CHAPTER II

THEORETICAL BACKGROUNDS

2.1 Nanoparticles

2.1.1 History of Nanoparticles

Although generally nanoparticles are considered an invention of modern science, they actually have a very long history. Specifically, nanoparticles were used by artisans as far back as in the 9th century Mesopotamia for generating a glittering effect on the surface of pottery. The lustre originates within the film itself, which contains silver and copper nanoparticles, dispersed homogeneously in the glassy matrix of the ceramic glaze. These nanoparticles were created by the artisans by adding copper and silver salts and oxides together with vinegar, ochre, and clay, on the surface of previously-glazed pottery. The object was then placed to a kiln and heated to about 600°C in a reducing atmosphere. There the reducing atmosphere reduced the ions back to metals, which then came together forming the nanoparticles that give the color and optical effects. Lustre technique shows that craftsmen had a rather sophisticated empirical knowledge of materials. The technique originates in the islamic world. As Muslims were not allowed to use gold in artistic representations, they had to find a way to create a similar effect without using real gold. The solution they found was using lustre. Michael Faraday provided the first description, in scientific terms, of the optical properties of nanometer-scale metals in his classic 1857 paper "Experimental relations of gold (and other metals) to light." Much of the modern day studies of these objects have been conducted at the ESRF laboratory. Several techniques were used to characterize the chemical and physical properties of these lustre, such as Rutherford Backscattering Spectrometry (RBS), optical absorption in the visible-ultraviolet region, ϵ microscopy (TEM and SEM), X-ray diffraction (Agam and Guo, 2007).

2.1.2 Properties of Nanoparticles

Nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures. A bulk material should have constant physical properties regardless of its size, but at the nano-scale this is often not the case. Size-dependent properties are observed such as quantum confinement in semiconductor particles, surface plasmon resonance in some metal particles and superparamagnetism in magnetic materials. The properties of materials change as their size approaches the nanoscale and as the percentage of atoms at the surface of a material becomes significant. For bulk materials larger than one micrometer the percentage of atoms at the surface is minuscule relative to the total number of atoms of the material. The interesting and sometimes unexpected properties of nanoparticles are partly due to the aspects of the surface of the material dominating the properties in lieu of the bulk properties (Ying and Jackie, 2001)

Nanoparticles exhibit a number of special properties relative to bulk material. For example, the bending of bulk copper (wire, ribbon, etc.) occurs with movement of copper atoms/clusters at about the 50 nm scale. Copper nanoparticles smaller than 50 nm are considered super hard materials that do not exhibit the same malleability and ductility as bulk copper. The change in properties is not always desirable. Ferroelectric materials smaller than 10 nm can switch their magnetization direction using room temperature thermal energy, thus making them useless for memory storage. Suspensions of nanoparticles are possible because the interaction of the particle surface with the solvent is strong enough to overcome differences in density, which usually result in a material either sinking or floating in a liquid. Nanoparticles often have unexpected visible properties because they are small enough to confine their electrons and produce quantum effects. For example gold nanoparticles appear deep red to black in solution (Whitesides, et al, 1991).

Nanoparticles have a very high surface area to volume ratio. This provides a tremendous driving force for diffusion, especially at elevated temperatures. Sintering can take place at lower temperatures, over shorter time scales than for larger particles. This theoretically does not affect the density of the final product, though flow difficulties and the tendency of nanoparticles to agglomerate complicates matters (Buffat and Burrel, 1976)

2.1.3 Classification of Nanoparticles

At the small end of the size range, nanoparticles are often referred to as clusters. Nanospheres, nanorods, and nanocups are just a few of the shapes that have been grown. Metal, dielectric, and semiconductor nanoparticles have been formed, as well as hybrid structures (e.g., core-shell nanoparticles). Nanoparticles made of semiconducting material may also be labeled quantum dots if they are small enough (typically sub 10 nm) that quantization of electronic energy levels occurs. Such nanoscale particles are used in biomedical applications as drug carriers or imaging agents. Semi-solid and soft nanoparticles have been manufactured. A prototype nanoparticle of semi-solid nature is the liposome. Various types of liposome nanoparticles are currently used clinically as delivery systems for anticancer drugs and vaccines (ASTM E 2456 - 06 Standard Terminology Relating to Nanotechnology).

2.1.4 Characterization of Nanoparticles

Nanoparticle characterization is necessary to establish understanding and control of nanoparticle synthesis and applications. Characterization is done by using a variety of different techniques, mainly drawn from materials science. Common techniques are electron microscopy [TEM,SEM], atomic force microscopy [AFM], dynamic light scattering [DLS], x-ray photoelectron spectroscopy [XPS], powder x-ray diffractometry [XRD], Fourier transform infrared spectroscopy [FTIR], Matrix-Assisted Laser-Desorption Time-of-flight mass spectrometry [MALDI-TOF], and Ultraviolet-visible spectroscopy. The technology for Nanoparticle tracking analysis (NTA) allows direct

tracking of the Brownian motion and this method therefore allows the sizing of individual nanoparticles in solution (ASTM E 2456 - 06 Standard Terminology Relating to Nanotechnology).

2.2 Superparamagnetic Nanopraticles

Superparamagnetism is a phenomenon by which magnetic materials may exhibit a behavior similar to paramagnetism even when at temperatures below the Curie or the Néel temperature. This is a small length-scale phenomenon, where the energy required to change the direction of the magnetic moment of a particle is comparable to the ambient thermal energy. At this point, the rate at which the particles will randomly reverse direction becomes significant. Normally, coupling forces in ferromagnetic materials cause the magnetic moments of neighboring atoms to align, resulting in very large internal magnetic fields. This is what distinguishes ferromagnetic materials from paramagnetic materials. At temperatures above the Curie temperature (or the Neel temperature for antiferromagnetic materials), the thermal energy is sufficient to overcome the coupling forces, causing the atomic magnetic moments to fluctuate randomly. Because there is no longer any magnetic order, the internal magnetic field no longer exists and the material exhibits paramagnetic behavior. If the material is non-homogeneous, one can observe a mixture of ferromagnetic and paramagnetic clusters of atoms at the same temperature, the superparamagnetic stage. Superparamagnetism occurs when the material is composed of very small crystallites (1–10 nm). In this case even when the temperature is below the Curie or Neel temperature (and hence the thermal energy is not sufficient to overcome the coupling forces between neighboring atoms), the thermal energy is sufficient to change the direction of magnetization of the entire crystallite. The resulting fluctuations in the direction of magnetization cause the magnetic field to average to zero. Thus, the material behaves in a manner similar to paramagnetism, except that instead of each individual atom being independently influenced by an external magnetic field, the magnetic moment of the entire crystallite tends to align with the magnetic field. The energy required to change the direction of

magnetization of a crystallite is called the crystalline anisotropy energy and depends both on the material properties and the crystallite size. As the crystallite size decreases, so does the crystalline anisotropy energy, resulting in a decrease in the temperature at which the material becomes superparamagnetic. The rate at which particles will lose their direction is governed by the Neel-Arrhenius equation. In particular, it is a function of the exponential of the grain volume (Kryder and M.H., 2005)

2.3 Descriptions of magnetic behaviors (Furlani, 2001)

There are many forms of magnetic behavior, and all materials exhibit at least one of them. Magnets vary both in the permanency of their magnetization, and in the strength and orientation of the magnetic field they create. This section describes, qualitatively, the primary types of magnetic behavior that materials can show. The physics underlying each of these behaviors is described in the next section below, and can also be found in more detail in their respective articles.

- Most popularly found in paper clips, **paramagnetism** is exhibited in substances which do not produce fields by themselves, but which, when exposed to a magnetic field, reinforce that field by becoming magnetized themselves, and thus get attracted to that field. A good example for this behavior can be found in a bucket of nails - if you pick up a single nail, you can expect that other nails will not follow. However, you can apply an intense magnetic field to the bucket, pick up one nail, and find that many will come with it.

- Unscientifically referred to as 'non-magnetic,' **diamagnets** actually do exhibit some magnetic behavior - just to very small magnitudes. In fact, diamagnetic materials, when exposed to a magnetic field, will magnetize (slightly) in the opposite direction, getting (slightly) repelled from the applied field. Superconductors are strongly diamagnetic.

- **Ferromagnetic** and **ferrimagnetic** materials are the 'popular' perception of a magnet. These materials can retain their own magnetization; a common example is a traditional refrigerator magnet. (The difference between ferro- and ferrimagnetic materials is related to their microscopic structure.)

2.3.1 Paramagnetism

Paramagnetism is a form of magnetism which occurs only in the presence of an externally applied magnetic field. Paramagnetic materials are attracted to magnetic fields, hence have a relative magnetic permeability greater than one (or, equivalently, a positive magnetic susceptibility). The force of attraction generated by the applied field is linear in the field strength and rather weak. It typically requires a sensitive analytical balance to detect the effect. Unlike ferromagnets, paramagnets do not retain any magnetization in the absence of an externally applied magnetic field, because thermal motion causes the spins to become randomly oriented without it. Thus the total magnetization will drop to zero when the applied field is removed. Even in the presence of the field there is only a small induced magnetization because only a small fraction of the spins will be oriented by the field. This fraction is proportional to the field strength and this explains the linear dependency. The attraction experienced by ferromagnets is non-linear and much stronger, so that it is easily observed on the door of one's refrigerator (Jackson, 1999)

2.3.2 Diamagnetism

Diamagnetism is weak repulsion from a magnetic field. It is a form of magnetism that is only exhibited by a substance in the presence of an externally applied magnetic field. All materials show a diamagnetic response in an applied magnetic field. In fact, diamagnetism is a very general phenomenon, because all paired electrons, including the core electrons of an atom, will always make a weak diamagnetic contribution to the material's response. However, for materials that show some other form of magnetism (such as ferromagnetism or paramagnetism), the diamagnetism is completely overpowered. Substances that mostly display diamagnetic behaviour are termed diamagnetic materials, or diamagnets. Materials that are said to be diamagnetic are those that are usually considered by non-physicists to be "non-magnetic", and include water, wood, most organic compounds such as petroleum and some plastics,

and many metals including copper, particularly the heavy ones with many core electrons, such as mercury, gold and bismuth.

Additionally, all conductors exhibit an effective diamagnetism when they move through a magnetic field. The Lorentz force on electrons causes them to circulate around forming eddy currents. The eddy currents then produce an induced magnetic field which opposes the applied field, resisting the conductors motion (Mulay and Boudreaux, 1976)

2.3.3 Ferromagnetism

Ferromagnetism is the "normal" form of magnetism with which most people are familiar, as exhibited in horseshoe magnets and refrigerator magnets. It is responsible for most of the magnetic behavior encountered in everyday life. The attraction between a magnet and ferromagnetic material is "the quality of magnetism first apparent to the ancient world, and to us today," according to a classic text on ferromagnetism. Ferromagnetism is defined as the phenomenon by which materials, such as iron, in an external magnetic field become magnetized and remain magnetized for a period after the material is no longer in the field. All permanent magnets are either ferromagnetic or ferrimagnetic, as are the metals that are noticeably attracted to them. Historically, the term ferromagnet was used for any material that could exhibit spontaneous magnetization: a net magnetic moment in the absence of an external magnetic field. This general definition is still in common use. More recently, however, different classes of spontaneous magnetization have been identified when there is more than one magnetic ion per primitive cell of the material, leading to a stricter definition of "ferromagnetism" that is often used to distinguish it from ferrimagnetism. In particular, a material is "ferromagnetic" in this narrower sense only if all of its magnetic ions add a positive contribution to the net magnetization. If some of the magnetic ions subtract from the net magnetization (if they are partially anti-aligned), then the material is "ferrimagnetic". If the ions anti-align completely so as to have zero net magnetization,

despite the magnetic ordering, then it is an antiferromagnet. All of these alignment effects only occur at temperatures below a certain critical temperature, called the Curie temperature (for ferromagnets and ferrimagnets) or the Néel temperature (for antiferromagnets) (Jackson, 1999).

2.4 Adsorption

Adsorption is the accumulation of atoms, molecules, or ions at the surface of a solid or liquid as the result of physical or chemical forces. It differs from absorption, in that an adsorbed substance remains at the surface while an absorbed substance spreads throughout the absorbing material. An adsorbed substance is termed an adsorbate while the material on which adsorption occurs is the substrate. The release of an adsorbate is termed desorption.

Chemists make a distinction between chemical adsorption, or *chemisorption*, characterized by the formation of chemical bonds with the substrate, and physical adsorption or *physisorption*, which results from the van der Waals force. Chemisorption plays an essential role in corrosion, heterogeneous catalysis, and electrochemistry. Physisorption is a factor to be dealt with in the design of vacuum systems and is also used as a tool to study highly irregular surfaces. Further distinctions can be drawn between localized adsorption, in which the adsorbed molecules remain at the sites at which they were initially adsorbed, and delocalized adsorption, in which the adsorbed molecules can move along the surface. A distinction can also be made between monolayer adsorption and multilayer adsorption. For some examples of this effect see liquid-liquid extraction, it is possible to extract from one liquid phase to another a solute without a chemical reaction. Examples of such solutes are noble gases and osmium tetroxide.

2.4.1 Physisorption (physical adsorption)

Adsorption in which the forces involved are intermolecular forces (van der Waals forces) of the same kind as those responsible for the imperfection of real gases and the condensation vapours, and which do not involve a significant change in the electronic orbital patterns of the species involved. The term van der Waals adsorption is synonymous with physical adsorption, but its use is not recommended.

2.4.2 Chemisoption (chemical adsorption)

Chemisorption is a type of adsorption whereby a molecule adheres to a surface through the formation of a chemical bond, as opposed to the Van der Waals forces which cause physisorption. It is characterized by:

1. High temperatures.
2. Type of interaction: strong; covalent bond between adsorbate and surface.
3. High enthalpy: 50 kJ/mol $<\Delta H<$ 800 kJ/mol
4. Adsorption takes place only in a monolayer.
5. High activation energy
6. Increase in electron density in the adsorbent-adsorbate interface.
7. Reversible only at high temperature.

The main way in which most chemists utilise the effect of chemisorption is in catalysed reactions. The process of chemisorption is actually pivotal to the role of heterogeneous catalysis where the catalyst is in a solid phase—particularly transition metal catalysts. In many cases the chemical reagents will both bind to the catalytic surface. The chemical bonds then form and draw electrons away from the chemisorption bonds. The molecule then desorbs and is free to leave the surface.

Examples of chemisorption:

1. Self Assembled Monolayers (SAMs) are often formed by chemisorbing thiols (RS-H) onto gold surfaces forming Au-SR bonds.

2. O_2 on carbon at high temperatures

3. Research on the adsorption of hydrogen onto carbon nanotubes with the aim of producing a fuel cell that can eventually replace our dependence on fossil fuels

Adsorption is also a key factor in electrochemical reactions. When a metal electrode is immersed in an electrolyte solution it is generally covered by physically adsorbed water molecules. Anions like chloride and bromide also adsorb on electrode surfaces while smaller cations like lithium, sodium and potassium are generally too strongly bound to a small number of water molecules to bind directly to the electrode. The number and arrangement of adsorbed ions and molecules is a function of the electrode charge and may strongly affect the approach of ions in solution to the electrode, and thus the rates of electrochemical reactions.

Absorption, in chemistry, is a physical or chemical phenomenon or a process in which atoms, molecules, or ions enter some bulk phase - gas, liquid or solid material. This is a different process from adsorption, since the molecules are taken up by the volume, not by surface. A more general term is sorption which covers adsorption, absorption, and ion exchange.

If absorption is a physical process not accompanied by any other physical or chemical process, it usually follows the Nernst partition law:

"the ratio of concentrations of some solute species in two bulk phases in contact is constant for a given solute and bulk phase"

$$\frac{[x]_1}{[x]_2} = constant = K_{N(x,12)}$$

The value of constant K_N depends on temperature and is called partition coefficient. This equation is valid if concentrations are not too large and if the species "x" does not change its form in any of the two phases "1" or "2". If such molecule undergoes association or dissociation then this equation still describes the equilibrium between "x" in both phases, but only for the same form - concentrations of all remaining forms must be calculated by taking into account all the other equilibrium. In the case of gas absorption, one may calculate its concentration by using e.g. the Ideal gas law, c = p/RT. Alternatively, one may use partial pressures instead of concentrations. In many technologically important processes, the chemical absorption is used in place of the physical process, e.g. absorption of carbon dioxide by sodium hydroxide - such processes do not follow the Nernst partition law.

2.4.3 Adsorption Kinetic (Eren Z. and Acar F.N., 2007)

2.4.3.1 The pseudo-first-order model

A simple kinetic of sorption is the pseudo-first-order equation of Lagergren expressed in equation 2.1.

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$
(2.1)

Integrating equation 2.1 and applying the boundary conditions $q_t = 0$ at $t = 0$ and $q = q_t$ at $t = t$, gives

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$$
(2.2)

Where k_1 = Lagergren rate constant (h^{-1})

q_e = Amounts of chemical sorbed at equilibrium (h)

q_t = Amounts of chemical sorbed at time t (h)

2.4.3.2 The pseudo-second-order model

The pseudo-second-order rate expression is used to describe chemisorption involving valency forces through the sharing or exchange of electrons between adsorbent and adsorbate as covalent forces. The rate of pseudo-second-order reaction may be dependent on the amount of solute sorbed on the surface of adsorbent and the amount sorbed at equilibrium. The kinetic rate equations can be written as equation 2.3.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

(2.3)

Where is Pseudo-second-order rate constant (g mg^{-1} h^{-1}). Separating the variables in the equation 2.3 gives integrating this for the boundary conditions $t = 0$ to t and $q_t = 0$ to q_t, gives

$$\frac{t}{q_t} = \frac{1}{2k_2 q_e^2} + \frac{t}{q_e}$$

(2.4)

The advantage of using this model is that there is no need to know the equilibrium capacity from the experiments. In addition, the initial adsorption rate can also be obtained from this model as equation 2.5.

$$h = k_2 q_e^2$$

(2.5)

Where h is the initial sorption rate (mg/(g min)).

2.4.4 Adsorption Isotherm

Sorption isotherms are plot between the equilibrium adsorption capacity (q) and the final equilibrium concentration of the residual sorbate remaining in the solution (C_e). The equilibrium adsorption capacity, q (mg/g), can be calculated with the equation 2.6.

(2.6)
$$q = \frac{(C_0 - C_e)V}{m}$$

Where C_0 is the initial concentration (mg/l), C_1 is the residual concentration at equilibrium (mg/l), V is the solution volume (l), and m is the adsorbent mass (g).The adsorption isotherm relationship can also be mathematically expressed. Langmuir and Freundlich isotherm are the most commonly used for describing relationship.

2.4.4.1 Langmuir Isotherm

In 1916, Irving Langmuir published a new model isotherm for gases adsorbed on solids, which retained his name. It is a semi-empirical isotherm derived from a proposed kinetic mechanism. It is based on four assumptions:

1.   The surface of the adsorbent is uniform, that is, all the adsorption sites are equivalent.

2.   Adsorbed molecules do not interact.

3.   All adsorption occurs through the same mechanism.

4.   At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent.

The Langmuir relationship is of a hyperbolic form as shown in equation 2.7:

Langmuir isotherm: $$q = \frac{q_m b C_e}{1 + b C_e}$$

(2.7)

The Langmuir relationship can be linearized by plotting either $(1/q)$ vs $(1/C_e)$ or (C_e/q) vs C_e. Where q_m is the maximum adsorption capacity, b is a Langmuir coefficient related to the affinity between the sorbent and sorbate.

The Langmuir isotherm considers sorption as a chemical phenomenon. It was first theoretically examined in the adsorption of gases on solid surfaces. Langmuir constant $b = 1/K$ which is related to the energy of adsorption through the Arrhenius equation. The higher b and the smaller K, the higher is the affinity of the sorbent for the sorbate. q_m can also to interpreted as the total number of binding sites that are available for sorption, and q as the number of binding sites that are in fact occupied by the sorbate ate the concentration C_e.

Although the Langmuir model sheds no light on the mechanistic aspects of sorption, it provides information on uptake capabilities and is capable of reflecting the usual equilibrium sorption process behavior. Langmuir assumed that the forces that are exerted by chemically unsaturated surface atoms (total number of binding sites) do not extend further than the diameter of one sorbed molecule and therefore sorption is restricted to a monolayer.

In the simplest case the following assumptions were made:

a) Fixed number of adsorption sites; at equilibrium, at any temperature and gas pressure a fraction of the surface sites θ is occupied by adsorbed molecules, and the fraction $1-\theta$ is free.

b) All sorption sites are uniform (i.e. constant heat of adsorption)

c) Only one sorbate.

d) One sorbate molecule reacts with one active site.

e) No interaction between sorbed species.

Assumption of a value for the surface area covered per molecule then could allow computation of the active specific surface area of the sorbent using Avogadro's number. As long as its restrictions and limitations are clearly recognized, the Langmuir equation can be used for describing equilibrium conditions for sorption behavior in different sorbate-sorbent systems, or for varied conditions within any given system.

2.4.4.2 Freundlich Isotherm

The Freundlich isotherm relationship is exponential form as shown in equation 2.8:

Freundlich isotherm: $q = kC_e^{(1/n)}$

(2.8)

Where: k and n are Freundlich constants.

The Freundlich relationship is an empirical equation. It does not indicate a finite uptake capacity of the sorbent and can thus only be reasonably applied in the low to intermediate concentration ranges. A simple sorption isotherm indicates that the highest fraction of the sorbate species sorbed is observed at the lowest sorbate concentration, corresponding to the steepest part of the isotherm plot. Such behavior is typical of all dissolved species. Stated differently, the lower concentration of a dissolved substance in water, the greater fraction of it will be sorbed on solids. This behavior is typical of trace organic and inorganic substances at µg/l concentrations or lower. However, it is easier to handle mathematically in more complex calculations (e.g. in modeling the dynamic column behavior) where it may appear quite frequently. Freundlich model can be easily linearized by plotting it in a (log-log) format.

2.4.5 Comparison of Sorption Performance

Performance of sorbing materials often needs to be compared. The simplest case is when there is only one sorbate species in the system. The comparison of single-sorbate sorption performance is best based on a complete single-sorbate sorption isotherm curve. In order for the comparison of two or more sorbents to be 'fair' it must always be done under the same conditions. These may be restricted by the environmental factors under which sorption may have to take place (pH, temperature, ionic strength, etc.).

By performance of the sorbent is usually meant its uptake (q). The sorbents can be compared by their respective q values which are calculated from fitting the Langmuir isotherm model to the actual experimental data (if it fits). This approach is feasible if there exists the characteristic q_m sorption performance plateau (the maximum sorbent saturation). A 'good' sorbent that one always looks for would feature a high sorption uptake capacity q_m. However, also desirable is a high affinity between the sorbent and sorbate reflected in good uptake values at low concentrations (C_e). This is characterized by a steep rise of the isotherm curve close to its origin. Performance in this region is reflected in the Langmuir coefficient b.

2.5 Nanotechnology and the environment

The report focussed only on the potential health risks from exposure to free engineered nanomaterials such as nanoparticles and nanotubes. This raises an obvious but important point: nanotechnology represents the development of an incredibly diverse range of structures and it is clear that a nanoparticle of titanium dioxide and an instrument such as a nanotweezer are quite different entities. By branding both as a single nanotechnology one runs the risk of tarring all with the same brush. Nanotechnology is very much a generic catchall term encompassing the development and commercial exploitation of a range of structures: these include nanoparticles (e.g. of carbon (fullerenes or buckyballs), TiO_2 and ZnO) and carbon

nanotubes. These nanomaterials are free, discrete structures. In fixed nanoproducts, the nanoscale active area forms part of a larger object, such as a computer chip.

Some information was available to the Royal Society working group to assess the potential human health impact of free engineered nanomaterials: this drew on studies of cellular toxicity and particle-induced lung diseases associated with air pollution (ambient particulates), mineral dusts, coal dusts, asbestos and a few recent studies on carbon nanotube pulmonary toxicity. What is very noticeable is the almost complete absence of scientific literature on environmental toxicity or exposure to allow the undertaking of even the most basic assessment of potential environmental and human health risks associated with environmental exposure to free, engineered nanomaterials. If the benefits of nanotechnology to society are to be realised it is clear that this issue needs to be comprehensively addressed.

The magnitude of the task associated with undertaking environmental risk assessments, even for the range of nanoparticles and nanotubes in current production alone, should not be underestimated: firstly, almost nothing is known about uptake, distribution and toxicity in non-human species. One concern is the potential unrestricted mobility of engineered nanomaterials such as nanoparticles within organisms (Nemmar et al., 2001). Indeed it is this translocatory potential that in part makes nanoparticles commercially attractive fordrug delivery into poorly accessible compartments of the body such as the brain.

There are almost no ecotoxicological (including marine) studies with engineered nanomaterials. One of the only studies conducted with aquatic species (fish) suggests that oxidative stress may be a potential mechanism of toxicity associated with free engineered nanoparticles such as carbon C60 fullerenes (Oberdorster, 2004). Oxidative stress and inflammatory reactions are known responses in the mammalian lung to ultrafine particulate exposure from inhalation of, for example, coal dust. Recent studies involving pulmonary exposure of carbon nanotubes in rodents (Lam et al., 2004; Warheit

et al., 2004) suggest that lung histopathological responses, including inflammation and granuloma formation, may also be significant. A more fuller understanding of basic mechanisms of toxicity at a cellular level for nanomaterials will be important in the initial phases of general toxicological research. In total such studies can provide provisional pointers as to further detailed areas for investigation in terrestrial, aquatic and marine species.

The above toxicological studies with carbon nanotubes highlight an important point: carbon nanotubes frequently contain residual catalytic metals (up to 27% by weight, Lam et al., 2004), often dependent on the method of manufacture. These studies show that the type and residual metal content of the nanotube may be important in terms of the relative toxicity. What this means is that each type of nanoparticle and nanotube may need to be assessed on a case by case basis, since, while toxicological effects may possess similarities, the exact nature and magnitude of that toxicity may be substance specific, and indeed may vary with size continuum for that particular substance. In light of this, there is a clear need to optimise or develop a range of generic standard test procedures that can be applied to a range of nanomaterials to assess their relative toxicities. This will require the reaching of a consensus on appropriate endpoints that should be measured.

Of course toxicity is only one part of the story: understanding exposure is equally important. But here again there is virtually no information to allow even the most basic assessment of nanoparticle or nanotube exposure in the environment.

There may be direct inputs into the aquatic, marine, terrestrial ecosystems and atmosphere from initial and downstream manufacturers (e.g. those who blend imported, engineered nanoparticles). There may also be non-industrial inputs e.g. consumer products including sunscreens and cosmetics from both direct (e.g. bathing) and indirect (sewer) sources, leaching from landfill or soil-applied sewage sludge and atmospheric sources from waste combustion. Central to this is the need to obtain

regularly updated information on the nature and magnitude of current and future sources of nanomaterials to the environment (a challenge since the nanoscale industrial landscape is rapidly changing) and understanding what happens to nanomaterials during their journey from manufacture to waste disposal. This

can help to focus studies that can tell us about transport pathways, biogeochemical cycling and environmental fate. Ultimately such work will help us to identify which, if any, environmental compartments are at risk of contamination by nanomaterials.

Underlying this is the need to develop cost effective, standardised methods for detecting and quantifying the levels of nanomaterials such as engineered nanoparticles in the environment and distinguishing these from those that are naturally occurring. These will need to be developed for a range of environmental media (from air to marine waters to sewage sludge), critically accounting for changes in behaviour within these media. And this behaviour may not be simple: the physical behaviour of nanoparticles and nanotubes tends to be quite different when they enter water, where they can readily clump together (Warheit et al., 2004) (although development of surface treatments may serve to prevent this clumping behaviour). In the absence of such treatment, formation of ultrafine colloids is likely to occur and methods will need to be optimised or developed to both measure these and to study how toxicity, persistence and bioaccumulation changes in aqueous media. Similarly, how nanomaterials influence the behavior and toxicity of existing chemicals present in the environment may be need to be addressed.