 2007a](#)). The strong EDA interaction may also cause rearrangement of CNT aggregates. Thus, the two mechanisms for resistant desorption may not be explicitly separated.

## 4.2. Inorganic manufactured nanoparticles

In comparison with CNTs, the adsorption of organic chemicals on other NPs was studied in a much lesser extent. Because of their hydrophilic surface, metal oxide NPs were believed to have low adsorption of nonpolar organic chemicals from water. The adsorption of pyrene on MNPs (Al<sub>2</sub>O<sub>3</sub>, ZnO, and TiO<sub>2</sub> NPs, [Wang et al., 2008b](#)) is more than one order of magnitude lower than pyrene adsorption on multiwalled CNTs with diameter of 15 nm (MWCNT 15, [Yang et al., 2006b](#)). [Wang et al. \(2008b\)](#) discussed that a layer of water molecules was chemically adsorbed on mineral particle surface which prevented hydrophobic chemicals from approaching and interacting with oxide surfaces. This is also the reason

that although surface roughness is expected for oxide particles, a linear adsorption of pyrene was observed. Pyrene adsorption on inorganic MNPs is at least one order of magnitude higher than regular particles. Surprisingly, [Fang et al. \(2008\)](#) observed very high adsorption of ZVI NPs for phenanthrene with  $K_d$  values in the range of 84.4–278 L/kg at equilibrated aqueous concentrations of 20–800  $\mu\text{g/L}$ . These values are comparable to the adsorption of phenanthrene on MWCNT 15 ( $K_d$  values in the range of 99–822 L/kg at the same equilibrated aqueous concentration range, [Yang et al., 2006b](#)). ZVI NPs even showed much lower surface area than CNTs (11.2  $\text{m}^2/\text{g}$  vs. 174  $\text{m}^2/\text{g}$ ). The authors did not make this comparison and thus explanation was not provided. But they did compare the adsorption of phenanthrene between different inorganic NPs. They observed linear and reversible adsorption on  $\text{SiO}_2$  NPs which was attributed to their hydrophilic properties. In the contrast, phenanthrene adsorption on ZVI and zerovalent copper (ZVC) NPs was nonlinear and irreversible because of their significantly heterogeneous surface energy distribution patterns. Based on the evidence of pH-dependent adsorption, the authors proposed that hydrophobic effect and dipole interactions were important mechanisms for phenanthrene adsorption on ZVI, ZVC, and  $\text{SiO}_2$  NPs.

For polar or amphiphilic molecules (such as DOM), the adsorption on these inorganic NPs was relatively strong ([Iorio et al., 2008](#); [Yang et al., 2009](#)). The adsorption of NOM on metal oxide NPs is controlled by the properties of these particles. NPs of aluminum oxide, titanium oxide, and zinc oxide showed significant adsorption with NOM, but the adsorption of NOM on silicate oxide NPs could be neglected ([Yang et al., 2009](#)). The adsorption of NOM on metal oxide NPs is mostly controlled by electrostatic interaction and ligand exchange ([Yang et al., 2009](#)). NOM is a complex mixture of small and macromolecule and the adsorption may result in fractionation of chemical fractions and conformation change of their physical organizations ([Hur and Schlautman, 2004](#)). The selective adsorption is also observed for NOM adsorption on metal oxide NPs. Phenol groups tend to be adsorbed on titanium oxide NPs, but carboxyl groups tend to be adsorbed on zinc oxide NPs ([Yang et al., 2009](#)).

Various studies have demonstrated that MNPs could enter organisms through skin, respiratory system, or gastrointestinal tract. The adsorption of enzymes and proteins on MNPs (such as  $\text{TiO}_2$ ,  $\text{Fe}_3\text{O}_4$ , and silica) and the consequent inhibition of enzyme activity can be the major mechanisms of MNP toxicity ([Sun et al., 2009](#); [Wang et al., 2009b](#)). The adsorption mechanisms of enzymes on MNPs include electrostatic interaction, van der Waals force, hydrogen bonds, and possible ligand exchange. The inhibition of enzyme activity was mostly attributed to the conformational change of enzyme macromolecules after adsorbed on NPs ([Kathiravan et al., 2009](#)). Human serum albumin (HSA) fluorescence was attributed to the presence of tyrosine, tryptophan, and phenylalanine residues. [Kathiravan et al. \(2009\)](#)

observed significant blue shift of HSA fluorescence spectra, indicating that HSA conformation was altered to a more polar and less hydrophobic environment around tyrosine residues. A loss in  $\alpha$ -helix content of chicken egg lysozyme structure was observed after adsorption on silica NPs (Vertegel *et al.*, 2004). The fraction of activity lost correlates well with the decrease in  $\alpha$ -helix content.

### 4.3. Natural nanoparticles

NNPs include vastly different types of NPs. This section will selectively discuss the ones that have strong interactions with organic chemicals. The strong nonlinear adsorption and sequestration of organic chemicals on black carbon and soot have been long recognized. This strong interaction leads to the nonideal adsorption between organic chemicals and soils/sediments (Cornelissen *et al.*, 2005; Koelmans *et al.*, 2006). However, naturally derived organic particles also show nonideal interactions with organic chemicals. The purified HA showed very strong nonlinear adsorption (Kang and Xing, 2005; Pan *et al.*, 2007b). Kerogen, which is one of the most condensed organic matter in soils/sediments, has very high adsorption affinity with organic chemicals (Ran *et al.*, 2007).

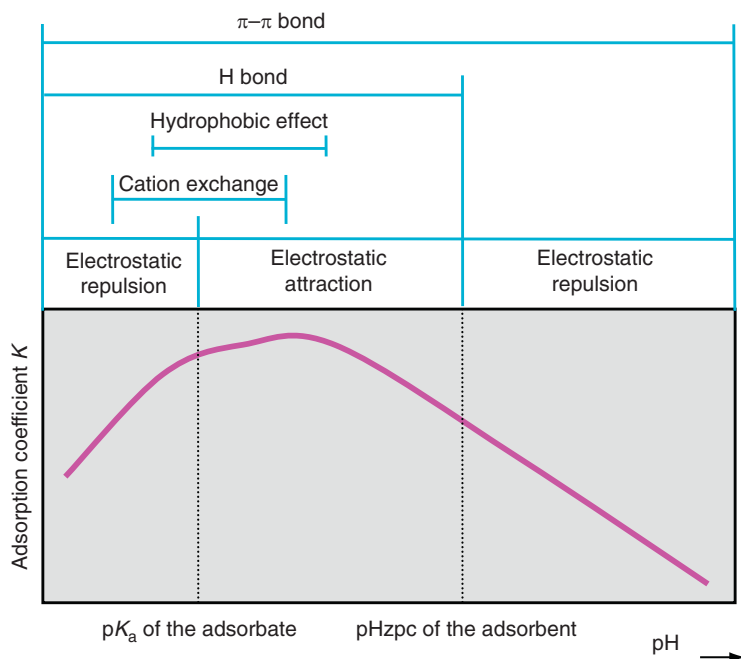
The interaction between dissolved organic matter and organic contaminants is believed to be linear partitioning. However, studies have reported strong evidence that the interaction between NOM and hydrophobic organic chemicals is nonideal as indicated by two stage desorption kinetics (Akkanen *et al.*, 2005; Schlebaum *et al.*, 1998), apparent nonlinear interaction (Eriksson and Skyllberg, 2001), competition with other chemicals and desorption hysteresis (Pan *et al.*, 2007a) for polar and even nonpolar compounds. Since hydrophobic interaction is the main interaction mechanism for nonpolar-NOM interactions, the investigators proposed that discrete hydrophobic microenvironment in NOM may provide adsorption regions with different adsorption energy. Then, adsorption exhibits nonlinear isotherms because of the unevenly distributed hydrophobic regions in terms of interaction energy (Pan *et al.*, 2007a).

### 4.4. Simultaneous functioning of various mechanisms

Various mechanisms have been proposed to be important for organic pollutant adsorption on CNTs. Hydrophobic interaction seems unable to totally explain the adsorption. For example, Chen *et al.* (2007a) reported poor correlations between the adsorption affinity and hydrophobicity of several aromatic derivatives. Pan *et al.* (2007a) also indicated that  $K_{\text{HW}}$  normalized adsorption coefficient varied more than 1000 times for several organic pollutants on CNT. A correlation study between adsorption coefficient and organic chemical properties failed to establish a satisfied

relationship (Pan and Xing, 2008). Obviously, various mechanisms need to be considered. For PAHs, hydrophobic interaction (simply because of CNT hydrophobic surface property) and  $\pi$ - $\pi$  bond (because of the benzene-ring structure of both PAHs and CNTs) are of the major importance (Yang *et al.*, 2006b). For ionizable organic chemical adsorption on CNTs, the involved mechanisms could be diverse. Besides hydrophobic and  $\pi$ - $\pi$  interactions, electrostatic interaction (because of the charged surface of both organic chemicals and CNTs) and hydrogen bond (because of the functional groups on both organic chemicals and CNTs) would all operate.

The discussion on adsorption mechanisms should also compare the adsorption systems at different pHs because  $pK_a$  of organic chemicals and pH<sub>Zpc</sub> of MNPs can affect the magnitude of adsorption. Different adsorption mechanisms may contribute at different pHs as presented in Fig. 4. This figure only discuss the system with  $pK_a$  of organic chemical < pH<sub>Zpc</sub>



**Figure 4** The contribution of different adsorption mechanisms at different pHs. The schematic figure highlights the adsorbent with a specific pH<sub>Zpc</sub> and adsorbate  $pK_a$  < adsorbent pH<sub>Zpc</sub>. At  $pH > pH_{Zpc}$  or  $pH < pK_a$ , electrostatic repulsion may be the dominant interaction mechanisms. H-bond and  $\pi$ - $\pi$  interaction are also possible interaction mechanisms. At  $pK_a < pH < pH_{Zpc}$ , the interaction is much more complicated and may be a combination of electrostatic interactions, cation exchange, hydrophobic effect, H-bond as well as  $\pi$ - $\pi$  interaction. (Reprinted from Zhang *et al.* (2010) with permission of the American Chemical Society).



of MNPs. At  $\text{pH} > \text{pH}_{\text{zpc}}$  or  $\text{pH} < \text{pK}_{\text{a}}$ , the electrostatic repulsion decreases the adsorption as pH increases (when  $\text{pH} > \text{pH}_{\text{zpc}}$ ) or pH decreases (when  $\text{pH} < \text{pK}_{\text{a}}$ ). But at  $\text{pK}_{\text{a}} < \text{pH} < \text{pH}_{\text{zpc}}$ , electrostatic attraction is an important interaction mechanism. In addition, in this pH range, cation exchange, hydrophobic interaction, hydrogen bond,  $\pi$ - $\pi$  interaction, and EDA system could all contribute to the overall adsorption. Hydrogen bond is considered as an attractive force between a hydrogen atom and an electronegative atom, for example nitrogen, oxygen, or fluorine. At pHs higher than  $\text{pK}_{\text{a}}$  of organic chemicals and  $\text{pH}_{\text{zpc}}$  of MNPs, both organic chemicals and MNPs are deprotonated, and thus hydrogen bond is negligible. Therefore, lack of pH-dependent adsorption is an evidence of minimal contribution of hydrogen bond (Chen *et al.*, 2007). It should be noted that there may not be much exchangeable cations on CNTs because of their hydrophobic surface; hence, cation exchange may not be an important interaction mechanism. If a dominant adsorption mechanism was not identified, a complete wrong conclusion may be obtained. For example, if the adsorption is controlled by hydrophobic interaction, CNT oxidation will decrease the adsorption. However, if the adsorption is controlled by hydrogen bond, CNT oxidation will increase the adsorption in the pH range where both organic chemicals and CNTs are not dehydrogenated. Therefore, it is of essential importance to identify the contribution of different adsorption mechanisms at a given environmental condition. However, up to now, the studies only indicate the possible mechanisms. No good methods have been proposed and developed to study and separate the contribution of different mechanisms.

Normalization of sorption coefficient by  $K_{\text{OW}}$  or  $K_{\text{HW}}$  could screen off hydrophobic effect, and thus investigators could focus on the factors other than hydrophobicity (Chen *et al.*, 2007). More directly, sorption experiments could be conducted in organic solvents. For the adsorption of organic chemicals on geosorbents (such as soil and sediment), a fraction of the adsorbent may be dissolvable in organic solvents. Thus, the experiment with organic solvents is not applicable for mechanistic study in those systems, and the data need to be analyzed carefully to exclude the hydrophobic effect (Borisover and Graber, 2002). However, the major portion of CNTs is well defined and the structure is explicit. Moreover, CNTs do not dramatically dissolve in organic solvent because of their rigid structure. Another benefit for the adsorption experiment with organic solvents is to ensure reliable detection by keeping the adsorbate concentration well above the detection limit due to high solubility in organic solvent. Therefore, the comparison of organic pollutant adsorption on CNTs between aqueous system and organic solvent system (such as in hexadecane) will provide important information for quantifying the relative contribution of hydrophobic interaction and other mechanisms.



Another useful method to investigate the adsorption mechanism of organic pollutants on CNTs is to conduct adsorption experiments on CNTs with various functional groups. For example, hydrophobic interaction may be depressed and H-bond may be enhanced after CNT oxidation. Comparison of organic pollutant adsorption on CNTs with different extents of oxidation or different types of functional groups would reveal the importance of individual mechanisms.

Molecular dynamic simulations were applied to investigate the adsorption of organic molecules on CNTs (Star *et al.*, 2001; Woods *et al.*, 2007; Zhao *et al.*, 2003). These methods seem promising in studying the explicit contribution of different mechanisms. However, theoretical simulations often use vacuum conditions, which is different from real environments. The modeling concept should be improved to integrate various environmental conditions.

## 5. MANUFACTURED NANOPARTICLE SORPTION PROPERTIES AS AFFECTED BY NOM

NOM is the decomposition compounds of the residuals of organisms (including animals and plants). These ubiquitous compounds will inevitably interact with MNPs and consequently alter MNP adsorption properties, environmental behavior, as well as their risks. Therefore, this line of study has attracted great research interest. Surface coating, three-phase interaction, and MNP dispersion as affected by NOM will be discussed in this section. The similar effects are also applicable to surfactants and polymers. Therefore, in the following discussion, information regarding surfactants and polymers will also be incorporated.

### 5.1. NOM coating

The interaction between NOM and organic chemicals could alter organic chemical environmental behavior and bioavailability. This research direction has been the focus of environmental scientists for more than three decades. In a typical soil–water system, NOM presents as two main forms. (1) NOM presents as solid phase such as precipitated humic acid and organomineral complex (humins). The adsorption of organic chemicals on these NOMs could decrease the mobility and bioavailability of organic chemicals. (2) NOM exists as dissolved organic matter in aqueous phase. The interaction between organic chemicals and dissolved NOM could enhance the solubility of organic chemicals, decrease their adsorption on solid particles, and possibly increase their environmental risk (Chiou *et al.*, 1986; Pan *et al.*, 2007a; Pan *et al.*, 2008a). In MNP–water system, NOM

may have the similar functions. Generally speaking, NOM coated on MNPs could adsorb organic chemicals on solid phase, while dissolved NOM could increase the solubility of organic chemicals in aqueous phase. However, for different types of MNPs, the apparent adsorption as affected by NOM could be quite different. Carbon-based NPs usually have very strong adsorption with organic chemicals (Pan and Xing, 2008). Thus, the adsorption of NOM on MNP surface may compete with organic chemicals. These interactions result in decreased adsorption of organic chemicals on MNPs (Chen *et al.*, 2008; Wang *et al.*, 2009a). According to relevant studies on activated and black carbon adsorption as affected by NOM coating, adsorption of organic chemicals were decreased through the mechanisms of molecular sieving, pore blockage and the competition between NOM and organic chemicals on the adsorption sites (Kilduff and Wigton, 1999; Kwon and Pignatello, 2005; Pignatello *et al.*, 2006).

But for metal oxides, their surface is hydrophilic and the adsorption of organic chemicals is very low. The MNP adsorbed NOM may adsorb organic chemical more strongly than MNPs themselves. Thus, the resulted apparent adsorption increased in comparison with pure MNPs (Iorio *et al.*, 2008; Li *et al.*, 2008; Yang and Xing, 2009). Li *et al.* (2008) observed significantly increased adsorption of diethyl phthalate (DEP) on both nano- and micro-alumina after NOM coating. The enhancement was more significant for nano-sized alumina. In addition, the adsorption was faster on coated nano-sized particles. These differences were attributed to the smaller size and higher surface area of NPs.

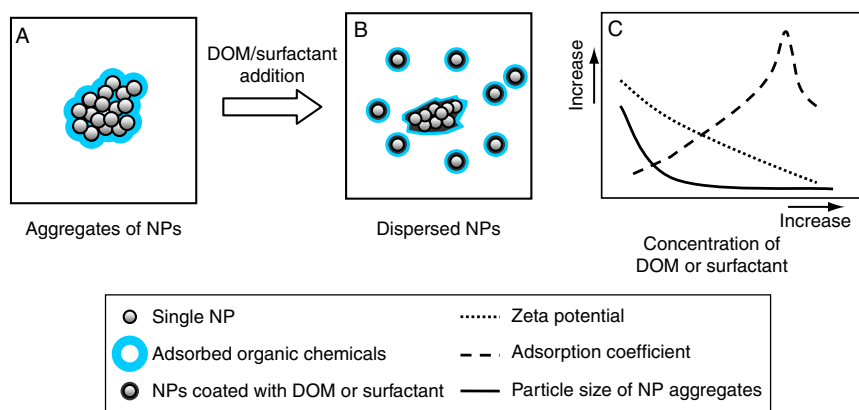
NOM is complex with different chemical components. The molecular weight ranged from thousands to millions Daltons (Schnitzer and Khan, 1978). The adsorption properties on MNPs of different components are different. Thus, fractionation is expected during NOM adsorption on MNPs. In addition, because the interactions between NOM fractions and organic chemicals are different, fractionation could result in significant different adsorption properties of coated NOM on MNPs and aqueous residual NOM (Yang and Xing, 2009). In these studies on NOM fractionation after adsorption on the particles of microscale, arguments exist regarding the fractions that will be selectively adsorbed. For example, aliphatic fraction was reported to be preferentially adsorbed by kaolinite and montmorillonite, while aromatic fraction left in the solution (Wang and Xing, 2005). On the other hand, a priority sorption of aromatic carbons on kaolinite and goethite was presented (Namjesnik-Dejanovic *et al.*, 2000). Different selectivities of NOM fractions on different types of mineral particles were observed in a single study. Polymethylene groups were prevalent at the surface of kaolinite, while aromatic groups on montmorillonite as shown with HR-MAS NMR (Feng *et al.*, 2006). As one can see, the selectivity of NOM fractions is dependent on the properties of mineral particles, such as surface area, functional groups, and charges. This line of study on NOM adsorption on MNPs

is just the beginning. However, the same research framework needs to be carried out for MNPs and the difference between nano-sized and micro-sized particles may provide valuable information to understand the interaction mechanisms between MNPs and NOM.

NOM may interact with MNPs through hydroxyl and carboxyl groups, and thus the physical conformation will be reorganized after coating on MNP surface (Yang and Xing, 2009). MNP-coated NOM showed more condensed structure than original NOM and thus stronger nonlinear interaction is expected (Yang and Xing, 2009). The reconfiguration of NOM on microscale particles results in a membrane-like structure with a hydrophobic interface between NOM and mineral particles (Wershaw, 1993) or a more condensed structure at low NOM loading (Gunasekara and Xing, 2003). Limited evidence is available to validate if these hypotheses are application in NOM adsorption on MNPs.

## 5.2. Three-phase system

Current studies regarding the effect of NOM on MNP–organic chemical interactions mostly focus on the coating of NOM on MNP particles. The interaction between aqueous NOM and organic chemicals has not been well investigated in current studies. As indicated in Fig. 5, at low NOM



**Figure 5** The role of dissolved organic matter (DOM) and surfactants in suspending MNPs and their adsorption for organic chemicals. Surface coated DOM/surfactant may decrease the zeta potential of MNPs (C) and thus facilitate the dispersion of MNP aggregates (B). The aggregate size may be decreased after surface coating. The availability of adsorption sites may be increased because of MNP dispersion. However, because of the interaction between DOM/surfactant and organic chemicals in aqueous phase, the adsorption on solid particles may decrease as DOM/surfactant concentration increase.

concentrations, the adsorption of organic chemicals on MNPs may be increased because of the dispersion (for both CNTs and inorganic NPs) or NOM coating (for inorganic NPs). However, as NOM concentration further increases, the adsorption of NOM on MNPs reaches saturation. In this case, the significant interaction between aqueous NOM and organic chemicals could result in decreased adsorption. Current studies applied limited NOM concentrations in the experimental design, and often reported a decreased adsorption of organic chemicals on CNTs (Ji *et al.*, 2009; Wang *et al.*, 2009a) or increased adsorption on oxide NPs (Iorio *et al.*, 2008) with the addition of NOM. No study was conducted to investigate the possible nonmonotonic influences of DOM on MNP adsorption characteristics.

Nonideal interactions between organic chemical–NOM, NOM–solid particles, and organic chemical–solid particles are a widely recognized phenomenon. These nonideal interactions result in nonlinear adsorption, competitive adsorption, and desorption hysteresis. Incorporation of these processes in organic chemical fate modeling could greatly increase the complexity and uncertainty of the model. Therefore, no study has attempted to completely consider all the processes.

### 5.3. Dispersion of manufactured nanoparticles

MNP aggregation could markedly decrease their available surface area and the convenience (or ease) for engineering processing. Therefore, various methods are proposed and practiced to disperse MNP aggregates. Coating with organic molecules is of the major concern. The practiced organic coatings include surfactants (Jiang *et al.*, 2003), biopolymers, such as alginic acid (Liu *et al.*, 2006), starch (Star *et al.*, 2002), proteins (Karajanagi *et al.*, 2006), phospholipids (Wu *et al.*, 2006) as well as NOM (Hyung *et al.*, 2007; Lin and Xing, 2008b; Lou *et al.*, 2004; Petrov *et al.*, 2003). Because NOM is ubiquitous in the environment, the discussion on NOM dispersing MNPs has generated tremendous research interest. Although ionic strength is another important environmental parameter, the ionic strength is normally less than 0.005 M in soil solution (Black and Campbell, 1982), at which MNP colloidal stability is hardly affected. Therefore, NOM may be a major controlling factor in addition to pH.

Two main dispersion mechanisms were proposed based on the studies on CNT dispersion by surfactants (Han *et al.*, 2008; Moore *et al.*, 2003; Tan and Resasco, 2005). One group of researchers stated that CNTs could be solubilized inside columnar micelles in aqueous solution as a result of energetic sonication of the mixture (O'Connell *et al.*, 2002). Another group of researchers believe that CNTs could not be dissolved in micelles, but the adsorption of surfactant molecules on CNT surface form one layer coating and thus CNT aggregates could be separated (Matarredona *et al.*, 2003).

The main evidence for this mechanism is that CNTs could not be dispersed unless violent disturbance is involved (such as ultrasonic) (Matarredona *et al.*, 2003; Yu *et al.*, 2007). Though exact suspension processes still remain unclear, the “unzippering” type of mechanism of dispersion has been proposed and widely adopted (Bandyopadhyaya *et al.*, 2002; Strano *et al.*, 2003). It is postulated to form gaps or spaces at the bundle ends in the high shear environment of ultrasonicated solution. Surfactant adsorption and diffusion then propagate this space along the bundle length, thereby separating the individual CNTs.

After the adsorption on NOM on MNPs, the zeta potential could decrease and the repulsion between MNPs could increase. Thus, MNP aggregates could be more easily dispersed (Chen and Elimelech, 2007; Hyung *et al.*, 2007; Yang *et al.*, 2009). The presence of NOM at environmentally related concentrations could increase C60 dispersion. After 10 days of mixing, C60 solubility increased to a few to tens of milligrams per liter (Li *et al.*, 2009). The dispersion mechanism was attributed to steric hindrance effect of the adsorbed NOM and the reduced surface hydrophobicity after NOM adsorption.

It is also worth noticing that the extent of MNP suspension is dependent on the properties of NOM. Better dispersion performance of NOM on MNPs was observed for NOM with higher content of surfactant-related component. While carbohydrate-dominated NOM showed much lower dispersion performance on MNPs (Chappell *et al.*, 2009). The properties of NOM to stabilize or destabilize MNP colloids include molecular size, charge, and rigidity of various functional groups (Wilkinson *et al.*, 1997). Up to now, limited study was conducted to relate the ability of NOM to disperse MNPs and NOM properties. Extended work is needed in this direction and the comparison between suspension performances of NOM with different properties may provide important information to understand suspension mechanisms.

Interestingly, NOM may promote the aggregation of MNPs at certain environmental conditions, and the aggregation is also controlled by NOM properties. For example, the coagulation rate of montmorillonite colloids is increased by aquagenic biopolymers, while the addition of fulvic acid could stabilize the colloids (Wilkinson *et al.*, 1997). NOM may disperse MNPs at neutral and alkaline pHs. But at acid pHs, MNPs may be aggregated (Ghosh *et al.*, 2008). At acid pHs, long-chain NOM molecules could form cross-linking structure, then capture MNPs and aggregate them. Short-chain NOM molecules could neutralize the surface charge of MNPs and promote the aggregation (at acid pH, NOM molecules are negatively charged while MNPs are positively charged). In the system with the presence of cations, MNP aggregation could be further promoted. Cations may decrease the repulsion between coated NOM molecules and thus promote aggregation of MNPs. In addition, cations could bridge NOM molecules and cause aggregation of NOM molecules. This enhanced cross-linking of NOM

molecules resulted in bigger network of NOM molecules and their ability to capture MNPs is enhanced (Chen *et al.*, 2006). Therefore, if environmental condition is to be considered, MNP dispersion by NOM becomes more complicated.

MNP dispersion may release more adsorption sites and increase the adsorption with organic chemicals (Carrillo-Carrion *et al.*, 2007; Gotovac *et al.*, 2006; Wang *et al.*, 2008a). Although the dispersion of MNPs by NOM has been widely reported, the adsorption characteristics could not be easily investigated using traditional adsorption experimental design. One of the major reasons is that aqueous/solid separation could not be achieved using centrifugation or normal filtering methods. One possible method for this goal is to apply ultrafiltration (Hyung and Kim, 2008) or dialysis equilibrium system (Pan *et al.*, 2007a) to separate suspended MNPs and the aqueous phase.



## **6. ENVIRONMENTAL MOBILITY OF ORGANIC CHEMICALS AND MANUFACTURED NANOPARTICLES AS AFFECTED BY ADSORPTION**

As discussed earlier, MNP environmental behavior is substantially controlled by their surface properties. The adsorption of organic chemicals could remarkably alter MNP surface properties and thus their mobility. Further, the environmental behavior and risks of organic chemicals will be strikingly changed by MNP adsorption. Therefore, understanding the change of the environmental behaviors of both MNPs and organic chemicals after the adsorption is vital to assess their exposure and risks.

### **6.1. Leaching of manufactured nanoparticles as affected by adsorption of organic chemicals**

Many studies have been conducted to obtain stable MNP suspensions for industrial applications. However, there is very limited information available for MNP dispersion/aggregation behaviors in natural environments, such as in soil and water. Because MNPs tend to aggregate and deposit in water, it may be reasonably expected that MNPs have limited mobility and transport in natural system after their release, hence having low exposure and risk. However, as has been discussed earlier in Section 5, MNPs may be dispersed through various ways in the environment. Dispersed MNPs could be stable in soil suspension for weeks to months without any change in particle size distribution (Gimbert *et al.*, 2007), and thus pose much higher environmental risks in comparison with aggregated MNPs. For example, the adsorption of ciprofloxacin could stabilize CNTs for over 1 month (Kumar and Wang, 2009). The presence of dissolved organic carbon and clay content in soil

solution could facilitate suspending of TiO<sub>2</sub> NPs (Fang *et al.*, 2009). In soil column containing relatively large particles and low solution ionic strength, 18.8–83.0% of the added TiO<sub>2</sub> NPs could pass through the soil columns. The authors estimated that TiO<sub>2</sub> NPs could transport as much as 41.3–370 cm in soil. NOM could decrease the deposition of MNPs in porous media by increasing electrostatic repulsion (Franchi and O'Melia, 2003) and steric repulsion (Jaisi *et al.*, 2008).

The dispersed MNPs may be transported to longer distances, have longer persistence, and potentially facilitate contaminant movement (Sen and Khilar, 2006; Zhuang *et al.*, 2003). In addition, application of MNPs in environmental remediation results in intensive dispersion of MNPs. For example, nano-ZVI particles are now used for groundwater remediation. The efficiency of these particles is restricted because of their aggregation. Therefore, many studies were devoted to investigate effective methods to disperse nano-ZVI. Water-soluble starch (He and Zhao, 2005), hydrophilic carbon or polyacrylic acid delivery vehicles (Schrack *et al.*, 2004), sodium carboxymethyl cellulose (He *et al.*, 2007), and polymers (Saleh *et al.*, 2007) are all used as organic coating to disperse nano-ZVI. The transport of these suspended MNPs is of great research attention for both engineering application and risk assessment of MNPs.

Although most of the studies considered a certain transport distance of MNPs in soil column, the limited MNP transport distance does not mean a zero risk of the retained particles. Even deionized water could rinse out the deposited MNPs (Jaisi *et al.*, 2008). Therefore, the retained particles can be released with the change of pH, ionic strength, DOM concentration, temperature, and flow rate. The redispersion and transport of the retained MNPs in soil column should be investigated in future studies.

## 6.2. Transport of organic chemicals after adsorbed by manufactured nanoparticles

Natural colloid facilitated transport of organic contaminants has been well studied. This line of research is summarized in several valuable reviews (de Jonge *et al.*, 2004; Sen and Khilar, 2006). Although quantitative description of this process is still under investigation, the methodology applied in natural colloids can be used to study organic chemical transport carried by MNPs. MNPs, especially CNTs, could strongly adsorb organic chemicals and directly affect their environmental concentration and behavior. For example, breakthrough of PCB was not observed after 120 pore volume of leaching. However, in the mixture of PCB and fullerene, breakthrough was observed after seven pore volume. Importantly, the leaching curves overlapped for PCB and fullerene. This experiment provided clear evidence that fullerene could enhance the mobility of PCB (Tomson, 2007).

One of the most important factors controlling the transport of organic chemicals as affected by MNPs is the rate of desorption. For example, if the



desorption reaches equilibrium much faster in comparison to MNP transport, the effect of MNPs on organic chemical transportation could be minimal. However, if the desorption rate is very slow, or negligible in comparison to MNP transport, MNPs may markedly enhance organic chemical transport (Hofmann and von der Kammer, 2009). Although the adsorption of organic chemicals on MNPs is being studied widely, few studies examine desorption, especially desorption kinetics. Lack of extensive information on desorption hinders our understanding on the effect of MNPs on organic chemical transport.

Various parameters should be considered in predicting the environmental behavior of organic chemicals in the presence of MNPs. However, because of the limited data from literature, current transport modeling is based on many simplifications, including some important processes. For example, MNPs were assumed to have no interaction with the stationary phase when assessing MNP relevance to organic chemical transport (Hofmann and von der Kammer, 2009). Clearly, this assumption is not valid in most of the environmental conditions, because MNPs could be significantly retained in the matrix through which they pass (Darlington *et al.*, 2009).



## **7. ENVIRONMENTAL EXPOSURE AND RISK OF ORGANIC CHEMICALS AND MANUFACTURED NANOPARTICLES AS AFFECTED BY ADSORPTION**

The adsorption of organic chemicals on MNPs can change the speciation and mobility of organic chemicals in environmental matrixes, and the surface properties and the aggregation state of MNPs. These changes will directly affect the environmental risks of both organic chemicals and MNPs. Therefore, toxicity and exposure studies of MNPs should consider the presence of organic chemicals.

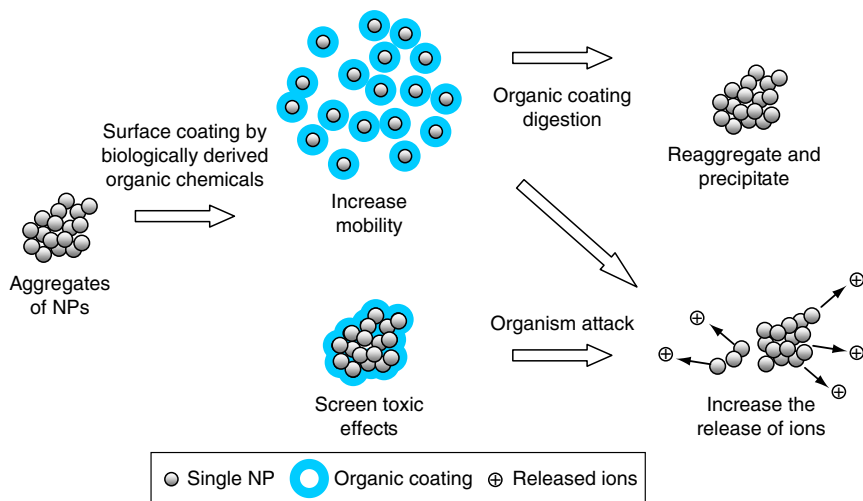
### **7.1. Uptake and toxicity of manufactured nanoparticles to organisms and the effect of organic chemical adsorption**

MNP dispersion by organic chemicals could decrease their aggregate size or even to individual particles, which may increase the penetration of MNPs through bio–nonbio interface. Thus, MNP toxicity may be increased. In addition, the surface properties of MNPs (such as redox reactivity) may be significantly changed after organic chemical coating. Thus, the attachment of MNPs on cell membrane and the electrons retaining by MNPs could all be decreased. All these processes could directly affect the toxicity of MNPs (Dong *et al.*, 2007). On the other hand, the suspension stability was reported to be affected by biological activities. SWCNTs could be well suspended



after being coated with lysophosphatidylcholine (LPC) (Roberts *et al.*, 2007). *Daphnia* activity decreased LPC–SWCNT concentration, indicating a strong effect of *Daphnia* on the solubility of LPC–SWCNTs. The authors proposed that *Daphnia* could ingest the water containing LPC–SWCNTs and utilize the lipid coating as their food source. After being subjected to digestive enzymes in the gut tract, LPC molecules were removed from SWCNT surface and thus, the uncovered SWCNTs may form big aggregates. The aggregated SWCNTs are not able to be taken up by *Daphnia* and dark precipitation was observed in the experiment, which is probably why the authors did not discuss about the toxicity of SWCNTs through uptake, but the accumulation of SWCNTs on the external surface of *Daphnia*. Similarly, other organisms (including grazing and filter-feeding aqueous organisms) as well as biofilms may facilitate the removal of surface coating and cause precipitation of suspended MNPs. This biologically facilitated precipitation could decrease MNP toxicity (Fig. 6).

Organisms may also react with MNPs and increase MNP dispersion or dissolution. For example, bacterial activity may promote the dissolution of ions from MNPs and increase the bioavailability of toxic elements (Ha *et al.*, 2006). In this case, the risk from the released ions instead of MNPs



**Figure 6** Biological process may increase or decrease MNP toxicity. Biologically derived macromolecules could form organic coatings on MNP aggregates. The organic coating may facilitate the dispersion of MNPs and thus increase their mobility, which may consequently increase MNP environmental exposure and risk. On the other hand, the coated organic molecules may screen off MNP toxic effects. Organisms may also digest the organic molecules. The bioactivities may strip the organic coating. MNPs could reaggregate and settle down, which eliminate their toxic effects. However, organisms may also react with MNP surface and promote the release of some toxic ions.

themselves increased. But natural organic coatings (environment-derived macromolecules) may protect MNPs from biological activities and thus extend the existence of MNPs in the environment. Then, the risk of MNPs could be increased. The fate of MNPs in actual environments such as soil and water requires direct field experiments.

## 7.2. Release, bioavailability and toxicity of organic chemicals after adsorption on manufactured nanoparticles

The bioavailability of organic chemicals usually decreased because of their adsorption on solid particles. For example, the toxicity of organic chemicals decreased significantly when they were adsorbed by black carbon (Knauer *et al.*, 2007; Koelmans *et al.*, 2006). However, because MNPs could be absorbed by organisms, various influences should be considered. If MNPs were aggregated and could not be taken up by organisms, the adsorption of organic chemicals on these particles would decrease the bioavailability of organic chemicals. However, if MNPs could be absorbed by organisms, the adsorption of organic chemicals on MNPs may increase the bioavailability. Further, the toxicity of organic chemicals is also dependent on the reversibility of the adsorption. If desorption hysteresis is observed, the adsorbed organic chemicals may show limited toxic effect to organisms. However, if the adsorption is reversible, the concentrated organic chemicals may release in high quantity. Then, MNPs act like a concentrator/collector of organic chemicals (Trojan horse effect) and the environmental risk of organic chemicals could be enhanced distinctively (Yang *et al.*, 2006b).

The effects of MNPs on the toxicity of organic chemicals are dependent on the chemical properties. For example, the bioaccumulation of phenanthrene increased with the addition of fullerene. However, the toxicity of pentachlorophenol decreased with the addition of fullerene. For other chemicals, such as atrazine and methyl parathion, the effect of fullerene on their toxicity was not significant (Baun *et al.*, 2008). Therefore, the effect of fullerene on the toxicity of organic chemicals was not solely controlled by fullerene–pollutant interactions, but also dependent on the mechanisms of toxicity and the physiology of the tested organisms. Another important implication of this study is that the interaction mechanisms between organic chemicals and MNPs need to be incorporated into this type of toxic studies. As we have discussed in previous text, the adsorption/desorption hysteresis is the key process controlling the fraction of the bioavailable chemicals. The four chemicals may bind with MNPs with different strengths and the release behavior from MNPs could be varied substantially. This process could control the toxicity of the chemicals. However, extended discussion could not be presented from the limited information on this topic.

It is interesting to note that uncoated alumina NPs could slightly decrease root elongation but phenanthrene-coated alumina NPs did not

(Yang and Watts, 2005). The authors excluded the possibility that changed NP aggregation size after phenanthrene loading contributed to the decreased toxic effect. Combining evidence from FTIR analysis and DMSO scavenging free hydroxyl radicals, the authors suggested that the loaded phenanthrene could change the surface characteristics of alumina NPs and decrease their toxicity. Therefore, in this study, the toxicity of both phenanthrene and Al NPs was decreased after adsorption. It is not unreasonable to speculate that the toxic effect may be strengthened in the presence of a secondary contaminant, which consequently results in synergistic effect between organic chemicals and MNPs. No evidence on this synergistic effect has been reported, yet.

## 8. SUMMARY AND PERSPECTIVES

### 8.1. Main points

With the fast development and application of nanotechnology, MNP production and discharge are increasing dramatically. From the discussion on MNP classification, application, and occurrence, it is expected that during their life cycle, MNPs can always find their way into the environment and transport in air, water, and soil systems. The interactions between organic chemicals and MNPs control greatly the environmental mobility, exposure, and toxicity and risk of both organic chemicals and MNPs. Among different types of MNPs, carbon-based NPs show the strongest interaction with organic chemicals. Various mechanisms operate simultaneously, including hydrophobic interactions,  $\pi$ - $\pi$  bonds, hydrogen bonds, electrostatic interactions, and cation exchange. Accurate prediction of organic chemical adsorption on MNPs depends on quantitative measurements of the contribution from individual mechanisms to the overall adsorption. The latter clearly merit more investigations.

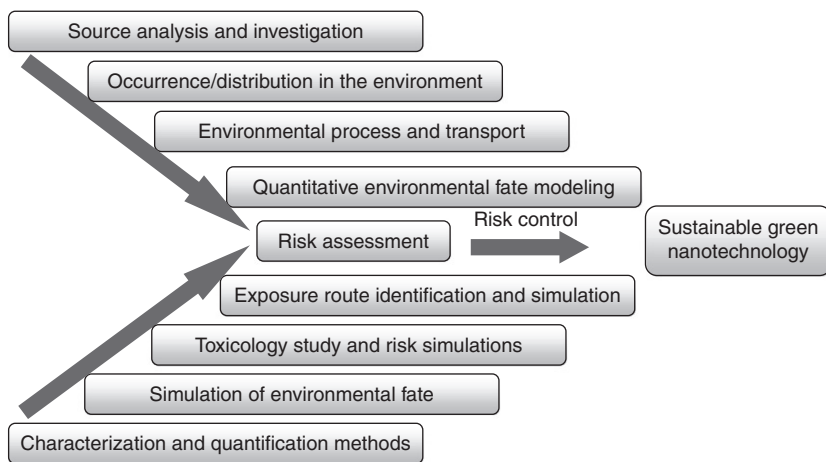
MNP colloidal behavior describes their aggregation status and regulates their adsorption properties. Higher density of MNP surface hydrophilic functional groups (mostly oxygen-containing functional groups), lower ionic strength, and organic coating may facilitate MNP suspension. The suspended MNPs could transport farther than the aggregated ones and thus carry organic chemicals to a longer distance. NOM will interact with MNPs upon contact, thus rendering the MNP colloidal stability, adsorption properties, environmental fate and transport, as well as their exposure and risks. NOM influences should be incorporated in the environmental risk assessment of MNPs.

Adsorption of organic chemicals could suspend MNPs, decrease their aggregate size, increase their mobility, and the possibility of penetrating through biomembranes. On the other hand, the colloidal behaviors of MNPs also determine the leaching and risks of organic chemicals associated with MNPs. Therefore, the adsorption characteristics (with emphasizing on

the contributions of individual mechanisms) and affecting parameters (such as pH, ionic strength, and temperature) should be outlined for organic chemical–MNP interaction in order to properly assess MNP environmental risks. This line of study is an opportunity and a challenge as well to environmental scientists.

## 8.2. Future directions

If we need to accurately assess the environmental risk of this newly emerging material, MNPs, two lines of studies are suggested as displayed in Fig. 7. Firstly, systematic work needs to investigate MNP properties. This type of work focuses on obtaining MNP property parameters and their apparent toxic effect as well as toxicity mechanisms. Another line of study will be the macroscale environmental behavior, including environmental concentrations and distribution in different compartments. The goal of this



**Figure 7** Overall outlook on environmental exposure and risk assessment of MNPs. Two lines of study are suggested. The status of MNPs in the environment needs to be systematically studied for their source, pathways they enter the environment, occurrence, and distribution in environmental compartments. MNP transport among environmental media has to be quantitatively described for a quantitative environmental fate modeling. Another line of study is to develop proper MNP characterization methods (quantitative and qualitative). The mechanisms of MNP interacting with other pollutants as well as their colloidal behavior need to be examined based simulation experiments with different scales. Toxicity study and exposure experiments are fundamental to understand MNP negative effects on ecosystems and the public health. The above mentioned two lines of study should be integrated to comprehensively assess MNP environmental risks and thus the regulatory strategies and policies for sustainable green nanotechnology could be proposed. The interactions between MNPs and organic chemicals are involved in all these processes.

type of study is to quantitatively describe MNP-involved environmental processes. The knowledge of interactions between MNPs and organic chemicals and their environmental implications will facilitate or is advanced by the progresses of all the lines of research outlined in Fig. 7. For example, the development of MNP characterization technologies could improve our understanding on MNP properties, which consequently provide valuable information to explain adsorption data. On the other hand, the adsorption of organic chemicals on MNPs may change MNP surface properties (such as surface charge, surface smoothness and fractal dimension, redox potential, aggregate size, and dispersion) and consequently their environmental exposure and risks. The information on the occurrence and fate of MNPs in the environment help us understand the extent and pattern that MNPs control organic chemical behavior, whereas organic chemical (including NOM) adsorption is an important process determining MNP colloidal behavior and transport. Therefore, studies on organic chemical–MNP interactions are fundamental for the whole framework and several urgently needed studies are discussed in the following paragraphs.

To estimate the environmental behavior and adsorption characteristics of MNPs, it is essential to quantitatively describe their environmental occurrence and physical/chemical properties. Understanding the pathways that MNPs enter the environment during production, storage, application, and disposal (i.e., life cycle) is the very first step. However, because of the lack of reliable MNP quantification techniques and methods, this type of study is at its infancy. Up to date, we do not have enough information to make any accurate estimation of their environmental occurrence and distribution. Several investigators tried to use mass balance calculation and simple distribution process to predict the source and behavior of MNPs (Gottschalk *et al.*, 2009; Mueller and Nowack, 2008). These trials are the only possible method at this stage of research. What makes this line of study more difficult is that the properties of MNPs are diverse, such as particle size distribution, solubility, elemental composition, morphological and crystal structure, surface area, surface charge, impurities, and surface coatings. In addition, MNPs may undergo dispersion–reaggregation, redox reactions and other transformations. All these MNP properties and processes cause uncertainties in recognizing and determining MNP environmental behavior (Isaacson *et al.*, 2009; Tiede *et al.*, 2009).

A general perplexity in understanding organic chemical–MNP interaction is the simultaneous operating of various mechanisms. Because different mechanisms may respond differently to a change in environmental conditions, accurate prediction of organic chemical adsorption on MNPs is not possible without knowing the exact contribution of individual mechanisms to the overall adsorption. This review suggested several ideas to separately measure the contribution of different mechanisms, for example, normalizing adsorption coefficients with  $K_{\text{HW}}$  or  $K_{\text{OW}}$ , performing experiments in

inert organic solvent, investigating adsorption as affected by pH and MNP functional groups, and conducting molecular dynamic simulations.

It is accepted that MNP colloidal behaviors are controlled by NOM coating. Although several studies has been conducted in this direction, it is still unclear what NOM properties affect their coating on MNPs, and how and in what extent NOM coating decrease or increase organic chemical adsorption. Limited information is available on NOM fractionation in aqueous and solid phases after their adsorption on MNPs. Consequently, to comprehensively determine the distribution of a given organic chemical in aqueous residual NOM and MNP-adsorbed NOM is difficult if not impossible.

The extent of organic chemicals on controlling MNP mobility is determined by their ability to suspend MNPs, which is examined in several engineering applications, such as macromolecules to suspend ZVI (He *et al.*, 2007; Saleh *et al.*, 2007), but not from the point of environmental risk. The transport of organic chemicals by MNPs was evaluated borrowing the concept and techniques of organic chemical transport by colloids. However, a few important processes were ignored, such as the interaction between MNPs and stationary phase, kinetic desorption from MNPs, MNP reaggregation and resuspension. Carefully designed experiments emphasizing the difference between MNPs and traditional colloids are demanded.

MNP dispersion affects their toxicity and most of the studies focus on this aspect. However, on the other hand, biological process may also change MNP aggregation state. Few studies recognize the importance of this topic. Thus, more studies are needed to examine the effect of biological processes on MNP surface properties and the change of their adsorption characteristics, and to elucidate how MNP aggregation promoted by biological process is related with organism defense systems to these emerging pollutants.

It is important to emphasize that the study on MNP environmental behavior and risk is not to restrict the development and application of nanotechnology. On the contrary, the goal is to build a guiding system for MNP risk control and promote the development of sustainable green nanotechnology. For this ultimate goal, many blanks are left to be filled. It could be very dangerous without knowing the flip side of MNPs before their wide application and disposal.

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