Occurrence, behavior and effects of nanoparticles in the environment

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Abstract

The increasing use of engineered nanoparticles (NP) in industrial and household applications will very likely lead to the release of such materials into the environment. Assessing the risks of these NP in the environment requires an understanding of their mobility, reactivity, ecotoxicity and persistency. This review presents an overview of the classes of NP relevant to the environment and summarizes their formation, emission, occurrence and fate in the environment. The engineered NP are thereby compared to natural products such as soot and organic colloids. To date only few quantitative analytical techniques for measuring NP in natural systems are available, which results in a serious lack of information about their occurrence in the environment. Results from ecotoxicological studies show that certain NP have effects on organisms under environmental conditions, though mostly at elevated concentrations. The next step towards an assessment of the risks of NP in the environment should therefore be to estimate the exposure to the different NP. It is also important to notice that most NP in technical applications are functionalized and therefore studies using pristine NP may not be relevant for assessing the behavior of the NP actually used.

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1. Introduction

Particles in the nano-sized range have been present on earth for millions of years and have been used by mankind for thousands of years. Soot for instance, as part of the Black Carbon continuum, is a product of the incomplete combustion of fossil fuels and vegetation; it has a particle size in the nanometer—micrometer range and therefore falls partially within the “nanoparticle” domain. Recently, however, nanoparticles (NP) have attracted a lot of attention because of our increasing ability to synthesize and manipulate such materials. Today, nanoscale materials find use in a variety of different areas such as electronic, biomedical, pharmaceutical, cosmetic, energy, environmental, catalytic and material applications. Because of the potential of this technology there has been a worldwide increase in investment in nanotechnology research and development (Guzman et al., 2006). Data on the current use and production of NP are sparse and often conflicting. One estimate for the production of engineered nanomaterials was 2000 tons in 2004, expected to increase to 58,000 tons in 2011—2020 (Maynard, 2006).

The forecasted huge increase in the manufacture and use of NP makes it likely that increasing human and environmental exposure to NP will occur. As a result NP are beginning to come under scrutiny and the discussion about the potential adverse effects of NP has increased steadily in recent years; in fact it has become a top priority in governments, the private sector and the public all over the world (Roco, 2005; Helland et al., 2006; Siegrist et al., 2007). Several reviews have
summarized the recent developments in this field. Most attention has thus far been devoted to the toxicology and health implications of NP (e.g. Oberdörster et al., 2005; Kreyling et al., 2006; Lam et al., 2006; Nel et al., 2006; Helland et al., in press), while the behavior of NP in the environment (Biswas and Wu, 2005; Wiesner et al., 2006; Helland et al., in press) and their ecotoxicology (Colvin, 2003; Moore, 2006; Oberdörster et al., 2006a) have been less often reviewed. However, no systematic description of natural and anthropogenic NP and their occurrence, fate and effects on the environment is yet available. This review therefore gives an overview on the behavior of NP in the environment, both manufactured and unintentionally produced, and also makes comparisons between them and natural NP. The knowledge gained with natural NP will be of invaluable help for assessing the behavior and effects of engineered NP in the environment.

In the following, first certain types of NP, their distribution and prevalence in the environment are highlighted. The analysis of NP is discussed next, followed by selected specific environmental processes in which certain NP play a key role. Finally the effects of NP on organisms and their ecotoxicity are presented.

2. Nanoparticle types

2.1. Classification

Nanotechnology is defined as the understanding and control of matter at dimensions of roughly 1—100 nm, where unique physical properties make novel applications possible (EPA, 2007). NP are therefore considered substances that are less than 100 nm in size in more than one dimension. They can be spherical, tubular, or irregularly shaped and can exist in fused, aggregated or agglomerated forms. Fig. 1 shows how the NP fit into other size-dependent categories that have been used for many decades. The commonly used definition of “dissolved” is in most cases operationally defined by all compounds passing through a filter, in many cases with a cutoff at 0.45 μm. The colloidal fraction is defined as having a size between 1 nm and 1 μm (Buffle, 2006), therefore overlapping with the NP. Separation between dissolved, colloidal and particulate matter in natural waters is normally given by the availability of analytical methods that can distinguish among these fractions without introducing artifacts during the measurement process (Lead and Wilkinson, 2006). Alternatively, Gustafsson and Gschwend (1997a) have also suggested a “chemcentric” definition of colloids and proposed that a colloid is any constituent that provides a molecular milieu into and onto which chemicals can escape from the aqueous solution and whose environmental fate is predominantly affected by coagulation—breakup mechanisms, as opposed to removal by settling. Particles in the atmosphere have normally been classified according to their size, e.g. PM$_{10}$ or PM$_{0.1}$, the latter corresponding to the definition of NP.

NP can be divided into natural and anthropogenic particles (Table 1). The particles can be further separated based on their chemical composition into carbon-containing and inorganic NP. The C-containing natural NP are divided into biogenic, geogenic, atmospheric and pyrogenic NP. Examples of natural NP are fullerenes and CNT of geogenic or pyrogenic origin, biogenic magnetite or atmospheric aerosols (both organic such as organic acids and inorganic such as sea salt). Anthropogenic NP can be either inadvertently formed as a by-product, mostly during combustion, or produced intentionally due to their particular characteristics. In the latter case, they are often referred to as engineered or manufactured NP. Examples of engineered NP are fullerenes and CNT, both pristine and functionalized and metals and metal oxides such as TiO$_2$ and Ag. Engineered NP are the main focus of the current research on NP in the environment, but some of them occur also naturally, e.g. as inorganic oxides or fullerenes. In the sections below the different types of natural and engineered NP are presented.

2.2. Organic colloids

The colloidal matter in natural waters includes particles, macromolecules and molecular assemblies and is defined as having a size of about 1 nm—1 μm (Buffle, 2006), and therefore falls to some extent into the size range of NP. This macromolecular colloidal organic matter is polymeric, polyfunctional and polydisperse (Guo and Santschi, 1997). Environmental colloids include three major types of compounds: inorganic colloids, humic substances and large biopolymers such as polysaccharides and peptidoglycans. Colloids must be seen as an essential building block of the abiotic medium supporting life in general (Buffle, 2006). Although the knowledge of the structure and the environmental impact of natural colloids have significantly increased in recent years, their precise function and composition are still poorly defined.

2.3. Soot

Natural and anthropogenic combustion processes that take place both in stationary and mobile sources emit a wide variety of particles. Of these particles only the so-called “ultra-fine” particles correspond to the standard definition of NP. This review is limited to the “soot” fraction out of the Black Carbon (BC) combustion continuum, and we use soot as the overall term for nano-sized BC. Soot as a product of re-condensation
processes during incomplete combustion of fossil and renewable fuels is mainly emitted into the atmosphere (Goldberg, 1985), from where it distributes hemisphere-wide and is deposited onto soils and water bodies.

Carbon Black (CB) is an industrial form of soot used in various applications such as filler in rubber compounds, primarily in automobile tires. The particle size of CB is partially in the nanometer range with average values between 20 and 300 nm for different materials (Blackford and Simons, 1987; Sirisinha and Prayoonchatphan, 2001; Tscharnuter et al., 2001).

2.4. Natural and unintentionally produced fullerenes and CNT

Although fullerenes and CNT are considered as engineered NP, they are also natural particles (fullerenes) or have close relatives in the environment (CNT). Whereas some of these fullerenes are of interstellar origin that have been brought to earth by comets or asteroids (Becker et al., 1996, 2001), the majority is believed to have formed from polycyclic aromatic hydrocarbons (PAH) derived from algal matter during metamorphosis at temperatures between 300 and 500 °C and in the presence of elemental sulfur (Heymann et al., 2003), or during natural combustion processes.

2.5. Natural and unintentionally produced inorganic NP

Natural inorganic NP can have atmospheric, geogenic or biogenic origin. Inorganic NP are present everywhere in soils and geologic systems (Banfield and Zhang, 2001; Waychunas et al., 2005). NP are also ubiquitous aerosols in the atmosphere and they are precursors for the formation of larger particles, which are known to strongly influence global climate, atmospheric chemistry, the visibility and regional and global transport of pollutants (Anastasio and Martin, 2001). Primary atmospheric NP can be, for example, soil dust and sea salt, although the major mass fraction is composed of coarse particles. The average particle size of airborne mineral dust, based on mass, is between 2 and 5 μm. However, based on the number of particles, the average size is approximately 100 nm with a considerable number below this value (Hochella and Madden, 2005).

A special class of unintentionally produced NP is composed of platinum and rhodium containing particles produced from automotive catalytic converters. Although most Pt and Rh are attached to coarser particles, about 17% was found to be associated with the finest aerosol fraction (<0.43 μm) (Zereini et al., 2001).

2.6. Engineered fullerenes and CNT

Of the large family of fullerenes, the buckminsterfullerene C_{60} is by far the most widely investigated. Fullerenes are mainly proposed to be used in fullerene—polymer combinations, as thin films, in electro-optical devices and in biological applications (Prato, 1999; Bosi et al., 2003). Due to the low water solubility of fullerenes, a lot of research is devoted to functionalization and a myriad of derivatives of C_{60} has been synthesized which all have their peculiar characteristics and properties (Wudl, 2002).

Carbon nanotubes (CNT) are considered as the hottest topic in physics (Giles, 2006). Depending on the synthesis method, the technique used for the separation from the amorphous by-products, subsequent cleaning steps, and finally different
functionalizations, a variety of different CNT are obtained that have very different properties (Dai, 2002; Niyogi et al., 2002). Especially biological and medical applications explore the potential of modifying the properties of CNT (Bianco and Prato, 2003).

Both fullerenes and CNT therefore have to be considered as a class of compounds where each single fullerene or CNT can have very different properties depending on the functionalization or the synthesis and cleaning method. This will have important implications for assessing the environmental behavior of these compounds.

2.7. Engineered polymeric NP

NP synthesized from organic polymers have gained widespread interest in medicine as carriers for drugs. The possibility to control size, surface charge, morphology and composition make polymers especially well suited for designing NP with tailored properties. These NP are taken up by a wide variety of cells and are studied for their ability to cross the blood–brain barrier (Kozia et al., 2003).

Several types of polymeric NP have also been developed and proposed for soil and groundwater remediation. Micelle-like amphiphilic polyurethane particles have a hydrophilic outer side and a hydrophobic inner core and are therefore very well suited for the removal of hydrophobic pollutants (e.g. phenanthrene) from soils (Kim et al., 2000, 2003a,b; Tungtithplakorn et al., 2004, 2005). The NP are able to extract the PAH in a similar manner to surfactant micelles but unlike the micelles they do not sorb to soil particles. Another polymeric nanoscale material is dendrimers that function as water-soluble chelators (Xu and Zhao, 2005, 2006).

2.8. Engineered inorganic NP

Engineered inorganic NP cover a broad range of substances including elemental metals, metal oxides and metal salts. Elemental silver is used in many products as bactericide (Morones et al., 2005), whereas elemental gold is explored for many possible applications and its catalytic activity (Brust and Liely, 2003). Metallic iron is very effective in degrading a wide variety of common contaminants such as chlorinated methanes, brominated methanes, trihalomethanes, chlorinated ethenes, chlorinates benzenes, other polychlorinated hydrocarbons, pesticides and dyes (Zhang, 2003). Successful results from field demonstrations using nZVI have been published, with injection of 1.7–400 kg of NP into the groundwater (Elliott and Zhang, 2001; Quinn et al., 2005). To date approximately 30 projects are under way where nZVI is used for site remediation (Li et al., 2006a).

Nanoparticulate metal oxides are among the most used NP (Aitken et al., 2006). Bulk materials of TiO₂, SiO₂ and aluminum and iron oxides have been produced for many years. However, recently they have also been manufactured in nano-sized form and have already entered the consumer market, e.g. ZnO in sunscreens (Rittner, 2002). TiO₂ NP are widely used for applications such as photocatalysis, pigments and cosmetic additives (Aitken et al., 2006).

A wide variety of other nanomaterials is under vigorous investigation by materials scientists. Nano-sized zeolites (Larbus et al., 2006), clays (Yaron-Marcovich et al., 2005) and ceramics (Cain and Morrell, 2001) are other NP that have been proposed for various applications. Several non-carbon nanotubes have also been synthesized (Pokropivnyi, 2001), for example, TiO₂ (Zhang et al., 2006). Quantum dots made from semiconductor materials such as CdSe, CdTe or ZnS have attracted wide interest in areas such as information technology, molecular biology and medicine (Gao et al., 2004).

3. Analysis of NP

3.1. Organic colloids

Today the development of analytical methods for engineered NP is still in its infancy. More experience is available on aquatic colloids (Lead and Wilkinson, 2006) and it is expected that many of the techniques applied there will also be useful for the determination of engineered NP. Several approaches have been used for aquatic colloids (Lead and Wilkinson, 2006): microscopic methods (e.g. electron microscopy, atomic force microscopy), size fractionation (e.g. ultrafiltration, field-flow fractionation (FFF) or centrifugation) and chromatography (e.g. size-exclusion or gel permeation chromatography (SEC and GPC)). The standard methods for separating colloids and particles are currently cross flow filtration, but FFF has gained increasing importance for the separation and characterization of aquatic colloids due to the ease of coupling the FFF to sensitive detection techniques such as ICP-MS (Lyven et al., 2003; Stolpe et al., 2005). Also laser-induced breakdown detection (LIBD) has been used to quantify natural aquatic organic NP in lake and drinking water samples (Wagner et al., 2003, 2004).

3.2. Black Carbon/soot

Extensive evaluations of methods for BC quantification in soils and sediments are available (summarized in Cornelissen et al., 2005). BC quantification methods in soils and sediments roughly fall into three categories: optical, thermal, and chemical. The first ones mainly resort to organic-petrographic or classical light microscopes and will not be discussed here further, as they are mainly restricted to BC particles >5–10 μm. In most methods, non-BC organic matter is first removed by selective oxidation (thermal or chemical). The remaining carbon residue is defined as BC and is quantified by various detection methods such as microscopic particle counting, titration, coulometry, ¹³C NMR, molecular marker analysis, or elemental analysis. The most important method artifacts are organic matter charring (overestimation of BC contents), and losses of soot BC during solution handling and “overoxidation” (underestimation).
Currently, the chemo-thermal oxidation at 375 °C (CTO; e.g., Gustafsson et al., 1997, 2001a; Elmquist et al., 2004) is a frequently used method and selective for the soot fraction of BC. Despite its possible limitations, this method has provided BC results for sediments that are consistent with geochemical characteristics. For instance, the spatial distribution of pyrogenic compounds such as PAH and polychlorinated dibenzodioxins and furans (PCDD/Fs) shows stronger correlations with BC than with bulk TOC contents (e.g., Gustafsson and Gschwend, 1997b; Gustafsson et al., 1997; Persson et al., 2002), and the 14C isotopic composition of CTO-isolated BC was identical to that of PAH but quite distinct from that of TOC in both sediments and aerosols (Gustafsson et al., 2001a; Reddy et al., 2002). Further, certain molecular combustion markers correlated significantly with CTO-isolated BC contents, but not with TOC in a set of Swiss soils (Bucheli et al., 2004).

3.3. Engineered carbon-containing NP

Quantification of C60 is usually performed by UV–vis measurements for high concentrations. Absorption bands of C60 are located at 336, 407, 540, and 595 nm, but this method is only applicable to defined laboratory systems. HPLC is used for the detection of low concentrations of C60 (Fortner et al., 2005) but also a method for the direct analysis by electrospray time-of-flight mass spectrometry has been developed (Kozlowski et al., 2004). The HPLC method has been used to detect fullerenes in natural samples, e.g. rocks and minerals (Becker et al., 1994; Heymann et al., 1995; Chijiwa et al., 1999).

No method for the quantification of CNT in natural media exists so far. Electron microscopy has been used to identify CNT in ice cores, but no quantification was done (Esquivel and Murr, 2004; Murr et al., 2004b,c). Several methods exist to analyze CNT under well-defined laboratory settings. The quantification is normally performed by UV–vis spectrometry at high concentrations (Sano et al., 2001; Jiang et al., 2003). CNT show strong absorption in the UV and visible region with peaks at 253 nm (Jiang et al., 2003), 266 nm (Liu et al., 2006a), 350 nm (Sano et al., 2001) and strong absorption extending up to 1200 nm (Karajanagi et al., 2006; Liu et al., 2006a). Wrapping of CNT with conventional fluorophores (Prakash et al., 2003; Kim et al., 2006), fluorescent polymers (Didenko et al., 2005) or with DNA-oligonucleotides (Heller et al., 2005) allowed their detection in biomedical applications. SEC with UV-detection was used for the separation of CNT from impurities and amorphous carbon (Duesberg et al., 1998a, 1999; Niyogi et al., 2001; Zhao et al., 2001). As mobile phase both organic solvents and aqueous solutions were applied.

3.4. Natural and engineered inorganic NP

Many techniques have been used to identify and characterize natural inorganic NP (Burleson et al., 2004). The ones most often used are transmission electron microscopy and scanning probe microscopy; images of individual NP can be obtained with both techniques. However, only a minute fraction of material is characterized, which means that it can be extremely difficult to ensure that a representative sample is examined. Also the sample preparation and the measurement conditions can often change the structure of the NP (Burleson et al., 2004). These methods have been used to detect NP produced by bacteria isolated from soils, sediments and waters.

Almost no reports about the analysis of inorganic engineered NP have been published so far. One study presents the characterization of CdSe quantum dots by SEC (Krueger et al., 2005). FFF was used to monitor the stability of nano-ZnO in soil suspension (Gimbert et al., 2007).

4. Formation, emission, occurrence and fate of NP in the environment

4.1. Overview

Assessing the risks imposed by the use of nanomaterials in commercial products and environmental applications requires a better understanding of their mobility, bioavailability, and toxicity. For nanomaterials to comprise a risk, there must be both a potential for exposure and a hazard that results after exposure. The important processes and pathways of NP in the environment are depicted in Fig. 2. Release of NP may come from point sources such as production facilities, landfills or wastewater treatment plants or from nonpoint sources such as wear from materials containing NP. Accidental release during production or transport is also possible. In addition to the unintentional release there are also NP released intentionally into the environment. nZVI, for example, is directly injected into groundwater polluted with chlorinated solvents. Whether the particles are released directly into water/soil or the atmosphere, they all end up in soil or water, either directly or indirectly for instance, via sewage treatment plants, waste...
handling or aerial deposition. In the environment the formation of aggregates and therefore of larger particles that are trapped or eliminated through sedimentation affects the concentrations of free NP (Fig. 3). Humans can be either directly influenced by NP through exposure to air, soil or water or indirectly by consuming plants or animals which have accumulated NP. Aggregated or adsorbed NP will be less mobile, but uptake by sediment-dwelling animals or filter feeders is still possible. Whereas the possibility of biomagnification of NP in the food-chain has been mentioned (EPA, 2007), no data are currently available.

4.2. Organic colloids

Colloidal organic matter is regularly around 10 times more abundant than larger particulate organic matter (filter defined >0.7 μm) in surface seawater (Sharp, 1973; Benner et al., 1992), and makes up about 10–40% of the filter passing DOC (Gustafsson et al., 2001b). Aggregation of colloids in water bodies and settling eliminates compounds from the water column and in soils the aggregation leads to porous microstructures that are essential for the development of microorganisms and for nutrient bioavailability. Colloids have also significant effects on pollutant, nutrient and pathogen chemistry, transport and bioavailability and may themselves be bioavailable (Lead and Wilkinson, 2006). They are internally and externally porous and charged. The overall charge is a function of pH and ionic strength and the surface is also hydrated to a variable degree, with hydrophilic and hydrophobic regions.

4.3. Soot

Incomplete combustion of fossil fuels leads to re-condensation reactions in the gas phase that produce highly aromatic globular structures in grape-like aggregates (soot) (Goldberg, 1985). Besides soot, incomplete combustion of biomass also yields less structured, carbonized residues from parental materials (chars, charcoal). The characteristics of BC vary widely (Goldberg, 1985; Middelburg et al., 1999; Schmidt and Noack, 2000; Morawska and Zhang, 2002), but generally, BC particles have a three-dimensional structure composed of stacked aromatic sheets, particle sizes in the nanometer—micrometer range, high but variable specific surface areas ranging from 2 to 776 m²/g, and sometimes plant residues (Cornelissen et al., 2005). Estimates of BC production from biomass burning range from 0.05 to 0.27 Gt/year (Kuhlbusch and Crutzen, 1995) and from fossil fuel combustion from 0.012 to 0.024 Gt/year (Penner et al., 1993). Reliable data on inventories of soot as a fraction of BC in final recipient media such as sediments and soils are largely missing or highly uncertain.

4.4. Fullerenes and CNT

Fullerenes have been detected in geological materials dating back 1.85 billion years (Becker et al., 1994). Most notably fullerenes are present in clays from the Cretaceous/Tertiary and the Permo-Triassic boundary, where they are believed to have formed in the extensive wildfires that resulted from the meteorite impact (Heymann et al., 1994; Chijiwa et al., 1999). Fullerenes have also been found in fulgurites, a glassy rock that forms when lightning strikes the ground (Heymann et al., 2003). CNT and fullerenes also occur in 10,000-year-old ice cores from Greenland (Esquivel and Murr, 2004; Murr et al., 2004b,c), indicating that even before the widespread use of fires by humans these compounds were present in ambient air. Natural CNT have been found in a coal—petroleum mix extracted from an oil well (Velasco-Santos et al., 2003). This finding shows that high temperature is not a prerequisite for synthesis of CNT, but that they can be produced under natural and albeit geologic conditions of elevated pressure and temperature. CNT have also been sampled from fuel-gas combustion streams (Bang et al., 2004; Murr et al., 2004a) and can be formed in alloys and steels during production and processing (Chernozatonskii et al., 1997; Reibold et al., 2006).

Fullerenes also occur in emissions from coal-burning power plants (Utsunomiya et al., 2002), in petrol, diesel and fuel-gas soot (Ishiguro et al., 1997; Lee et al., 2002; Murr and Soto, 2005). They have also been found in quite high concentrations (3 mg/kg to 1 g/kg) in Chinese ink sticks made from soot obtained by the slow burning of oils (Heymann et al., 2003). The stability of the fullerenes under geologic conditions for hundreds of millions of years shows that they are truly recalcitrant in the environment. However, this also implies that life has been exposed to low concentrations of these compounds for hundreds of millions of years.

Pristine fullerenes are virtually insoluble in pure water (Heymann, 1996; Beck and Mandi, 1997), but fullerenes derivatized with ionizable or hydrophilic groups exhibit a much greater water solubility (Wudl, 2002). Not derivatized fullerenes can be solubilized in water by forming clusters of C₆₀ with a size of about 25–500 nm (nC₆₀; nano-C₆₀). The color, hydrophobicity, and reactivity of individual C₆₀ are substantially altered in this aggregate form. These aggregates are crystalline in order and remain as underivatized C₆₀.

![Fig. 3. Release of NP from products and (intended or unintended) applications:](image-url)
throughout the formation/stabilization process that can later be chemically reversed (Fortner et al., 2005). The standard method of producing nC_{60} clusters uses C_{60} dissolved in organic solvents (Scrivens et al., 1994; Deguchi et al., 2001; Fortner et al., 2005), but it is also possible to produce nC_{60} by extended vigorous mixing (several weeks to months) of C_{60} in water (Brant et al., 2005; Labille et al., 2006). The particle size can be affected by formation parameters such as the pH of the water. Once formed, nC_{60} remains stable in solution at or below ionic strengths of 0.05 I for months. nC_{60} carry a strong negative charge (zeta potential of about –50 mV) and they remain negatively charged in the presence of monovalent and also divalent cations such as Ca and Mg in the concentration range between 0.01 and 10 mM (Brant et al., 2005). The zeta potential increased to zero at about 100 mM ionic strength (Brant et al., 2005), resulting in aggregation into even larger clusters, whereas at lower concentrations the size of nC_{60} remained constant (Fortner et al., 2005). The negative charge of nC_{60} is likely acquired through charge transfer from an organic solvent or surface hydrolysis reactions involving the hydration shell of the cluster and the strong electron-accepting properties of C_{60} (Brant et al., 2005). Almost all studies of the environmental behavior and effects of fullerenes have been carried out with this form of C_{60}.

Single, dissolved molecules of fullerenes are also formed by interaction with host molecules. Cyclodextrin, for example, can solubilize C_{60} in a host–guest interaction (Andersson et al., 1992; Sundahl et al., 1993). Fullerenes are also easily taken up by micellar or colloidal solution of tensides (e.g. Triton X-100) or phospholipids (Hungerbuhler et al., 1993; Beeby et al., 1994; Bensasson et al., 1994; Guldi et al., 1994).

Untreated CNT as received from the producing companies are not dispersable in water (Chen et al., 2004). A standard procedure for solubilizing CNT is cutting pristine CNT in strong acid under sonication. The resulting shortened CNT are hydroxyalted at the ends and at defects and can reasonably well be suspended in water, however, they rapidly aggregate in the presence of cations (Sanó et al., 2001). Solubilized CNT can be obtained in a similar way to the fullerenes by interaction with organic molecules, e.g. by wrapping them with linear polymers such as surfactants (Duesberg et al., 1998b; Jiang et al., 2003; Moore et al., 2003). Biopolymers such as alginate acid (Liu et al., 2006b), starch (Star et al., 2002), proteins (Karajanagi et al., 2006) and phospholipids (Wu et al., 2006) have been found to solubilize CNT. A recent study shows that humic and fulvic acids are able to solubilize single CNT and that a stable suspension in water containing humic acids can be obtained (Hyung et al., 2007).

Underivatized CNT were reported to have a point of zero charge of around pH 7 and a zeta potential of less than 30 mV (Hu et al., 2005). Acid-treated and therefore hydroxylated CNT were negatively charged over the whole pH range with a zeta potential between –30 and –70 mV (Hu et al., 2005). The low or even absent charge on pristine CNT around neutral pH values is the main reason for their inability to form a stable suspension in water.

4.5. Natural inorganic NP

Nucleation is a process that can result in the formation of secondary aerosols, which are to a large extent in the nanoparticulate size range (Biswas and Wu, 2005). The key species in the atmosphere are sulfuric acid, nitric acid and organic gases. The growth of the NP is the main process that affects their lifetime in the atmosphere, accomplished by the condensation of low volatile gases, coagulation with other NP and surface reactions that increase particle mass (Anastasio and Martin, 2001). Anthropogenic emissions have more than doubled the flux of fine particles into the atmosphere (Anastasio and Martin, 2001). The dominant anthropogenic source is primary emissions from combustion sources and secondary aerosol formation from the oxidation of species such as gaseous SO2 or organic compounds (Kittelson, 1998).

Chemical weathering processes of silicates, oxides and other minerals frequently produces NP such as amorphous silica, hydrous aluminosilicates such as allophane, clays such as halloysite, and oxides such as magnetite and hematite. UO_2 NP particles are formed by reaction of uranyl with green rust, a Fe(II)/iron(III) phase (O’Loughlin et al., 2003). In acid mine drainage, the very low pH solutions derived from weathering of sulfide-rich rocks forms a variety of different NP when mixed with natural waters due to changes in temperature, pH and higher oxygen concentrations. Ferrhydrate, amorphous iron oxide, and goethite (a-FeOOH) are typical examples of NP formed during this process. Polynuclear complexes and nanoclusters of aluminum, e.g. Al_{13} or Al_{30} (Casey et al., 2001; Furrer et al., 2002), and of sulfides, e.g. Cu_S nanoclusters, have been found in natural waters.

Microorganisms can also generate NP through the generation of metabolic energy by pathways involving inorganic ions that participate in redox reactions. Oxidation of Fe(II) results in the formation of iron oxide NP. A variety of different manganese oxide NP are formed, both inside and outside the cell (Matsunaga and Sakaguchi, 2000). Also sulfides can be produced by the action of sulfate-reducing bacteria, e.g. ZnS, but also UO_2 NP have been observed on the surface of bacteria (Gilbert and Banfield, 2005).

The physical properties (e.g. melting point, electrical conductivity) and reactivity (e.g. catalytical activity, sorption capacity) of such NP vary dramatically as a function of size and can be very different from the bulk material (Madden and Hochella, 2005). The minerals in the size range of approximately a few to several tens of nanometers are in the transitional range where properties are expected to be variable and deviate from bulk behavior (Waychunas et al., 2005).

5. Selected specific processes of NP in the environment

5.1. Aggregation of organic colloids and NP in water

In the environment natural colloids or NP interact among themselves and with other natural NP or larger particles (Figs. 2 and 3). The formation of aggregates in natural systems can be understood by considering physical processes, i.e.
Brownian diffusion, fluid motion and gravity. Aggregation is particle-size dependent and results in efficient removal of small particles in environmental systems (Omelia, 1980). To quantify the stability of NP in the environment we have to predict the stability of their suspension and their tendency to aggregate or interact with other particles (Mackay et al., 2006). Twenty nanometer-sized nZVI particles aggregated, for example, within 10 min to micrometer-sized clusters (Phenrat et al., 2007). The nature of the NP is modified by adsorption processes (Fukushi and Sato, 2005) and especially the surface charge plays a dominant role (Kallay and Zalac, 2001, 2002). Cations, for example, are able to coagulate acid-treated CNT with critical coagulation concentrations of 37 mM for Na, 0.2 mM for Ca and 0.05 mM for trivalent metals (e.g. La\(^{3+}\)) (Sano et al., 2001). Aggregation of CNT added as suspension to filtered pond water has been reported (Zhu et al., 2006c).

NP are not necessarily released as single NP (see Fig. 3). In many applications NP are embedded in a matrix and release of NP will occur through release of matrix-bound NP (Koehler et al., in press). As many NP are functionalized, release of functionalized NP is also possible. In the environment the released NP are affected by environmental factors such as light, oxidants or microorganisms. This can result in chemical or biological modification or degradation of the surface functionalization or the embedding matrix and may result in free NP. The surface of pristine NP can also be modified by environmental factors (e.g. coating by organic matter) or functionalized by chemical or biological processes. The effect of humic and fulvic acids to inhibit the aggregation of CNT has been recently shown (Hyung et al., 2007) and also nZVI is efficiently coated with humic acids (Giasuddin et al., 2007). Nanoparticulate ZnO which was coated with the surfactant sodium dodecyl sulfate was stable in soil suspension for 14 days without changes in particle size distribution (Gimbert et al., 2007).

5.2. Behavior of NP in porous media

The transport of colloids in porous media and the colloid-facilitated transport of contaminants have received a lot of attention in the past (McGechan and Lewis, 2002; Sen and Khilar, 2006). The movement of colloids — and therefore also of NP — in porous media is impeded by two processes: straining or physical filtration where the particle is larger than the pore and is trapped and true filtration where the particle is removed from solution by interception, diffusion and sedimentation. However, particles removed from solution by such processes can readily become resuspended upon changes in the chemical or physical conditions (e.g. changes in pH, ionic strength, flow rate) (Sen and Khilar, 2006).

Several studies have investigated the transport of a wide range of engineered NP through porous media (Lecoanet et al., 2004; Lecoanet and Wiesner, 2004; Dunphy Guzman et al., 2006). Particles smaller than 100 nm are predicted to have very high efficiencies of transport to collector surfaces due to Brownian diffusion. If all particle-collector contacts were to result in particle attachment to the collector, these small particles would be retained to a large extent by the porous medium. However, nano-sized silica particles were not appreciably removed and also anatase NP were only removed between 55 and 70%, depending on the flow velocity (Lecoanet and Wiesner, 2004). Fullerol (hydroxyxylated fullerene) and surfactant-stabilized CNT were almost completely mobile and only removed to a very low percentage (Lecoanet et al., 2004). The most efficient removal was observed for an iron oxide and for fullerene clusters (nC_{60}). The deposition efficiency for nC_{60} increased with time and after 60 pore volumes virtually no nC_{60} were detected in the effluent, an effect ascribed to “filter ripening”, the increased filter efficiency by deposition of particles (Cheng et al., 2005a). These studies show that the collector efficiency for NP can be very different and that especially the surface-modified NP displayed high mobilities. Also the environmental conditions are important, though, and efficient removal of titania NP was observed close to the pH at the point of zero charge (Dunphy Guzman et al., 2006).

Because the nZVI particles used for groundwater remediation have the strong tendency to aggregate and adsorb to surfaces of minerals, a lot of effort has been directed towards methods to disperse the particles in water and render them mobile. In one approach water-soluble starch was used as stabilizer (He and Zhao, 2005); in another hydrophilic carbon or polyacrylic acid delivery vehicles were used (Schrick et al., 2004). Modified cellulose, sodium carboxymethyl cellulose (CMC) was found to form highly dispersed nZVI (He et al., 2007) and also several polymers have been tested and found to be very effective (Saleh et al., 2007). These modified NP were found to be mobile under natural conditions, indicating the importance of knowing the exact surface properties of NP for a prediction of their potential mobility in the environment.

5.3. NP as adsorbents

The unique structure and electronic properties of some NP can make them especially powerful adsorbents. Dissolved organic carbon and organic colloids in the sub-micron size range have been recognized as a distinct non-aqueous organic phase to which organic pollutants are partitioning (Burkhard, 2000), which leads to their reduced bioavailability. Most data on dissolved organic carbon partition coefficients (\(K_{DOC}\)) are available for PAH. In general, \(K_{DOC}\) values for any individual compound vary widely over several orders of magnitude, depending on the characteristics of the sorbents such as size, conformation, and chemical composition, and probably also the experimental method applied. Moreover, they are significantly lower than predictions from octanol–water partition coefficients and partitioning relationships developed primarily from natural organic matter of sediments and soils (Burkhard, 2000). Still, by their shear abundance, such sorbents may significantly attenuate the truly dissolved exposures of organic pollutants. Note also that the partitioning of organic pollutants into colloidal organic carbon is not restricted to hydrophobic organic pollutants such as PAH, but also of relevance for
more polar compounds such as steroid hormones (Zhou et al., 2007a) or modern herbicides (Irace-Ouigand and Aaron, 2003). The distribution of metal ions between solution and colloids strongly influences metal speciation and therefore metal bioavailability (Lead and Wilkinson, 2006). Colloids act therefore as metal buffer that keep free metal ions, e.g. of Cu$$^{2+}$$, within a range that is beneficial for life.

Also soot is a powerful adsorbent for organic compounds. The nonlinear adsorption of organic compounds onto BC can completely dominate total sorption at low aqueous concentrations in soils and sediments (Cornelissen et al., 2005). The extremely efficient sorption to BC pulls highly toxic polycyclic aromatic hydrocarbons, polychlorinated biphenyls, dioxins, polybrominated diphenylethers and pesticides into sediments and soils (Koelmans et al., 2006). The increased sorption is general but strongest for planar and most toxic compounds at environmentally relevant, low aqueous concentrations. The presence of BC can explain that the sorption of organic compounds into soils and sediments is much higher than expected based on adsorption into organic matter alone (Cornelissen et al., 2005).

CNT have received a lot of attention as very powerful adsorbents for a wide variety of organic compounds from water. Examples include dioxin (Long and Yang, 2001), PAH (Gotovac et al., 2006; Yang et al., 2006b,c), DDT and its metabolites (Zhou et al., 2006c), PBDEs (Wang et al., 2006), chlorobenzenes and chlorophenols (Peng et al., 2003; Cai et al., 2005), tribhalomethanes (Lu et al., 2005, 2006), bisphenol and nonylphenol (Cai et al., 2003b), phthalate esters (Cai et al., 2003a), dyes (Fugetsu et al., 2004), the pesticides thiamethoxam, imidacloprid and acetamiprid (Zhou et al., 2006a) and the herbicides niclosulfuron, thifensulfuron, metsulfuron, triasulfuron (Zhou et al., 2006b, 2007b), atrazine and simazine (Zhou et al., 2006d), and dicamba (Biesaga and Pyrzynska, 2006). It was found that purification (removal of amorphous carbon) of the CNT improved the adsorption (Gotovac et al., 2006). The available adsorption space was found to be the cylindrical external surface, neither the inner cavity nor the inter-wall space of multi-walled CNT contributed to adsorption (Yang and Xing, 2007). Different to fullerene no adsorption—desorption hysteresis was observed, indicating reversible adsorption (Yang and Xing, 2007).

Oxidized and hydroxylated CNT are also good adsorbers for metals. This has been found for various metals such as Cu (Liang et al., 2005a), Ni (Chen and Wang, 2006; Lu and Liu, 2006), Cd (Li et al., 2003; Liang et al., 2004), Pb (Li et al., 2002, 2006b), Ag (Ding et al., 2006), Am(III) (Wang et al., 2005) and rare earth metals (Liang et al., 2005b). In most cases adsorption is highly pH-dependent with increasing sorption with increasing pH as expected for adsorption of metals onto hydroxyl groups. Adsorption of organometallic compounds on pristine multi-walled CNT was found to be stronger than for CB (Munoz et al., 2005). Chemically modified NP have been proposed for environmental cleanup and may therefore be released into the environment (Obare and Meyer, 2004). TiO$$\text{2}$$ functionalized with ethylenediamine was tested for the ability to remove anionic metals from groundwater (Mattigod et al., 2005).

Fullerenes have also been tested for adsorption of organic compounds. Adsorption depends to a great extent on the dispersion state of the C$$\text{60}$$ (Cheng et al., 2004). Because C$$\text{60}$$ forms cluster in water there are closed interstitial spaces within the aggregates where the compounds can diffuse into which leads to significant adsorption—desorption hysteresis (Cheng et al., 2005b; Yang and Xing, 2007). Fullerenes were found not to be very good sorbents for a wide variety of organic compounds (e.g. phenols, PAH, amines) while they are very efficient for removal of organometallic compounds (e.g. organolead) (Ballesteros et al., 2000).

Many materials have properties that are dependent on size (Hochella, 2002). Hematite particles with a diameter of 7 nm for example adsorbed Cu at lower pH values than particles with 25 or 88 nm diameter, indicating the uniqueness of surface reactivity for iron oxide particles with decreasing diameter (Madden et al., 2006). However, an investigation of Pb adsorption onto TiO$$\text{2}$$ NP showed that the bulk material exhibited stronger adsorption and higher adsorption capacity (Giammar et al., 2007).

6. Effects on organisms
6.1. Uptake and toxicity

A consistent body of evidence shows that nano-sized particles are taken up by a wide variety of mammalian cell types, are able to cross the cell membrane and become internalized (Lynch et al., 2006; Rothen-Rutishauser et al., 2006; Smart et al., 2006). The uptake on NP is size-dependent (Limbach et al., 2005; Chithrani et al., 2006). Aggregation and size-dependent sedimentation onto the cells or diffusion towards the cell were the main parameters determining uptake (Limbach et al., 2005). The uptake occurs via endocytosis or by phagocytosis in specialized cells. One hypothesis is that the coating of the NP by protein in the growth medium results in conformational changes of the protein structure, which triggers the uptake into the cell by specialized structures, limiting uptake to NP below about 120 nm (Lynch et al., 2006).

Within the cells NP are stored in certain locations (e.g. inside vesicles, mitochondria) and are able to exert a toxic response. The small particle size, a large surface area and the ability to generate reactive oxygen species play a major role in toxicity of NP (Nel et al., 2006). Inflammation and fibrosis are effects observed on an organism level, whereas oxidative stress, antioxidant activity and cytotoxicity are observed effects on a cellular level (Oberdörster et al., 2005). Several respiratory and cardiovascular diseases in humans are caused by BC (Avakian et al., 2002; Morawska and Zhang, 2002; Armstrong et al., 2004). Ultra-fine soot globules migrate deep into the lungs and carry very toxic, often carcinogenic compounds such as polycyclic aromatic hydrocarbons (PAH) (Avakian et al., 2002; Morawska and Zhang, 2002; Armstrong et al., 2004). Air pollution related illnesses causes “premature death” among especially asphalt-, coke plant-, and gas-workers, chimney sweeps, carbon electrode manufacturers,
or victims of smoke related accidents, as well as the general public (Armstrong et al., 2004).

6.2. Uptake under environmental conditions and ecotoxicity

Most toxicology studies have been carried out with mammalian cells, and the NP were exposed to a cell culture medium containing a mixture of proteins and other biological compounds. Results from such in vitro studies can therefore not be directly transferred to environmental conditions where uptake of NP into the aquatic biota is a major concern. Potential uptake routes include direct ingestion or entry across epithelial boundaries such as gills or body wall. At the cellular level, prokaryotes like bacteria may be largely protected against the uptake of many types of NP since they do not have mechanisms for transport of colloidal particles across the cell wall (Moore, 2006). However, for eukaryotes, e.g. protists and metazoans, the situation is different since they have processes for the cellular internalization of nanoscale or microscale particles, namely endocytosis and phagocytosis (Moore, 2006). The uptake of different NP has indeed been observed. CNT were taken up by a unicellular protozoan and were localized with the mitochondria of the cells (Zhu et al., 2006c). Latex NP were taken up by eggs of the fish Oryzias latipes and adult fish accumulated the NP in gills and intestine but particles were also detected in brain, testis, liver and blood (Kashiwada, 2006). Another study reported that C60 adsorption onto the gram-negative E. coli was 10 times higher than on gram-positive Bacillus subtilis (Lyon et al., 2005). Also inorganic NP are taken up by cells. Nano-sized ZnO, for example, was internalized by bacteria (Brayner et al., 2006). Also nano-sized CeO2 particles were adsorbed onto the cell wall of E. coli, but the microscopic methods were not sensitive enough to discern whether internalization had taken place (Thill et al., 2006).

Ecotoxicological studies show that NP are also toxic to aquatic organisms, both unicellular (e.g. bacteria or protozoa) and animals (e.g. Daphnia or fish). CNT induced a dose-dependent growth inhibition in a protozoan (Zhu et al., 2006c) and were found to be a respiratory toxicant in rainbow trout (Smith et al., 2007). However, also growth stimulation of a unicellular protozoan by CNT was observed in a growth medium containing a yeast extract medium. This was explained by uptake of CNT-peptide conjugates where the additional peptide was responsible for the stimulation (Zhu et al., 2006b). With copepods purified CNT did not show any effect, whereas unpurified CNT with all their by-products increased mortality (Templeton et al., 2006). CNT coated with lipids were readily taken up by Daphnia magna and they modified the solubility of the CNT through digestion of the lipid coating (Roberts et al., 2007). Acute toxicity was only observed at the highest concentration.

For C60 more information about the interaction with several aquatic organisms is available, e.g. bacteria (Lyon et al., 2005, 2006), Daphnia (Lovern and Klaper, 2006) and fish (Oberdörster, 2004; Oberdörster et al., 2006b; Zhu et al., 2006a). However, in most studies only toxicity and sometimes stress biomarkers were determined. Fullerenes have only little impact on the soil microbial community and function, based on soil respiration, soil enzyme activity and changes in community structure (Tong et al., 2007). Bacterial cell walls show a physiological adaptation to the presence of fullerenes and they show a response in lipid composition and membrane phase behavior (Fang et al., 2007).

Quite a lot of information is available for nano-sized silver particles due to their use as bactericides. The cells of bacteria are damaged in the presence of nano-Ag, finally resulting in death of the organisms (Sondi and Salopek-Sondi, 2004). The interaction with the cells is size-dependent (Morones et al., 2005) and seems to depend also on the shape of the particles (Pal et al., 2007). Nano-Ag appears to be significantly more toxic than Ag ions towards E. coli (Lok et al., 2006).

Inorganic nanoparticulate TiO2, SiO2 and ZnO had a toxic effect on bacteria, and the presence of light was a significant factor increasing the toxicity (Adams et al., 2006). Whereas bulk TiO2 is considered to have no health effects on aquatic organisms, this is clearly the case for nano-sized TiO2 (Lovern and Klaper, 2006). NP that damage bacterial cell walls have been found to be internalized while those without this activity were not taken up (Stoimenov et al., 2002).

6.3. Interaction of NP with plants

To date research on interaction of NP with plants is almost non-existent. One study reports the effect of aluminum oxide NP on root elongation in hydroponic studies (Yang and Watts, 2005). A slight reduction in root elongation was found in the presence of uncoated alumina NP but not with NP coated with phenanthrene. It was proposed that the surface characteristics of the alumina played an important role in phytotoxicity. However, the study is problematic as pointed out by Murashov (2006) because the author did not take into account that soluble Al3+ is a potent root toxicant and known to inhibit root growth. The solubility of aluminum oxide is known to increase with decreasing particle size and modification of the surface by adsorbed compounds is known to affect the dissolution rate.

Several articles by Hong et al. (2005a,b), Zheng et al. (2005), Gao et al. (2006) and Yang et al. (2006a) have shown that nano-sized TiO2 can have a positive effect on growth of spinach when administered to the seeds or sprayed onto the leaves. Nano-TiO2 was shown to increase the activity of several enzymes and to promote the adsorption of nitrate and accelerate the transformation of inorganic into organic nitrogen. Normal-sized TiO2 did not have these effects.

One study reported the interaction of NP with green algae, which have a cell wall similar to plants (Hund-Rinke and Simon, 2006). Only information on toxicity of nano-sized TiO2 under illumination is reported in this study, whereas neither uptake of the NP nor the dark reaction was studied.

The few data that are available indicate that at least inorganic, oxidic NP are able to interact with plant cells or green algae with a similar cell wall structure. To date no information about cellular internalization has become available. Plant cell
walls differ from those of mammalian cells, for which internalization of NP is known (see above). Possible interactions of NP with plant roots are adsorption onto the root surface, incorporation into the cell wall, and uptake into the cell. The NP could also diffuse into the intercellular space, the apoplast, and be adsorbed or incorporated into membranes there. Plant cells carry a negative surface charge, which allows the transport of negatively charged compounds into the apoplast. The Casparian strip poses a barrier to the apoplastic flow and transport and only symplastic transport is possible into the xylem. However, this barrier is not perfect and compounds can enter the xylem through holes or damaged cells without ever crossing a cell membrane and be further transported to the shoots. This process has been found to be the dominant process for the uptake of metal complexes with chelators such as EDTA and their translocation to the shoots (Nowack et al., 2006; Tandy et al., 2006). Based on this knowledge about root physiology we could therefore hypothesize that negatively charged NP could enter the apoplasm of the root cortex and eventually also the xylem, but are not taken up by the cells.

6.4. Interactions among organisms, NP and contaminants

The interaction of NP with toxic, organic compounds can both amplify as well as alleviate the toxicity of the compounds. In contrast to harmful effects, NP can therefore also have an advantageous role in the environment. The possible interactions in systems with organisms, NP and pollutants are shown schematically in Fig. 4. The influence of pollutants on organisms is well studied (Fig. 4a) and the interaction with (or absorbed) pollutant and possible uptake of pollutant-NP. (c) adsorption (or absorption) of pollutants onto NP and reduction in pollutant uptake by organisms and (d) adsorption of NP with adsorbed (or absorbed) pollutant and possible uptake of pollutant-NP.

Fig. 4. Scheme of the interactions of pollutants, NP and organisms (algae as example). (a) Adsorption and uptake of pollutant, (b) adsorption and uptake of nanoparticle, (c) adsorption (or absorption) of pollutants onto NP and reduction in pollutant uptake by organisms and (d) adsorption of NP with adsorbed (or absorbed) pollutant and possible uptake of pollutant-NP.

NP with the adsorbed pollutants are taken up by the cells (Fig. 4d), then a toxic effect could be the consequence, either caused by the NP, the pollutant or in a synergistic way by both together. However, it could also be that no effect is observed if the bound pollutant is not bioavailable and the NP itself is not toxic.

The strong sorption of organic compounds to BC was shown to be a dominant factor for the low and variable biota to sediment accumulation factors and the limited potential for microbial degradation (Cornelissen et al., 2005). BC generally comprises about 9% of total organic carbon in sediments and may reduce uptake in organisms by up to two orders of magnitude (Koelmans et al., 2006). Decreased bioavailability of organic pollutants in sediments and benthic invertebrates in presence of BC was reported in a number of papers (Maruya et al., 1997; Jonker et al., 2004; Lohmann et al., 2004; Rust et al., 2004; Sundelin et al., 2004; Voparil et al., 2004). Much less has been done with plankton from the open water column (Knauer et al., 2007).

Growth stimulation of a unicellular protozoan by CNT was observed in a growth medium containing a yeast extract medium and was explained by uptake of CNT—peptide conjugates and the additional peptone was responsible for the stimulation (Zhu et al., 2006b). A slight reduction in root elongation was found in the presence of uncoated alumina NP but not with NP coated with phenanthrene (Yang and Watts, 2005). It was proposed that the surface characteristics of the alumina played an important role in phytotoxicity and that adsorption of phenanthrene shielded the toxic alumina surface from the plant roots. When exposed to As(V)-contaminated water in the presence of nano-sized TiO₂, carp accumulated considerably more As than without NP (Sun et al., 2007).

6.5. Environmental risk assessment of NP

Environmental exposure varies on the basis of conditions such as the way in which materials are handled in the workplace, how nanomaterials partition to various phases (e.g., water and air), the mobility of nanomaterials in each of these phases, their persistence, and the magnitude of the sources. A lot of research is currently devoted to these topics. This basic information about the behavior and toxicity is needed, but is not sufficient to allow for a realistic risk assessment of NP in the environment. What is also needed is an evaluation of the expected quantities and concentrations of NP in environmental systems. To date nothing is known about this issue, neither from an analytical point of view (e.g. actual measurements of NP in the environment) nor with respect to theoretical or modeling studies. Only few products containing NP are actually on the market, but this is expected to change rapidly in the next years as more and more nano-products are sold. It is therefore not only necessary to get an overview on current exposure, but also more important to anticipate future scenarios on the use of nano-products and exposure to released NP. As a starting point to risk assessment, exploring the sources and environmental pathways helps to identify relevant applications and situations where a subject deserving protection may face exposure to NP (Reijnders, 2006; Koehler et al., in press).
7. Conclusions

There is currently a lot of attention being paid to the behavior and effects of engineered NP, but there is still only limited solid information. Nonetheless, there is quite a vast amount of work being done with natural NP, e.g. soot and aquatic colloids, and the knowledge gained there will be of invaluable help in assessing the fate of engineered NP. Analytical methods developed for natural NP are now beginning to be applied to engineered NP. The discussion of NP in the environment is therefore different from organic micropollutants, where often advances in analytical techniques and detection of compounds in the environment have been the starting point for scientific and public discussions. For NP the public discussion predates the possibility of their analysis.

Compared to conventional or other emerging contaminants, NP particles pose some new challenges for scientists. Whereas it is already obvious that particle size plays an important role with respect to toxicity, much less is known how size affects the behavior and reactivity of NP. It is also important to realize that many engineered NP are functionalized and these significantly affects their behavior. Changes in functionalization by environmental factors or the coating of the surface by natural compounds is clearly an important process in the environment which has, however, been studied only marginally so far. These new issues and concepts need to be incorporated into the experimental design and the choice of appropriate analytical methods (Holsapple et al., 2006; Powers et al., 2006). When applying established toxicity tests to NP the results should always be interpreted with great care especially to avoid the reporting of false positive results (Wörle-Knirsch et al., 2006).

Finally, the use of limited resources such as Pt, Pd, and other scarce metals in nanoform might pose a problem because once applied and emitted, these metals are inadvertently lost to mankind because they are dispersed to yield infinitely low concentrations in the environment (Gordon et al., 2006). Recycling will in many cases not be possible and future generations will not have these elements at their disposal anymore. In contrast to organics, the number of metal elements is finite and substitution often not possible.

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