

Figure 7.3. The global distribution and flux of NPs throughout the atmosphere, geosphere, and hydrosphere have been estimated by Hochella et al. (2012). All numbers are in units of teragrams ($Tg = 10^{12}$ g) and italicized numbers are fluxes per year. The two component systems associated with atmospheric and volcanic deposition are split into aerosols and mineral dust components SOURCE: Data from Hochella et al. 2012

Inorganic NMs are transported from terrestrial reservoir by wind-blown mineral dust, volcanic eruptions, and rivers (Hochella et al. 2012). Mineral dusts are derived from arid and semi-arid lands, which comprise approximately 30% of the land surface on earth and include deserts in northern Africa, the Middle East and Tibet. Desertification and forest clearing increases the input of mineral dust into the atmosphere by enhancing wind erosion in these areas (Hochella et al. 2012). Nanominerals and mineral NPs with sizes that are less than 40 nm make up approximately 90% mineral dust particles and feldspars, quartz, and clays are the dominant phases (Engelbrecht and Derbyshire 2010). Other minerals including carbonates, sulfates and oxides are also observed, resulting in a total amount of mineral dust injected into the atmosphere by winds as approximately 1,600 Tg (Buseck and Adachi 2008). Volcanic eruptions produce a significant amount of sulfate based aerosols and approximately 10³⁻⁴ Tg of inorganic NMs, or 0.1-0.001% of the total reservoir within the continents are transported from soils to the continental shelf via rivers (Ludwig and Probst 1998; Hochella et al. 2012). Estimates for riverine fluxes are based upon clay-silt fraction, which contain fine grained silicates, iron-oxide and clay particles, which comprises approximately 58 Tg year (Mossa 1996).

Only about 1.5% of this material will be transported to the deep ocean because of the increased ionic strength and mixing in estuaries and continental shelves

leads to aggregation and settling (Hochella et al. 2012). The predicted reservoir associated with continental shelf regions account for 10^{2-3} Tg of NMs and the flux to the open ocean is still in question. A significant amount (10^9 particles per milliliter) of 2–150 nm aggregates were observed in surface and subsurface water collected offshore San Diego, California. These particles were often composed of smaller particles of 2–5 nm in size and contained organic matter, metal oxides, and clay minerals (Wells and Goldberg 1991).

Other fluxes to the ocean include glacial run off and atmospheric deposition of mineral dusts, and hydrothermal vents (Hochella et al. 2012). These additional inputs only represent approximately 100 Tg/yr, with atmospheric deposition contributing a significant portion of the nanominerals flux into open ocean. The only identified flux of NPs from the ocean is sea-spray, which may be equivalent or an order of magnitude higher than mineral dust. Sea-sprays are also composed of aggregated NPs and typically are found in the 30–40 nm range. Of the total sea-spray particles approximately 15% are in the nano-size range and contribute a total flux of approximately 2 Tg per year. Overall, it is predicted that oceans may represent a net sink for NPs within the global budget (Hochella et al. 2012).

7.4.3 Important Processes Influenced by Natural NPs

The importance of NPs in natural systems is widespread and encompasses fundamental geochemical processes. Some of the more essential geochemical and aquatic processes that are impacted by natural NMs include elemental distribution, biological interactions, contaminant transport, catalytic transformations, mineral growth, structural transformation, and weathering (Hochella 2008). Chemical reactions in the atmosphere are also influenced by natural NMs because they are a precursor to the formation of larger particles that impact global climate and transport of pollutants and nutrient. In addition, atmospheric NPs are the critical particle size that cause significant human health problems associated with air pollution (Anastasio and Martin 2001).

Even basic phenomena, such as the thermodynamic stability of mineral phases are impacted by nanoparticle, as illustrated by crossovers in stabilities for polymorphs. Calorimetric studies performed by Navrotksy et al. (2008) showed that the complexity within the iron oxyhydroxide group of mineral is related to the differences in the surface energy that impart stability to nanomineral phases and energy crossovers can exist that are dependent on particle size. Hematite (Fe₂O₃) is the most thermodynamically stable bulk mineral phase, but as the particle size decreases to 60 nm, an energy crossover occurs, favoring the formation of the goethite (FeO(OH) phase. Similarly, lepidocrocite (γ -FeO(OH) and akageneite (β -FeO(OH) become the thermodynamically stable phase when particle sizes decrease to 12 and 5 nm, respectively. The hydration state of ferrihydrite varies, but the stability field for ferrihydrite is comparable to the other iron oxide phases, particularly at particle sizes less than 5 nm (Navrotsky et al. 2008).

Ferrihydrite and other iron oxides are an extremely important class of natural NMs that have been implicated on in an array of key Earth systems processes. One important example of these vital activities includes the role of iron oxide NPs in global carbon cycle. Iron is a limiting nutrient for the growth of phytoplankton in the open ocean and traditionally, dissolved iron was thought to be the important species that influence the growth of these communities (Schlesinger 1997). However, a significant amount of iron in the ocean is observed as nanoparticle with sizes between 2 and 20 nm that far exceed the amount of dissolved iron via riverine input (Wells and Goldberg 1991; Poulton and Raiswell 2002; Raiswell et al. 2008; Raiswell 2011; Hochella et al. 2012). Much of the nanoparticulate iron is deposited into the ocean via mineral dust as well as melting icebergs and glaciers (Raiswell et al. 2008). It is also important to note that nanoparticulate iron is bioavailable to marine phytoplankton, thus providing an important nutrient that greatly impacts the carbon cycle, particularly in the world's oceans.

Iron oxide and other metal oxide species also impact the adsorption, mobility and transport of contaminants in aqueous systems. Small (1–10 nm) NPs exhibit enhanced adsorption of contaminants from larger surface areas and increased mobility due to lowered settling rates. Enhanced transport of heavy metals (Cu, Zn, As, Pb, Cd) and radionuclides due to the presence of metal oxide has been documented in several systems, with one of the welldocumented studies involving Pu(IV) (Novikov et al. 2006; Hassellov and von der Kammer 2008). Tetravalent actinides are predicted to be insoluble and relatively immobile in natural system, yet are observed kilometers from point sources (Kersting et al. 1999). In subsurface waters impacted by a processing plant at Mayak, Russia, approximately 80% of the Pu(IV) was associated with small iron oxide NPs that were less than 15 nm in diameter (Novikov et al. 2006). These small NPs flow quite freely through groundwater systems, enhancing the transport of Pu(IV) within the system.

Catalytic oxidation and reduction of contaminants is also impacted by the presence of NMs in environmental systems. An example of this the importance of this catalytic process is the interaction of arsenic with ferrihydrite (Zhao et al. 2011). Arsenic is observed in two oxidation states, As(III) and As(V), with the reduced species exhibiting increased mobility and toxicity in natural waters. As (III) will bind to the surface of ferrihydrite and subsequently undergo oxidation to As(V) through a catalytic reaction with oxygen detailed below:

$$= \operatorname{Fe}(O_2)(\operatorname{As}(\operatorname{III})(\operatorname{OH})^- + O_2 + H_2O)$$

$$\rightarrow = \operatorname{Fe}(O_2)(\operatorname{As}(V)(O)(OH)^- + 2OH^-)$$

where = Fe represents the surface of ferrihydrite (Pereira et al. 2012). Similar catalytic reactions have also been reported for the oxidation of organic pollutants and can be observed on the surface of nanoscale manganese oxides as well (An and Zhao 2012). Catalytic oxidation processes that are impacted by nanoscale mineral

species represent an important mechanism for the transformation of chemical pollutants in environmental systems.

Catalytic reactions, such as the Fenton reaction, can also be linked to health effects associated with air pollution (Anastasio and Martin 2001). Iron oxide NPs or particles with adsorbed iron species can create reactive hydroxyl radicals through the following reaction:

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + OH^{\bullet} + OH^{-}$$

If these particles are inhaled, then hydroxyl radicals can be produced in vivo within the lungs and cause cardiovascular and pulmonary morbidity (Vidrio et al. 2008). The presence of peroxide in the system does not necessarily need to be present because hydroxyl radicals were also documented just in the presence of naturally occurring pyrite (FeS) NPs (Cohn et al. 2010).

7.5 ENGINEERED AND ANTHROPOGENIC NPs IN NATURAL SYSTEMS

Alleviating concerns over the presence of engineered NPs entering natural ecosystems is hampered by our lack of knowledge regarding their influx and the transformations that can occur in environmental systems. Release rates are currently unknown, but are modeled to range from 0.003 ng/L for fullerene to 21 ng/L for TiO₂ in natural surface waters (Gottschalk et al. 2009). Release of sewage effluent into natural waters is expected to increase concentrations of engineered nanoparticulates, particularly for TiO₂, which is expected to be present at $\mu g/L$ levels. The deposition of solid effluents onto agricultural fields may also introduce anywhere from 1 ng-89 µg of engineered NMs per kg of biosolids annually for Europe and the United States (Gottschalk et al. 2009). The chemical complexity and diverse mechanisms for transformation of engineered NPs in the environment, lead to additional uncertainty in the potential environmental health risks. Each class of engineered nanoparticle possesses unique chemistries and can also behave differently based upon the method of preparation or type of surface coating. Once these particles are released into the environment, they can undergo transformations, including chemical, biological, physical aggregation, and interactions with macromolecules (Figure 7.4) (Lowry et al. 2012). Some transformations could lead to decreased mobility or toxicity, but others can lead to increased concentrations of heavy metals in the environment and cellular stress to impacted biota. Due to this uncertainty, the impact of engineered nanoparticle on ecosystem and environmental health, remain a controversial topic.

To highlight the complexity of engineered NPs in the environment, two classifications (carbon nanotubes and Ag NPs) of NMs will be discussed in the following section. These two classes were chosen due to their wide use in



Figure 7.4. The major transformation pathways for engineered NPs in the environment include physical, biological, chemical and molecular interactions SOURCE: Lowry et al. (2012); reproduced with permission from American Chemical Society

commercial products, insignificant quantities of natural analogues, and the large amount of initial research into their transformation in environmental systems. In addition, the consequences of anthropogenic, NPs that are unintentionally produced during human activities will also be briefly touched upon, as they are also directly released into the environment and can also undergo a variety of transformations.

Carbon Nanotubes. Carbon nanotubes are used in composite materials and are also being investigated for drug delivery aspects. Pure carbon nanotubes are minimally soluble and will resist dispersion in water (Bahr et al. 2001), thus are not expected to be mobile in environmental systems. Due to their limited solubility, carbon nanotubes are expected to accumulate in soils and sediments and interact with organism, particularly soil bacteria. Studies using pure microorganism cultures, such as *Escherichia coli* find that unadulterated nanotubes suppress metabolic activity and are quite toxic, as over 80% of the cells attached to the nanotubular walls were dead after a 60 minute incubation time (Ahmed et al. 2012). Studies on microbial communities suggest that dose rates are significant, but that the presence of organic matter can decrease the impact of carbon

nanotubes on the microbial responses of these nanominerals (Tong et al. 2012). Transformation of carbon nanotube surfaces can also occur within the environmental system, including oxidation of pure carbon nanotubes can occur through interactions with naturally occurring hydroxyl radicals. This oxidation process has been demonstrated by interactions of the nanotubes with the horseradish peroxidase enzyme (Allen et al. 2008).

Surface functionalization can have significant impact on the interaction of carbon nanotubes with natural systems. Carbon nanotubes are typically modified in commercial products to improve solubility, with oxidation reactions (formation of carboxylate groups) or the additional functionalization with ligands such as polyethyleneglycol or sulfonic acid. Functionalized surfaces have been reported to decrease overall toxicity to microbial communities as these organisms are able to recover from chronic exposure (Tong et al. 2012). The composition of the recovered community also changes, which could have impacts on overall carbon and phosphorus cycling in the environment (Rodrigues et al. 2013). Functionalized nanotubes are also subject to biotranformations, including degradation of the PEG coatings that cased the carbon nanotubes to aggregate and precipitate from solution (Kirshling et al. 2011). The addition of hydrophilic functional groups could increase interactions with mineral surfaces or natural organic matter which can either increase or decrease transport based upon exact environmental conditions (Chowdhury et al. 2012).

Silver NPs. Silver NPs are used in a wide range of commercial products, including textiles and cosmetics. Release of silver NPs occurs through public water system either as primary particles or as the oxidized cation, Ag^+ (Stark 2011). Silver flux into the environment is expected to be 20 ta⁻¹ in the United States, but much of the aquatic input immobilized as a sparingly soluble salt (AgCl or Ag₂S) or through aggregation upon entry into higher ionic strength solutions (Gottschalk et al. 2009; Zook et al. 2011). A majority of the nanoparticulate silver will be found in sewage sludge where in may be mobilized into the soil environment again after disposal in the landfill (Gottschalk et al. 2009; Kim et al. 2010; Kaegi et al. 2011).

The antimicrobial properties of silver NPs are a main driver in their use in commercial products; however, it is this beneficial property that may negatively impact environmental systems (Chernousova and Epple 2013). Silver NPs themselves turn out to be relatively non-toxic (200 mg/L) under anaerobic conditions (Ziu et al. 2012). Exposure to oxic environments results in the chemical oxidation of the Ag^0 metal to $Ag^+(aq)$, which has known bactericidal properties. For eukaryotic cells in vitro, toxic concentrations are 1–10 mg/L for Ag⁺, compared to 10–200 mg/L for silver NPs (Chernousova and Epple 2013). Dissolution of the Ag nanoparticle is impacted by the surface coatings that are generally used to prevent aggregation during the manufacturing process. Upon degradation of the surface coating, the silver particle can dissolve incongruently, leaving the outer shell in solution. Reactions with inorganic sulfur, thiols, or sulfur-containing biomacromolecules can also impact dissolution and result in more release of $Ag^+(aq)$ into the surrounding environment. The inverse reaction is also a

possibility as other organics may lead to the aggregation and deposition of the particles from the water column (Kim et al. 2010; Levard et al. 2011; Liu et al. 2012).

Anthropogenic NPs. In addition to the discharge of engineered NPs produced for industrial and commercial applications, anthropogenic NPs can also be released into the environment, often through unintended means (Wiesner et al. 2011). A major source of anthropogenic NPs includes combustion processes, which produce ultra-fine or the soot fraction of black carbon (Nowack and Bucheli 2007). The combustion of fossil fuels or biomass is often incomplete, leading to re-condensation reactions in the gas phase and the formation of large aromatic compounds. In manufacturing environments, ultrafine soot particles are common and originate from processing of material, vehicle emissions, welding, and infiltration of outside air. Concentrations of these particles vary widely (724-23,000 l/cm³) depending on the industrial activities and air flow throughout the facility (Peters et al. 2006; Peters et al. 2009; Methner et al. 2010). Anthropogenic soot is also released directly to the environment through automobile exhaust, energy production, industrial processes, and biomass burning. Worldwide production of black carbon and secondary organic aerosols are 0.22 and 0.19 Tg and have a climate forcing of +0.51 to +0.8 W/m² (Chung and Seinfeld 2002).

7.6 OCCURRENCE OF NMs FOR ENVIRONMENTAL REMEDIATION

At the same time that concerns over the release of NPs in natural systems are being voiced, their novel use in environmental remediation efforts are continuously being discovered. The use of NMs in environmental remediation applications again stems from their high surface areas that increase the chemical degradation, adsorption, and photocatalytic activities of these materials (Hotze and Lowry 2011). Enhanced chemical reactivity leads to higher removal rates and increased catalytic degradation of a wide range of toxic and problematic contaminants.

Most remediation efforts center on water remediation in built reactive barriers, filtration systems, and within soils and sediments. As water resources become scarcer, more efforts to remediate and purify potable water sources with advanced technologies become more important. This includes difficult contaminants, such as persistent organic pollutants that are recalcitrant to many degradation protocols and metal such as As(III) that do not strongly bind to adsorbents (Sato et al. 2002; Oulton et al. 2010). A wide range of NMs are being developed for reactive barriers and filtration systems as listed in Table 7.3. Many of these materials are still under development, although some, such as the zero-valent iron particles and clay NMs, are currently being utilized for a variety of pollutants (Kanel et al. 2006; Yuan and Wu 2007; Dickinson and Scott 2010; Wei et al. 2010). In addition, to build environments, bioremediation efforts in soils and sediments create insoluble NPs that limit transport of contaminants into groundwater systems. Each of these remediation environments and the NMs utilized in these technologies will be detailed below.

Nanomaterial	Pollutant	Reference
Zero Valent Iron	Alachlor, Atrazine, Chlorinated and brominated organic compounds, heavy metals, nitrate, nitrite, perchlorate, radionuclides, PCBs, dioxins	Kanel et al. (2006), Xiong et al. (2007), Lin et al. (2008), Bezbaruah et al. (2009), Shih et al. (2009), Berge and Ramsburg (2010), Dickinson and Scott (2010), Wei et al. (2010), Singh et al. (2011), Zhang et al. (2011), Kharisov et al. (2012), and Xie and Cwiertny (2012)
Bi-metallic particle	Nitrate, chlorinated organic compounds	Shih et al. (2009), Xu et al. (2009), Sakulchaicharoen et al. (2010), and Kang et al. (2012)
Surface modified	Trichloroethylene, chlorinated organic compounds Cr(VI)	Wang and Zhou (2010), and Xie and Cwiertny (2010) 5,
Zeolites	Heavy metals, toluene, nitrogen dioxide	Song et al. (2004, 2005), and Ghrair et al. (2009, 2010)
Carbon Nanotubes	Organic compounds, virus, bacteria	Gao and Vecitis (2011), Deng et al. (2012), and Rahaman et al. (2012)
Functionalized w/organic	Heavy metals, chlorinated organic compound	Shao et al. (2011), Adolph et al. (2012), and Seymour et al. (2012)
Support for metal	2,4 dichlorophenol, organic pollutants, arsenic	Shao et al. (2010), Chen et al. (2011), Tawabini et al. (2011), Wilson et al. (2012), Xu et al. (2012), and Zhang et al. (2012)
Metal oxides		
TiO2	Organic pollutants, fluorinated compounds, heavy metals	Linsebigler et al. (1995), Chow et al. (2005), Liu et al. (2005), Pena et al. (2005), and Li et al. (2012)
Doped TiO ₂	Azo dyes, phenol	Liu et al. (2005), and Nahar et al. (2006)

Table 7.3. Examples of NMs used in environmental remediation efforts

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Table 7.3. Examples of NMs used in environmental remediation efforts (Continued)

Nanomaterial	Pollutant	Reference
Aluminum	Heavy metals, organic pollutants	Sato et al. (2002), Kang et al. (2003), Ma et al. (2009), Stewart et al. (2009), Giles et al. (2011), Henneberry et al. (2011), Maria Valente et al. (2012), and Mertens et al. (2012)
Iron (III)	Heavy metals, radionuclides	Filip et al. (2007), Genovese and Mellini (2007), Violante et al. (2007), Shipley et al. (2009), Amofah et al. (2011), Giles et al. (2011), Shipley et al. (2011), An and Zhao (2012), Li and Kaplan (2012), and Maria Valente et al. (2012)
Manganese	Heavy metals, radionuclides, organic pollutants	Pal et al. (2011), Clarke et al. (2012), Johnson et al. (2012), and Watanabe et al. (2012)
Nanoclays	Heavy metals, phosphate	Isoyama and Wada (2007), Yuan and Wu (2007), and Maria Valente et al. (2012)
Nanopolymers	PAHs, cyanotoxins	Krupadam (2012), and Krupadam et al. (2012)

Zero Valent Iron (ZVI) particles have been used in reactive barriers to remediate chlorinated and bromated organic compounds, nitrate, and toxic heavy metals (Kanel et al. 2006; Xiong et al. 2007; Lin et al. 2008; Bezbaruah et al. 2009; Dickinson and Scott 2010; Wei et al. 2010; Singh et al. 2011; Zhang et al. 2011). To create the ZVI barriers, metallic (Fe⁰) NPs are placed into packed bed reactors or permeable reactive barriers within the contaminated groundwater plume (Zhang 2003). Under remediation conditions, the contaminant such as carbon tetrachloride will readily accept the electrons from iron oxidation:

 $\mathrm{CCl}_4 + 4\mathrm{Fe}^0 + 4\mathrm{H}^+ \rightarrow \mathrm{CH}_4 + 4\mathrm{Fe}^{2+} + 4\mathrm{Cl}^-$

This reaction will also reduce soluble U(VI) to form insoluble U(IV) oxides to limit the transport of toxic radionuclides from contaminated sites (Dickinson and Scott 2010). Bi-metallic iron particles, including Pd/Fe, Fe/Ni, Fe/Co, and

Fe/Cu particles are also utilized in environmental remediation efforts to provide catalytic enhancement of the reduction process (Xu et al. 2009; Kharisov et al. 2012). In addition, the surface of the ZVI particles can be modified with a polymer coating, which prevents aggregation and adhesion of the particle to mineral surfaces, but still allows the exchange of electrons between the iron metal center and the contaminant phase (Xie and Cwiertny 2010). Reactor beds have been extensively used to reduce chlorinated organic pollutants from groundwater systems, but the concern over the release and toxicity of ZVI in natural systems has resulted in their reevaluation as an environmental remediation strategy (Lee et al. 2008; El-Temsah and Joner 2012; Kadar et al. 2012; Keller et al. 2012; Tilston et al. 2013).

Single-walled and multi-walled carbon nanotubes have been extensively explored as a means for advanced filtration for water remediation. The benefits of carbon nanotubes for purification efforts include their ability to intertwine to create filters for use in water treatment facilities or point source contaminant remediation scenarios (De Volder et al. 2013). In addition, carbon nanotubes can electrochemically oxidize organic contaminants, bacteria, and viruses, and can serve as a substrate for the deposition of redox active or photocatalytic metal particles (Zhang 2003; Gao and Vecitis 2011; Rahaman et al. 2012). Surface functionalization with carboxylate groups also enables the hydrophobic nanotubes to attract metal contaminants. Other surface functional groups such as thiols can attract softer metals, such as Pb^{2+} and Hg^{2+} , to remove additional metals from natural water systems. Alignment of single-walled carbon nanotubes may also enhance permeability and find use in lower energy water desalination by reverse osmosis processes, although the diameter of the nanotubes will need to be carefully controlled to reject salt at seawater concentrations (Holt et al. 2006; Corry 2008).

Metal oxide material, such as TiO₂, Fe₃O₄, FeO(OH), and MnO₂, can be used as filtration membranes for passive treatment of aqueous solutions, or in active redox or photocatalytic applications. Iron (III), Al(III), and Mn(IV) oxide and oxyhydroxide particles are naturally abundant, limiting concerns regarding introduction of engineered materials into environmental systems, and can act as an adsorbent for a wide range of heavy metals, radionuclides, and organic pollutants. Some iron oxides contain mixed oxidation states, which enables catalytic redox reactions that lead to the oxidation of organic pollutants. In addition, the metal oxide material can be doped with various amounts of other metals to tune the adsorptive capability of the overall adsorbent (Warner et al. 2012). Nanophase TiO₂ also possesses photocatalytic properties and can be used to reduce contaminants in water through surface mediated effects (Liu et al. 2005; Nahar et al. 2006). Processing of TiO_2 into nanorods or through electrospinning techniques creases highly porous reactive filters advanced water purification activities (Chen and Mao 2007). Metal oxides can also be supported by carbon nanotubes, aluminum oxide scaffolds, or polymer composite to creation of unique technologies for water purification. Examples metal oxide supported NMs are the development of magnetically driven floats for removal of oil slicks from surface