Nanopollutants, their effects on the environment, and potential impacts on the South African water treatment and supply infrastructure

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1. Introduction

Nanotechnology research and development is rapidly expanding into a full-scale industry that includes building materials, automotive parts, sports equipment and consumer products. This technology promises significant technological advantages, including less expensive and cleaner production processes. Nanotechnology also shows potential for environmental pollution remediation through catalytic degradation and adsorption processes [Borm, 2008].

Due to economic pressures the availability of nanotechnology-based consumer products are increasing rapidly while the development of regulatory frameworks and environmental impact assessment tools regarding nanotoxicity to the environment are lagging behind. Unfortunately this lack of regulatory control means that increasing environmental exposure to nanotechnology occurs without an increase in the knowledge of the general public regarding both exposure and potential environmental toxicity of nanoparticles [Rejeski & Lekas, 2007]. The study of nanotoxicity and its effects on the future sustainability of the environment is a relatively new field in science, unfortunately hampered by a lack of funding [Morrissey, 2006; Uskovic, 2007]. However, the available information regarding nanotoxicity indicates that the potential dangers associated with uncontrolled release of nanoparticles into the environment must not be ignored.

This report is concerned with the rapidly growing availability of nanotechnology and related products in South Africa. Although nanotechnology-related industries are not currently widely distributed in this country, imported nanotechnology-related products are freely available and represent an increasing potential for environmental pollution. Examples of the applications and toxicity of nanoparticles and materials will be provided together with information regarding the potential environmental impacts of nanotechnology.

Although very little research is available regarding the impact of nanotechnology on water and waste treatment systems it must be regarded as an important area of future research by local scientific institutions. The potential effects of this growing industry on water sanitation and waste water treatment systems will be discussed based on the available information. Future research efforts in the field of waste water treatment should be aimed at raising awareness with municipal authorities regarding the dangers inherent to uncontrolled nanopollution. Local regulations and by-laws should be developed as soon as possible to protect the environment against the pollution potential of imported nanotechnology.

2. Definitions and types of nanoparticles

Research into the unique properties of nanomaterials and the development of techniques and analytical tools to increase the knowledge base regarding these properties has expanded rapidly in the last decade. The emergence of nanotechnology from laboratory research to widely available consumer products and appliances has been so fast that the general population is already being exposed to this new technology without having had the time to understand all the potential implications [Borm, 2008]. Unfortunately this rapid expansion of nanotechnology has also led to the confusing and often inaccurate use of the word "nano" [Borm, 2008]. Currently accepted definitions regarding the crucial aspects of this new field of scientific development are provided in this section.

- Nanoscience (NS)
  - Study of phenomena and manipulation of materials at the atomic, molecular and macromolecular scale whose properties differ significantly from those at the larger scale [Public Available Specifications, British Standards Institution 2005].

- Nanotechnology (NT)
  - The understanding and control of material with dimensions of between 1 – 100 nm [Nowack, 2007] in more than one dimension and the design, characterisation, production and application of structures, devices and systems by controlling shape and size at the nanoscale [Public Available Specifications, British Standards Institution 2005].
  - NT (what it is) should include all of the following:
    - Research and technology development at the atomic, molecular or macromolecular levels in the length scale of 1-100 nm [Romig et al, 2007].
    - Creation and use of structures, devices and systems with novel properties and functions because of their small or intermediate size [Romig et al, 2007].
    - Ability to control or manipulate at the nanoscale [Romig et al, 2007].
    - The use of- or application of nanoscale science to produce novel materials and devices for biological or medical applications [Romig et al, 2007].

- Nanomaterial (NM)
  - Material with one or more external dimensions or an internal structure on the nanoscale (smaller than 100 nm) that could exhibit novel characteristics compared to the bulk or parent material [Public Available Specifications, British Standards Institution 2005].

- Nanoparticles (NPs)
  - Particles with one or more dimensions at the nanoscale (100 nm or less) [Public Available Specifications, British Standards Institution 2005].
  - Shapes can be spherical, tubular or irregular and particles can be fused, aggregated or agglomerated [Nowack, 2007].
  - NPs can occur naturally or be of anthropogenic (engineered NPs or as by-products of certain processes) [Nowack, 2007] origin.
  - NPs can be classified as organic or inorganic [Nowack, 2007]:

    - Organic (carbon containing) NPs can have different origins that can be used in their classification:
        - Biogenic [Nowack, 2007]
        - Geogenic [Nowack, 2007]
        - Atmospheric [Nowack, 2007]
        - Pyrogenic [Nowack, 2007]
    - Inorganic
        - Metals and metal oxides as well as various other inorganic materials like SiO_2 [Nowack, 2007].
    - Colloidal matter of nanometer scale
        - Colloidal material is defined as separate from dissolved or particulate suspended material [Nowack, 2007].
        - Dissolved material is defined as capable of passing trough a 0.45 µm cut-off filter [Nowack, 2007].
        - Some colloidal material can also pass through such a filter but is generally regarded as < 1 µm [Nowack, 2007].
        - The "chemcentric" definition of colloids define such particles as "a constituent providing such a milieu into and onto which chemicals can escape from the aqueous medium and whose environmental fate is predominantly affected by coagulation/break-up mechanisms, rather than removal by settling" [Gustafsson & Gschwend, 2007a].
        - Nanoparticles fall into the size-range of both dissolved and colloidal particles [Nowack, 2007].

- Nanopollutants
    - A pollutant must be considered to be any substance that is released (on purpose or accidental) from a specific area of safe confinement and/or handling and has the potential to cause harm to the environment [Nowack, 2007].
    - For nanomaterials to be classified as pollutants, the possibility of environmental exposure to such nanoparticles must exist [Nowack, 2007].
    - Furthermore, such exposure must result in a hazard to the environment [Nowack, 2007].
    - Analogous to the natural disaster precipitated release of conventional hazardous substances, NPs may be released unintentionally in large quantities. Population and industrial growth in areas where natural disasters may occur, as well as the effect natural disasters may have on storage or nano-related production facilities [Young, 2004], may well become a major environmental risk factor.

- Nanotoxicity
    - The identification of naturally occurring NPs, the improving technical ability to synthesize both organic and inorganic NPs as well as improving methods for evaluating the environmental impact of such particles have led to the realisation that some of these NPs are toxic to biological

systems. NPs are of similar dimensions as biologically active molecules and structures involved with chemical control (proteins), information storing (DNA and RNA) and support structures (membranes, actin and microtubules). The potential impact of such particles on the environment has led to the study of nanotoxicity. Early *in vitro* studies demonstrated that both polymeric dendrimeres as well as metal NPs can be cytotoxic due to the disruption of- and nanopore formation in cell membranes [Hong et al,. 2005]. Such NP/cell membrane interaction is dependent on the surface charge as well as the size of the NP [Nel et al., 2006]. Both cationic gold and positively charged dendrimere particles exhibited this ability to disrupt the phospholipid cell membrane [Hong et al., 2005]. More recent publications indicate that metal and metal oxide NPs cause cytotoxicity by adsorbing to cell membranes where interaction with sulphidoproteins disrupt these membranes. In some cases ion formation causes severe cytotoxic effects. The formation of reactive oxidant species (ROS), by both organic and inorganic NPs, causes oxidative damage to cell membranes and its effect on cellular anti-oxidant defence mechanisms also plays a role in the cytotoxicity of NPs [Hong et al. 2005; Park et al 2008].

- Different types of NPs
  - NPs can be subdivided into organic (made up of carbon) and inorganic NPs (minerals and metals) [Nowack, 2007].
  - NPs can occur naturally (black carbon, fullerenes and carbon nanotubes have existed in the environment at low concentrations since prehistoric times) or accidentally due to mechanical actions or processes. Anthropogenic NPs are manufactured as part of the growing NT activities world wide or as by-products of unrelated industrial chemical and mechanical processes [Nowack, 2007].
  - Naturally occurring organic NP
    - Soot or black carbon (BC) is a NP derived naturally from the incomplete burning of fossil fuels and one of the materials studied in order to gain more insight into the behaviour of both natural and anthropogenic NPs [Nowack, 2007].
    - Fullerenes also occur naturally due to the combustion of organic matter. This includes coal-burning power plants, petrol, diesel and fuel gas soot. Fullerenes are very stable in the environment which implies a long period (since the invention of fire and volcanic activity) of co-existence at very low concentrations with biological life. These NPs are insoluble in water in the native form but derivatization with ionisable or hydrophilic side-groups may render them more water soluble. Aggregates of fullerenes become more water soluble as their physical characteristics changes substantially from the single molecule. Fullerenes dissolve easily in phospholipid micelles [Nowack, 2007].
    - Carbon nanotubes (CNT) are another example of NPs that existed long before man. Currently produced as a by-product of alloy and steel manufacturing, single and multi-walled CNT's are also water insoluble unless cut into a strong acid solution under sonication. Such hydroxylated CNT's can be suspended in water but

aggregate in the presence of cations. Certain biopolymers can solubilise CNT [Nowack, 2007].

- Naturally occurring inorganic NP
  - Chemical weathering processes of silicates, oxides and other minerals often produces naturally occurring NPs. Acid mine drainage (AMD) may lead to the formation of NPs as sulphate-reducing bacteria can produce ZnS and UO_2 NPs. Physical properties of such NPs vary according to particle size and can be very different from the bulk material [Nowack, 2007].

- Anthropogenic or engineered NPs are manufactured from metal oxides, silicon and carbon. Drug delivery systems include the use of lipids, liposomes and polyethyleneglycol-based molecules. NPs are also manufactured accidentally in the modern society due to fuel combustion, diesel burning, metal smelting, frying food and heating of polymers [Reijnders, 2006].

- NPs used in manufactured products can be classified as inherently dispersive or inherently fixed
  - Inherently dispersive - free and easily lost to the environment
    - Silver NPs in consumer products and hydroxyapatite in toothpaste [Reijnders, 2006].
    - Fullerenes and/or TiO_2 and ZnO NPs in sunscreens. Coating of these NPs to facilitate containment and limit environmental exposure may in some cases even increase hazardous potential and alternatives should be considered [Reijnders, 2006].
    - Fullerenes with modified surfaces may change cytotoxicity by many orders of magnitude [Reijnders, 2006].
    - Safe use of cosmetics with inorganic NPs is under investigation [Reijnders, 2006].
    - Washing machines with silver NPs will discharge these particles to sewer systems and although diluted will extend the bactericidal effects of these NPs. Must pass through WWTW's and will probably be discharged into the environment. This also means that a scarce resource is lost forever and probably cannot be considered sustainable practice. Alternatives are available [Reijnders, 2006].
    - NPs used in drug delivery systems should remain stable long enough to accomplish its intended function but should biodegrade fast enough to avoid unintended side effects. Degradation by-products must have very low toxicity [Reijnders, 2006].
    - Coatings of lipids and liposomes to reduce negative character of the outer surface of NPs reduce toxicity but completeness and longevity of coating must be considered [Reijnders, 2006].
    - Quantum CdSe dots are coated with ZnS but this coating must be intact to be effective [Reijnders, 2006].
    - Biodegradation into low-hazard compounds and coating must be considered as the best preventative measures [Reijnders, 2006].

    - Inherently fixed (Not inherently dispersive)
        - Inherently fixed and therefore not easily lost [Reijnders, 2006].
        - However, can be lost due to wear, tear, corrosion and cleaning.
            - 20 washing cycles only leads to the loss of 60% of bactericidal activity from silver NP impregnated textiles [Reijnders, 2006].
        - More examples include glass, ceramics, polymer matrix – UV or IR filter layers, nanoplastisizers, stabilizers in concrete, window sprays and self-cleaning layers [Reijnders, 2006].
        - The hazard to the environment lies in when and how these particles are released [Reijnders, 2006].
        - NP release may also occur with the use of materials like stainless steel although not manufactured through the use of NT [Reijnders, 2006].
        - Wear and tear, cleaning and friction may release NPs or clusters of NPs. This should be taken into consideration for future manufacturing mechanisms [Reijnders, 2006].

- Functionalization of NPs
    - The exact nature of physical and chemical characteristics of the surface of any NP will determine its functionality and behaviour in different environments. Such knowledge is therefore crucial when trying to determine the nature of NP-environmental interaction [Nowack, 2007].
    - NPs are often functionalised through the addition of functional or reactive chemical groups to their surfaces.
        - Hydroxylation of the surface of CNT's to render them more soluble in an aquatic environment is such an example [Nowack, 2007].
        - Coating of NPs is also used to change the inherent and sometimes unfavourable characteristics of a NP for a specific purpose [Nowack, 2007].
    - This surface modification and sometimes the loss of these functional groups of NPs may change their reactivity and surface characteristics completely and this makes it difficult to determine the exact nature of its fate and effect on the environment [Nowack, 2007].
    - Aggregates of NPs are often released to form single NPs due to microbial organisms, light and oxidants. This activity may result in chemical or biological modification or degradation of the surface functionalization or release of NPs from a matrix. Chemical, biological and/or environmental factors may also change the functionality of NPs [Nowack, 2007].

These definitions and explanations are provided to increase awareness and understanding of the current terms and concepts used in the field of nanotechnology and nano-related research. Although the industrial sector has been quick to take advantage of the financial implications of NT, research regarding the environmental impacts of NT has not kept pace [Rajeski, 2007]. Government sponsored research into the safe and environmentally friendly use and release of nano-products has not been funded adequately and a much bigger effort in this regard from the industrialised nations in Europe and North America must be considered a priority. Future research into the environmental impact of NT could ultimately be the determining factor regarding the successful and sustainable utilisation of NT. NT is expected to play an important role in establishing new standards in clean manufacturing and improved waste disposal practices [Borm, 2008]. Products developed from the application of NT are also expected to improve in quantity, quality and affordability resulting in increased consumer utilization and therefore increased contact between NPs and the environment [Reijnders, 2006; Nowack, 2007].

3. Potential environmental exposure to nanotechnology

As mentioned in the previous paragraph the large-scale release of NPs into the environment is considered to be inevitable based on the increasing industrial exploitation of NT [Nowack, 2007]. Personal care products (PCP) like sunscreens and cosmetics as well as food products and packaging are examples of the increasing use of nanomaterials associated with future impact on the environment. Probably the outstanding feature of NPs is the change in surface characteristics of the nano-scale particles compared to the bulk or "parent" material [Nowack, 2007]. This increase in the surface to volume ratio increases surface reactivity and factors such as particle size and shape also influence the nature of NP interaction with its immediate environment. Differences in the character of the different available NPs will also lead to differences in toxicity and the potential routes of exposure of the environment to these NPs [Hansen et al., 2007]. Oberdorster et al. [Oberdorster et al., 2005] therefore made a valid point when suggesting that the environmental toxicity of the different NPs will have to be investigated and treated separately in order to produce meaningful results in this regard. Many studies are available regarding the possible toxicity of NPs to humans, based mostly on work with human or mammalian cell-lines [Fischer, 2007]. Some cases of NP toxicity to the ecology include studies on Zebrafish [Zhu et al., 2008], Rainbow trout [Federici et al., 2007], algae [Hund-Rincke, 2006] and daphnids [Hund-Rincke, 2006; Lovern, 2007], to name but a few examples. With toxicological studies of NPs lagging far behind the production, modification and use of nano-products the uncertainty of the potential impact of NPs on the environment needs to be addressed without delay.

Accurate evaluation of the potential of NPs to contribute to environmental pollution and nanotoxicity demands that all possible sources of introduction of any specific NP into the environment be taken into account, combined with a thorough investigation regarding the chemical and physico-chemical characteristics of that specific type of NP [Nowack, 2007]. The development of test protocols and toxicity evaluation systems that will allow the comparison of the toxicity of NPs must also be considered to be a high priority [Borm, 2008].

Point source release of NPs into the environment will occur from production facilities, landfills or waste water treatment plants. Non-point sources of NPs include accidental release during the production or transport as well as NPs released due to natural, chemical or mechanical wearing of NP containing products [Young]. The intentional release of NPs during NT-based environmental remediation treatment may also occur more and more frequently. For example, zero-valent iron NPs (nZVI) show great potential in the treatment of chlorinated organic solvents and arsenic adsorption [Nowack, 2007]. Although such environmental remediation is to be encouraged, the fate of the NPs as well as possible by-products resulting from the contact between the NPs and the pollutant and/or by-product formation due to contact with organic or inorganic components during the treatment must be studied carefully and extensively. Additional environmental contamination, even if due to the beneficial use of NPs must be avoided.

4. Nanotechnology and NPs in industry

The following sections will first explore current nanotechnology related products already manufactured and used in industry. The most prevalent NM's and therefore the most likely types of NPs currently at risk of being released into the environment will be identified. The potential impacts of nanopollution on both human health and the ecology will be discussed as well as the beneficial aspects of NT that can improve human life quality and mitigate ecological pollution.

Industrial applications of NT have already advanced to the point where NT has become commonplace in areas ranging from building material to consumer products. This has occurred under the pressure of the demand for superior and/or new products and applications in these sectors. NM's used in industry already totalled 2 000 tons in 2004 and is expected to grow to 58 000 tons between 2011 and 2020 [Maynard, 2006]. According to Borm [Borm, 2008], Lux Research estimates the current European nanoproduct market of €2.5 billion to increase to hundreds of billions of euro's in 2015 and trillions of euro's in the years to follow. Nanotechnology is estimated to be part of 15% of all manufactured products by 2014 worth approximately €2.6 trillion and an estimated 10 million jobs are expected to be created by the manufacturing of nano-related products alone [Borm, 2008]. Unfortunately, the pollution or toxic potential as part of the environmental health and safety (EHS) aspects of many of these nano-based products have not been adequately researched prior to release to the general consumer market. Unless there is a world wide initiative to develop human understanding regarding the risk factors involved with NT and adequate EHS regulations and development plans for such regulations are put in place, the risks regarding nanotechnology to the environment are considered to be incalculable [Morrissey, 2006]. In the absence of well-informed regulators such as national and even international EHS procedures the obvious economic potential of NT may not be realised to the full due to public pressure in response to poor EHS management. An example of the power of negative public sentiment regarding new technology can be found in the poor handling of the genetic modification (GM) technology issues [Uskovic, 2007].

Tables one and two provide information regarding the use of NT in industry, science and technology as well as consumer products. These tables highlight the wide-spread use of NT related products and therefore the increasing possibility of associated environmental impacts. Both organic and inorganic NPs with the potential of having a negative impact on the environment due to its toxicity as well as the frequency of application in NT can be identified from the information in tables 1 & 2. These NPs can be expected to have a higher impact on environmental pollution than those occurring less frequently and will be discussed in more detail in the next section of this report.

- Examples of industries already using NT
    - Electronic [Nowack, 2007; Hoyt, 2008]
    - Pharmaceutical [Nowack, 2007; Hoyt 2007]

- Cosmetics [Nowack, 2007] and sunscreens [Hoyt, 2008]
- Energy [Nowack, 2007]
- Environmental [Nowack, 2007]
- Catalytic [Nowack, 2007; Hoyt, 2008]
- Food
- Biomedical [Nowack, 2007; Hoyt, 2008]
- Defence
- Material and Textiles [Nowack, 2007; Hoyt, 2008]

5. The potential for environmental pollution by the NPs most frequently used in industry

From the information in tables 1 & 2 it is evident that the most prevalent NPs currently used in industry include organic NPs like CNT and fullerenes as well as metals like silver and gold NPs and metaloxide NPs, for instance TiO_2. These types of NPs are therefore the most likely sources of future environmental pollution. Although a number of very useful applications for NT have been developed including exiting and ongoing development in the medical field [Chan, 2006; Hagens, 2007; Sahoo, 2007; Sanvicens, 2008; Kelly, 2008; Jabr-Milane, 2008; Azarmi, 2008; De Jong, 2008], the potential harmful effects of NPs on the environment has also been recognised [Nowack, 2007]. Although many current and prospective nano-dependent technologies and products relies on non-dispersive nanoparticles, dispersal into the environment due to damage, friction, long-term exposure to unfriendly conditions and wearing must be expected. This means that even inherently non-dispersive NPs may be released into the environment over time. Inherently dispersive NPs in contact with the environment include drugs, PCP and environmental remediation products [Reijnders, 2006].

Governments, industry and the general public show increasing awareness of the growing potential for direct contact between NM's and the environment and the possibility of adverse consequences cannot be ignored [Nowack, 2007; Uskovic, 2007]. The information and examples cited in the following sections is by no means complete but can be used to form a general assessment of potential future impacts of NT on the environment. The available information regarding nanotoxicity also highlights the importance of research and the development of regulatory frameworks for industry regarding the handling, storage, recovery and the ultimate disposal of NMs.

Unfortunately very little funding is currently available for the investigation of possible ecotoxicity and ethical questions surrounding the nano-industry. For instance, environmental impact assessment (EIA) studies [Uskovic, 2007]. However, despite this lack of funding, the list of scientific publications regarding the potential negative environmental impact of engineered NPs keeps growing and should serve as motivation for both governments and private industry, especially in developed countries, to drastically increase the funding available in this regard. A serious draw-back regarding EIA work is the lack of a universal evaluation system for nanotoxicity of the different NPs and NM's as well as a method to evaluate NP impact on the environment. Although natural NPs can be used to model the possible occurrence, fate and effects of anthropogenic NPs in the environment, specifically with regard to possible environmental toxicity [Nowack, 2007] this is not sufficient. Moore [Moore, 2006] warns against the validity of such comparative studies as these naturally occurring NPs that have co-existed with biological life forms for a very long time have been present at very low concentrations.

6. Nanotoxicity and Human health

6.1 General mechanisms of human exposure to NPs

The information in tables 1 & 2 clearly indicate how wide spread the use of NT has become. Human exposure to NT and NPs must not be considered a future problem but a current reality. Increasing human contact with NPs is as inevitable as the rapidly accelerating growth of the NT related industry [Nowack, 2007]. Hoyt & Mason [Hoyt, 2008] estimate that around 2 million researchers and workers will be exposed to NPs due to the nature of their work by 2023. These numbers exclude environmental exposure of the general populace. Human contact with such NPs can occur *via* air, water or soil while bioaccumulation and bio-magnification of NPs in the environment threaten contamination of future human food supplies [Reijnders, 2006; Nowack, 2007]. The bioaccumulation of TiO_2 and BC NPs observed in *Daphnia* is but an example of the potential impact of nanopollution on the environment [Lubick, 2006].

The potential toxicity of free NPs as well as the increasing risk of environmental exposure to these NPs has been discussed extensively by Reijnders [Reijnders, 2006], and Nowack [Novack, 2007]. Fischer *et al.* [Fischer et al, 2007] focus on the importance of *in vivo* toxicological studies of NPs in order to provide valid data for future regulatory legislation in this field. *In vitro* studies that use cultured cell lines as evaluation tool may not provide all of the data required to determine the effects of nanotoxicity on the environment.

In the environment, NPs released into water/groundwater sources or into the atmosphere will tend to form aggregates, enhancing the possibility of NP elimination through sedimentation. Natural or artificially enhanced aggregation will reduce but not necessarily eliminate all free NPs. The concentration, environmental distribution, mobility and reactivity of such NP aggregates will differ significantly from that of the original free NPs. However, it cannot be assumed that the NP aggregates will be non-toxic to the environment unless proven by thorough scientific investigations. Another factor that may impact on environmental nanotoxicity is the changes that may occur once NPs is released. Loss of functionalization and chemical/structural changes that may occur due to its exposure to metabolic or other processes prior to environmental release may completely change the nature of a specific NP compared to its characteristics prior to release. Very little is known regarding the environmental fate and chemical stability of many of the NPs in use today. It is this unknown quantity and lack of information regarding the fate of NPs released into the environment, combined with the lack of regulation of the rapidly expanding nano-industry that is causing concern with interest groups world wide. It is therefore understandable that much of the available data on NP toxicity is aimed at its impact on human health. However, not nearly enough data is available at present and much of the relevant experimental data is generated using human cell cultures and animals [Hoyt, 2008]. This makes investigations into nanotoxicity to humans difficult to quantify with precision.

Nanotoxicity can be subdivided into organic and inorganic nanotoxicity although these different types of NPs may have similar cytotoxic effects. Some human health effects occurs independent of whether the NPs are organic or inorganic and synergistic effects between the two types of NPs may lead to increased levels of toxicity [Reijnders, 2006; Hoyt, 2008]. NP toxicity is mainly due to its large surface areas and ability to generate reactive oxygen species (ROS). Inflammation and fibrosis are indications of nanotoxicity noticed at organism level while oxidative stress, antioxidant activity and cytotoxicity occurs at the cellular level [Hoyt 2008].

Currently, inhalation is the primary method of airborne NP ingestion by humans as the lungs are in direct contact with the environment [Yang 2008]. NPs exist easily as aerosols due to their small size and are considered to be part of the respirable fraction (the amount of fine and ultra-fine particles < 5 μm inhaled on a regular basis) [Hoyt, 2008]. Although small particles in the micron and sub-micron range have been implicated in human pulmonary and cardiac diseases, NPs and NP aggregates (< 100 nm) penetrates even further than these ultrafine particles and may cause even more severe symptoms [Thrall, 2006]. All particles that make up the respirable fraction reach the alveoli in the lungs and due to the small size of NPs, Brownian motion will largely determine their fate. According to the particle deposition curve for particles in the lungs, 50-80% of NPs will attach to the alveoli compared to the 10 – 20% of larger particles. Macrophages tasked to ingest these contaminants fail to cope with these large numbers or fail to recognise them as invasive entities. Large numbers of NPs entering the lungs are therefore not removed by the body's primary defence system for inhaled small particulate matter [Hoyt, 2008]. These NPs may enter the bloodstream [Nowack, 2007] where it will circulate and if toxic, may cause severe renal and cardiovascular damage as the large numbers of NPs cannot be removed efficiently by the kidneys. Oxidative stress caused in blood vessels and tissue by the circulating NPs may lead to a loss of dilation in blood vessels resulting in cardiac stress [Nowack, 2007; Hoyt, 2008].

The observed translocation of inhaled carbon NPs along the olfactory nerve to the olfactory bulb in the brain has been observed [Reijnders, 2006] and NPs capable of crossing the blood-brain barrier are associated with neurological damage [Nowack, 2007; Hoyt, 2008]. Mouse microglia, specialised cells protecting the brain from external stimulae, were shown to suffer damage due to oxidative stress from the NP induced formation of reactive oxygen species (ROS). Microglia engulfs chemical particles *via* phagocytosis and destroys them by releasing chemicals in an oxidative burst mechanism. Prolonged stimulation by ROS was implicated in severe brain cell damage, similar to that observed for degenerative diseases like Parkinson's and Alzheimer's [Thrall, 2006].

Adsorption through the skin and ingestion are also recognized as alternative routes of human exposure to NPs [Hoyt, 2008]. NPs may reach the epidermis and penetrate to the blood stream through diffusion but ingestion remains a poorly understood mechanism for NP adsorption [Hoyt, 2008]. However, Reijnders [Reijnders, 2006] cites several authors indicating the possibility of NPs to cross the intestinal barrier for uptake into the lymphatic system (2-3% of ingested dose). The surface characteristics of the NPs will determine their uptake into liver, spleen and kidneys through the blood stream and inflammation of these areas may occur. Similar toxic effects as described for the inhalation of NPs are expected even if exposure occurs through these alternative routes [Hoyt, 2008]. Treatment of nanotoxicity is mainly symptomatic unless chronic illness develops and is based to great extent on experience with ultrafine particles [Hoyt, 2008].

The aggregation of NPs, size dependent sedimentation onto cells or diffusion towards cells is the main parameters determining NP uptake by mammalian cells [Nowack, 2007]. NP adsorption to cell membranes, determined by the surface characteristics of the NPs, also appears to play an important role. Active cell uptake includes endocytosis or phagocytosis by specialised cells while NPs can also penetrate non-phagocytic mammalian cell membranes like that of red blood cells and become internalised at vesicles and mitochondria causing serious cell damage and cell death [Thrall, 2006]. One characteristic common to both organic and inorganic NPs is that the finer the NP, the stronger the adverse health response seems to be. NP size (surface area), surface charge and chemical nature influence the severity of adverse health reactions [Reijnders, 2006].

Although some of the effects of NP pollution on human health have similar consequences whether caused by organic or inorganic NPs, the different types of NPs and their effect once taken up by living organisms will be discussed separately. Due to the different physicochemical surface characteristics of organic and inorganic NPs, regulations and control mechanisms for the protection of the environment may differ substantially in some respects depending on the type of NP.

6.2 Nanotoxicity caused by organic NPs

As mentioned in the previous section, the inhalation of NP contaminated air is associated with pulmonary infections, inflammations and other diseases. Human exposure to NPs like BC and PTFE is a well documented example of solid particles' ability to penetrate deep into the lungs where they show high deposition potential. Due to its relatively small size and surface activity, NPs not only penetrate cell membranes but may carry additional toxic materials with them [Reijnders, 2006]. Carbon based NPs are especially prone to adsorption of the highly toxic polycyclic hydrocarbons [Yang, 2008].

CNT are associated with interstitial granulomas that may increase in severity with time and fullerenes are toxic to macrophages in experimental studies while ozone and BC NPs also cause damage in a synergistic fashion [Reijnders, 2006]. Native CNT's may concentrate on the skin or protective gloves in the lab or workplace to cause dermal toxicity due to oxidative stress [Reijnders, 2006]. NPs originating from the use of medical implants or dental work are another source of internal NP pollution as is nano-sized polyethylene particles [Reijnders, 2006]. Drug delivery systems dependent on NT may cause hypersensitivity reactions, possibly due to complement activation. Although NP drug delivery systems will increase the capacity of future medical treatment, careful selection of these particles will be vital to reduce the occurrence of inflammation and oxidative damage. An example is soluble polyalkylcyanoacrelates where the long alkyl chain molecules are less susceptible to hydrolytic degradation and therefore less likely to cause toxicity [Reijnders, 2006].

Water soluble fullerenes are used in medical technology and optical, mechanical and electronic applications. Future exposure of the environment to these C_{60} molecules is therefore increasingly likely. C_{60} produces oxygen radicals in water and its effect on cell membranes is therefore important. Fullerenes are normally not soluble in water but the addition of functional groups (for instance hydroxyl and carbonyl groups) on the surface can make these NPs sparingly soluble [Sayes et al, 2005]. Interestingly, Sayes et al [Sayes et al, 2005] reports that the functionalisation of fullerenes decreased its toxicity in human cell lines. The pristine inner structure of the fullerenes however, proved highly toxic even without interaction with mitochondria but through the generation of reactive oxygen species (ROS) resulting in oxidative cell membrane damage. Fullerenes are strong electron acceptors in biological systems and can probably act as pro-oxidants for the formation of superoxide anions, responsible for oxidative damage to the cell membrane [Sayes et al, 2005]. BC particles are associated with oxidative stress at a cellular level [Reijnders, 2006].

6.3 Nanotoxicity caused by inorganic NPs

Several of the inorganic NPs already in use by industry for the manufacturing of a variety of consumer products (see tables 1 and 2) are toxic to humans. TiO_2 is often used as an anti-caking agent in foodstuffs as well as a reflective material in sunscreens and cosmetics [Thrall, 2006]. Dermal UV protection using agents containing TiO_2 and ZnO NPs have been classified safe to use by the SCCNFP of the European Union (EU) although recent publications indicate high levels of penetration of mammalian skin within 8 hours of application. These metal oxides can be photocatalytically active upon exposure to sunlight and is often coated with Al_2O_3 or SiO_2. Such NPs may be active in causing DNA damage due to its penetration potential. TiO_2 is linked with allergic reactions and impaired lung defence mechanisms, nickel and other metal NPs cause lung illnesses and iron salts are associated with oxidative stress at a cellular level [Reijnders, 2006].

CdSe semiconductor quantum dots are used to replace fluorescent dyes but exhibit cytotoxicity with liberation of Cd^{2+} ions [Reijnders, 2006].

Although popular as anti-bacterial agent, silver nanoparticles also exhibit toxicity to mammalian cells, especially if ingested through respiratory channels and the gastro-intestinal tract. Preliminary data suggests that these NPs react with the thiol groups of certain proteins and other enzymes within mammalian cells which include glutathione, thioredoxin, SOD and thioredoxin peroxidase. These proteins form an important part of cellular anti-oxidant defences, responsible to neutralize the oxidative stress that may result from the formation of ROS, primarily generated by mitochondrial energy metabolism. Damage to this defence mechanism will lead to ROS accumulation, inflammatory response and mitochondrial destruction. The resulting release of apoptogenic cytochrome C leads to programmed cell death. Cell membrane damage is also associated with Ag NPs that must penetrate the membrane to reach the mitochondria. Proteins with thiol groups exist in large concentrations in the cell membrane and Ag NP damage of these proteins as well as lipoperoxidation may be implicated in membrane damage and NP penetration [Chen, 2006]. Recent work corroborates Ag NPs and/or colloid inhibition of bacterial growth [Hu et al, 2003]. Nitrifying bacteria, crucial to the successful operation (nutrient removal) of modern activated sludge plants were shown to be vulnerable to silver NP toxicity although the mechanism of toxicity could not be associated with bacterial cell membrane damage [Choi, 2008].

Zero-valent iron NPs, already seen as an important factor in future environmental remediation activities will have to be used with circumspection as these NPs are also toxic to bacteria like *E. coli* and may therefore have undesirable impacts on activated sludge processes [Lee, 2008; Auffan et al, 2008].

6.4 Oxidative stress

It is clear from recent experimental research that NPs cause damage at a cellular level (cytotoxicity) through different mechanisms. These include disruption of mitochondrial activity, destruction of microstructures in the cells and oxidation damage to cell organelles and membranes due to oxidative stress. Oxidative stress appears to be a very important factor in NP cytotoxicity and will be discussed in more detail.

Excessive ROS production or the failure of the cellular anti-oxidant defence system may cause oxidative stress. Li et al. [Li et al, 2008] postulates that low levels of oxidative stress serves as a cellular defence mechanism while high levels of oxidative stress causes injury and cell death [Li et al, 2008]. Xia [Xia, 2006] describes oxidative stress as a state of redox disequilibrium where ROS production is higher than what the antioxidant defense mechanisms of the cell can handle. The transcriptional activation of more than 200 antioxidant and detoxification enzymes (phase II response) is triggered by the appropriate glutathione (GSH)/glutathione disulfide (GSSG) ratio, the main regulator of cellular redox homeostasis. However, NP dependent ROS production may reach levels where the cellular responses are inadequate to deal with the problem, leading to pro-inflammatory and cytotoxic effects [Xia, 2006]. Cytotoxic effects are mediated by the mitochondria through the release of pro-apoptotic factors. However, several NPs are known to target the mitochondria directly [Xiao, 2003], thereby negating these protective cellular mechanisms.

Determining the levels of cellular oxidative stress caused in human cell lines and animal studies may constitute an excellent method for determining the potential toxicity of NPs [Xia, 2006; Li et al, 2008].

7. Ecological toxicity potential of NPs

7.1 Potential impacts of nano-pollution on the ecology

Compared to the potential human health impacts of NPs the ecological impacts have so far received little attention by comparison, a fact also emphasised by Reijnders [Reijnders, 2006]. Recent studies have highlighted the fact that human health may be closely related to the wellbeing of aquatic biota. This association does not exists solely through bioaccumulation and the food chain but the general health of aquatic biota can be used as a reliable indicator of the exposure of all life-forms to an increasingly toxic environment [Jha, 2004]. The preservation and sustainability of the ecology should therefore be considered as an integral factor in the future sustainability of human existence. Although nanopollution of the ecology has only become a recent subject of scientific investigation, some examples of the impact of NPs on the ecology are available and will be discussed in the following sections. The potential toxicity of NPs to biological systems is due largely to the fact that NPs are of a similar size than many biological molecules and macromolecules. The large surface to volume ratio of NPs sets it apart from its bulk or parent material as it is the surface characteristics of particles that determine their chemical or physico-chemical reactivity [Moore, 2006]. Polycationic macromolecules, both organic and inorganic, are capable of penetrating cell membranes *in vitro* and NP interaction with surface lining layers of tissue is due to surface chemistry and reactivity [Hoet et al, 2004]. Fibre length is another critical parameter for adverse cellular interaction with NPs and particle size, mobility and biodegradability also influence the ecotoxicity of NPs in the aquatic environment [Moore, 2006]. The rapid mixing and distribution of nanopollutants in aquatic systems cause additional concern as it will cause fast and widespread distribution of nano-pollutants from industry, PCP and rain water run-off [Lovern, 2007]. The effective distribution of NPs also implies rapid dilution and therefore a probable degree of mitigation. It is cause for concern that organisms like *Daphnia magna* exhibited behavioural changes due to exposure to NPs, even at sub-lethal concentrations. Such behavioural changes lead to alterations in reproduction, predation and feeding patterns and might have far-reaching consequences on food web interactions [Lovern 2007]. Much of the available information regarding the behaviour of NPs in the environment and their interaction with biological life forms are generated through model NPs like BC, fullerenes and CNT. Although these NPs may have been present in the past, giving some indications that their existence is not intolerable to biological life, the current anthropogenic NPs produced by industrial activities are present at far higher concentrations and is often surface-modified. Studies based on the low levels of NPs occurring naturally prior to the industrial revolution is therefore of limited value for predictive studies of the future effects of nanopollution on the ecology [Moore, 2006].

7.2 Specific examples of ecological nano-toxicity

7.2.1 Organic NPs

The utilization of fullerenes in anything from commercial to medical applications is hampered by the lack of information regarding its human health and ecological impacts [Brant, 2007]. Although highly insoluble, fullerenes can exist in an aquatic environment as aggregates [Brant, 2007] or in clusters with modified (hydrophilic functionalized) C_{60} on the outside and unmodified C_{60} on the inside. These organic NPs cause lipid oxidation in the brain of juvenile bass and bactericidal activity of C_{60} and MgO NPs was also observed [Nowack, 2007]. Fullerenes also have a very low adsorption potential in soil and are therefore more easily absorbed by earthworms which causes concern regarding their environmental fate after release or disposal [Nowack, 2007]. The lipophilicity of these molecules allows relatively easy penetration of cell membranes and collection areas in the cell include mitochondria, cytoplasm, lysosomes and nuclei. Organic solvents like tetrahydrofuran may be trapped inside the fullerene structure and has been linked to observed cytotoxicity. [Nowack, 2007]. The fate of these molecules may also change in biological fluids and through exposure to UV light. This potential for unpredictable behaviour of fullerenes in solutions of different types, ionic strength, pH and temperatures suggests that a more stable variant of this NP is required to decrease its potentially harmful impact on the ecologically [Brant, 2007].

Although environmental contact and adsorption of xenobiotics by organic NPs (C_{60}, BC and CNTs added to aqueous solutions) may reduce the environmental availability of these compounds, such interaction may also result in increased toxicity, decreased toxicity or no change whatsoever. The partitioning and toxic mechanisms of the different toxic substances as well as their interaction mechanisms with the NPs they encounter must be understood thoroughly prior to using NT for the removal of such pollutants [Baun, 2008].

7.2.2 Inorganic NPs

Silver NPs have bactericidal properties and are used in consumer products like washing machines, food contact devices, medical applications and textiles [Blaser, 2008]. With this increased use of nanosilver in consumer products, food and medical technology, increased environmental exposure to silver NPs will occur [Blaser, 2008] and may well serve as a model of how NPs in the environment can be monitored and regulated.

Particle size and shape of silver NPs appear to be important to its potential bacterial toxicity, a feature common of a variety of different NPs [Nowack, 2007]. Although silver NPs are often embedded in a matrix or applied as a coating to polymeric devices [Blaser, 2008] its bactericidal effects are ascribed to the release of Ag^+ ions due to oxidation of metallic silver (Ag^0) [Kumar 2005]. Silver ions disrupt the phosphate, sulphur and nitrogen cycles of nitrifying bacteria through enzyme inhibition. This inhibition probably occurs due to silver ions binding to the thiolate groups found in these enzymes. Silver ions also directly cause the blocking of DNA transcription and disrupt bacterial respiration and ATP synthesis. However, Ag NPs were found to be much more bacterially toxic than silver ions [Nowack, 2007] and *E.coli* cultures sensitive to both Ag and Cu nanoparticles were identified. Although Ag NPs were more effective in these studies, Cu NPs proved more responsive to certain surface active groups of the *Ruparelia* strain [Ruparelia, 2008]. Ag NPs also showed antimicrobial activity against both *Escherichia coli* (Gram-negative) and *Staphylococcus aureus* (Gram-positive) [Maneerung, 2008]. Silver has been reported to be effective against certain types of viruses, algae and fungi [Blaser, 2008]. Silwer NPs were also found to inhibit the embryo development of Zebrafish in a dose dependent manner [Asharani, 2008].

Enough evidence regarding silver toxicity to the aquatic environment exists. However, due to the high affinity of silver for reduced sulphur compounds and the fact that these compounds are almost three times higher in natural water than silver ions, very low silver concentrations are normally in evidence in freshwater ecosystems [Blaser, 2008].

Of the metals found in freshwater systems, only Hg has a higher affinity for sulfides than Ag. Ag therefore occurs in the aquatic environment as colloidal silver sulphide clusters or as silver sulphide – organic material complexes. Organic silver thiolate complexes occur in the interstitial water content of sediments. In WWTW silver thiolate complexes are mostly converted to insoluble and very stable silver sulfides. Ag_2S binds strongly to suspended particles and is therefore removed from WWTW's in the sludge while it will occur mainly in the sediment of aquatic systems. Most of the Ag present in the dissolved phase is associated with colloids [Blaser, 2008]. Risk assessment of silver NPs remains uncertain at this point but nanosilver products disposed of in landfills may create future problems as microbes for the degradation of waste may be inhibited [Blaser, 2008].

Both micro and nano Zn particles are responsible for renal toxicity in mice. [Wang, 2005]. Mice also show moderate toxicity to copper NPs and ions but not copper microstructures. According to this study, copper toxicity of mice shows a gender dependency as male mice suffered more from nano copper toxicity than females [Chen, 2006].

Apart form silver NPs, many of the metal and metal oxide NPs tend to be toxic to bacteria. TiO_2 NPs also show bactericidal properties and as non-aggregated NPs tend to be very mobile in an aquatic environment and may combine with certain species of persistent organic pollutants (POPs), this association will tend to create an additional transport and perhaps uptake mechanism for the undesirable POPs [Reijnders, 2006].

7.3 Experimental data applicable to environmental toxicity

- As most studies regarding mammalian cell uptake of NPs were done *in vitro* and involved growth medium containing protein and other biological compounds, direct application of such data to the uptake of NPs by aquatic biota is difficult. Possible routes of uptake include direct ingestion and crossing of epithelial cells in gills, olfactory organs and skin [Moore, 2006].
- Prokaryotes like bacteria may be protected against some types of NPs due to a lack of transport mechanism for colloidal particles and macromolecules across its cell walls [Moore, 2006]. Gram positive bacteria also seem far better protected than gram negative ones regarding C_{60} uptake [Novack, 2007].
- Eukaryotes like protists and metazoans do have mechanisms for endo- or phagocytosis of nanoscale or microscale colloids and macromolecules.
- Inorganic NPs of ZnO was taken up by bacteria and CeO_2 adsorbed onto the cell wall of *E. coli* although internalisation could not be confirmed.
- Both unicellular aquatic organisms and animals like fish were shown to be susceptible to NP toxicity although some conflicting data were observed.
- Respiratory toxicant to rainbow trout and growth inhibitor to protozoans. Observed unicellular protozoan growth-stimulation explained by CNT-peptone complex and therefore increased uptake of peptone. CNT unpurified synthesis mixtures shown to increase mortality.
- Metal NPs of TiO_2, SiO_2 and ZnO are proven to be toxic to bacteria, especially in the presence of light. Bulk TiO_2 shows no toxic effects but NP-sized TiO_2 is toxic.
- The toxic effect of the above metal NPs are associated with internalisation.
- Several factors appear to determine the potential toxicity hazard of NPs. Persistence in biological matter may lead to bioaccumulation and long term toxicity while NPs that are biodegraded and secreted in low toxicity forms may well cease to be hazardous. Solubility will be important as is shape, size and also dose levels of exposure. In the absence of genotoxic compounds NPs may be tolerable at reasonably high doses. Air pollution *via* NPs is another issue altogether. Significant correlation between NP breathing contamination and disease and death exists [Reijnders, 2006].

Oxidative damage to aquatic organisms caused by surface active NPs seems likely and as additional toxic interaction between these life forms and newly manufactured NPs are inevitable, the Royal Society and Royal Academy of Engineering propose a precautionary approach, the testing of all existing and new nanomaterials for individual levels of impacts on the environment [Moore, 2006].

- Interaction of NPs and other contaminants
    - Interaction of NPs and toxic organic compounds can both increase and/or alleviate the toxicity of the newly formed combination [Nowak, 2007].
    - NPs may absorb or adsorb the organic toxin, reducing its free concentrations and therefore reducing the toxic effects [Nowak, 2007].
    - NPs bound to organics (adsorption) and taken up by the cell may have a toxic effect due to the nature of the NP, the organic substance or synergistically due to the presence of both[Nowak, 2007] .
    - No toxicity may also result if neither of the compounds is toxic. BC is a good example of reducing the uptake of organic material by micro-organisms. Another example is the reduced uptake of As(V) by carp in the presence of TiO_2 NPs [Nowak, 2007].
    - NPs can therefore also benefit certain toxic environmental conditions [Nowak, 2007].

- Environmental risk assessment
    - Environmental risk assessment of NPs
        - Environmental risk assessment studies for nanoparticles are still in its infancy [Nowak, 2007].
        - Various factors like partitioning of NPs to different phases and the mobility of NPs in each phase plays an important role [Nowak, 2007].
        - Persistence in secreted form and concentrations in which NPs is released will be important [Nowak, 2007].
        - Behaviour and toxicity regarding the different NPs are needed and analytical techniques are still in the development phase for many NPs [Nowak, 2007].
        - Products containing NP's and therefore capable of secreting NPs to the environment is still relatively few but expanding at a rapid rate [Nowak, 2007].
        - Nowak suggests that such assessments should start with a study of the sources of NPs and its environmental pathways. Such an approach should help to identify the subject needing protection from the relevant NP [Nowak, 2007].

The current opinion amongst scientists can be summarized as although NT can provide breakthrough development impacts in many areas, not all impacts will be benign to the environment. NPs will eventually have to be disposed of after use and will in all probability end up in landfills and incinerators and from these final treatment and storage areas be distributed to the atmosphere, soil and water. Life-cycle assessment of individual NPs will be the only way to determine the required changes needed regarding regulatory frameworks and laws governing the disposal of NPs. Information regarding the safety of NPs for use in humans and its final impacts on the environment is still lacking to a large degree and this will have to be addressed as soon as possible [Breggin & Pendergrass, 2007].

8. Technologies for the removal of environmentally hazardous NPs

8.1 Current problems in dealing with nanopollution

Existing waste water treatment and water purification technologies are not primarily designed to deal with nanopollution. Due to adsorption and other chemical interactions with NPs, dissolved chemicals may well escape in the treated water. Pre-coagulation and membrane filtration represent suitable treatment options but increased fouling by sub-micron particles may interfere with efficiency.

End-of-pipe treatment is yet to be implemented on a significant scale and will rely on the producers of nanomaterials with significant pollution potential to commit to the cost implications of such treatment. Evaluation of source reduction mechanisms will allow the implementation of process specific treatments but special attention should be given to capturing NPs in liquid rather than gaseous medium as well as the recycling of NPs. Containment of NPs in the process is important, therefore good filtration technology will be required. End of pipe treatment at production facilities includes filtration and electrostatic precipitation. This is mainly for aerosol NPs and not very effective, especially as NPs decrease in size. Carbonaceous NPs respond well to catalytic oxidation filters and continuously regenerating traps but actually increase the secretion of volatile droplets of less than 30 nm. Magnetic NPs can theoretically be scavenged using magnetic filters but the efficiency is reduced with decreasing particle size < 200nm [Reijnders, 2006].

Coating may render NPs much less hazardous and must be considered [Reijnders, 2006]. This treatment option will of course depend on specific characteristics and applications of NPs. Regulation of NP release will have to be enforced by governmental agencies and it is doubtful that such enforcement will be possible prior to the development of adequate life-cycle and toxicity information.

Mass based risk assessment parameters may be inappropriate as NPs of smaller mass may differ radically from the bulk or larger particles of the same material. A number based system as for air-pollution quality would be more appropriate [Reijnders, 2006].

8.2 Examples of technology for the removal of NPs from the environment

Silica NPs are used in slurries for chemical-mechanical metal polishing and chemical-mechanical planarization (CMP) [Yang, 2007; Chin, 2006]. Such waste water contains high solid loads and conventional coagulation is difficult due to changes in turbidity and the production of high sludge volumes [Chin, 2006]. Composite TiO_2/Al_2O_3 membranes can also be used successfully to remove SiO_2 NPs from oxide CMP waste *via* electrofiltration [Yang, 2007]. Magnetic seeding aggregation with magnetite NPs proved to be very effective and provide results similar to membrane filtration. Recycling and reuse of the magnetite particles proved possible but still requires optimization [Chin, 2006].

Al(III) is used for the preparation of polyaluminium chloride (PAC) used in flocculation and coagulation processes for water and waste water treatment. Al_{13} (a nanosized particle) is believed to be the most effective form of Al(III) available. However, the separation and purification of this "forced hydrolysis" PAC product presents difficulties. Fractionation of the different nano-sized particles using UF membranes with a MWCO of alternatively 1 and 3 kDa can be used to purify Al_{13} from a mixture of Al(III) hydrolysation products [Huang et al, 2006].

An industrial park in Taiwan produces effluent in which the levels of COD are closely related to the number of NPs present in the effluent. This NP fraction comprises mainly of CaF_2 and silica. Poor coagulation performance of NPs using poly-aluminium chloride, high sludge volumes and the poor settling characteristics of these NPs do not allow for adequate treatment using biological methods. Although increased dosage of PAC improved the removal of the NPs it was established that charge neutralization was not the mechanism of choice for destabilisation in this system. Si particles in filtered, chemically treated water tended to agglomeration and possibly associate with compounds responsible for the high COD load. Rapid sand filtration of this fraction with particles > 0.45 µm was suggested for the adequate removal of the Si NPs [Chang, 2007].

9. Effects of NP pollution of water and aquatic biota

Direct release or accidental spillage of industrial effluent containing NPs into waterways or aquatic systems will impact on human health. Direct contact with such water will lead to ingestion of nanopollutants through skin contact, ingestion and water aerosols. Ingestion of vegetable matter irrigated with contaminated water or aquatic organisms like fish and shellfish could also lead to humans being exposed to the effects of bioaccumulation [Moore, 2006]. Research and development of technology suitable for the effective removal of various types of NPs from the aquatic environment must therefore be treated as a very high priority.

10. Ecological mitigation and remediation using NT

10.1 Environmental remediation

NT, except for its growing potential in the manufacturing industry can also play a large role in future environmental remediation. NT is not only expected to provide cleaner manufacturing processes thereby decreasing industrial pollution but also offers exiting possibilities for the direct treatment of environmental pollution. Several NT dependent applications have been identified with regard to pollution remediation and for use in water and wastewater treatment. This application of NT in the water treatment sector can be expected to grow rapidly in the future as the availability of treated water of good quality is at a premium world wide. The magnitude of this problem is illustrated by the fact that around 1.7 million fatalities (mainly children) occurs around the world every year due to unsafe water use. Approximately 4 billion cases of diarrhoea occur annually representing 4.5 % of the global health burden and an estimated 1/6 of humanity lacks any form of improved water within 1km from home [Smith, 2006]. This disturbing information illustrates the importance of high quality, affordable water treatment technology and NT can be expected to play an important role in alleviating the global shortage of potable water.

Nanotechnology for use in pollution treatment or water purification must be environmentally benign, capable of remediation of materials contaminated with hazardous substances and serve as sensors for environmental agents. Available adsorptive and reactive treatment options based on NT can be applied *in situ* or *ex situ*, similar to conventional treatment options [Tratnyek, 2006] and will be discussed in more detail in the following sections.

10.2 Filtration and adsorption technology

Nanofiltration (NF) is a membrane dependent, pressure driven process that removes bacteria, viruses, cysts, organic material [Costa, 2006] and some dissolved ions like As and metals, also nitrates, dyes and specialty chemicals [Smith, 2006]. NF is also effective in reducing COD loads and removing salt ions from textile waste waters for reuse, at much lower operating costs than reverse osmosis (RO). Pre-treatment with UF allows optimal permeate production rates and fouling protection for NF systems [Gozalvez-Zafrilla, 2008]. Coatings made from nanomaterials can also be used to minimize bio-fouling of existing membrane technologies [Smith 2006]. Zhang [Zhang, 2006] showed that composite Al_2O_3 membranes with $Mg(OH)_2$ nanotubes as active adsorbent could be used to remove almost 90% of Ni^{2+} ions from wastewater and repeated use of these membranes were possible prior to regeneration [Zhang, 2006].

The high surface area of clays, nanofibres and ceramic NPs allows efficient adsorption of pollutants, [Smith, 2006]. Nanoporous zeolites, polymers and attapulgite clays are useful in removing pollutants through adsorption. Magnetic nanoparticles are also being investigated for use in water treatment [Smith, 2006]. Organic carbon NPs and organic colloids are exceptionally strong adsorbents for organic pollutants and may provide a future method for the reduction of steroid hormones and herbicides in the environment [Nowack, 2007].

Nanofibre technology used in the filtration industry offers high specific surface area, interconnectivity of pores with the added potential to add functional or active groups on the surface at the nanoscale [Ramakrishna 2006; Barhate, 2008]. The large surface to volume ratio enables effective adsorption of organic materials, bacteria, viruses and protozoan cysts although these nanofibers also can be structurally modified to remove inorganic species as well. Nanofibers' surface to volume ration can be further increased by synthesis of porous nanofibers. Nanofiber based filtration experiments reports minimal fouling and flow restriction compared to membrane dependent processes which reduces the energy demand of related technologies [Smith, 2006].

10.3 Metal NPs used for environmental remediation

Cadmium released into the environment mainly originates with the metal finishing industry. This metal is highly toxic and although less prevalent than mercury, prone to bio-accumulation which poses a serious future environmental risk. Conventional processes for its removal include membrane filtration and alkaline metal hydroxide precipitation. These technologies are vulnerable to changes in pH, high salt concentrations and complex formation in the presence of organic and inorganic compounds. Pacheco et al [Pacheco et al, 2006] describes the highly efficient adsorption of Cd to Si-core, Al-shell NPs used as a cationic flocculant.

Hexavalent chromium Cr(VI) considered the third most prevalent inorganic contaminant at hazardous waste sites and second most prevalent inorganic contaminant after lead. Cr(VI) is acutely toxic, mutagenic and carcinogenic and can cross cell membranes. Reduction to Cr(III) is an important step in aqueous media and soil to eradicate its environmental impact [Omole, 2007]. Reducing agents include ferrous sulphate, sulphur dioxide, and sodium bisulfite, followed by Cr(III) precipitation [Xu, 2007]. Reduction with Pd NPs and formic acid are an effective method, specifically at 45 °C and low pH values [Omole, 2007]. Zero valent stabilised iron (nZVI) NPs can oxidise Cr(VI) in both water and soil and resin stabilisation of nZVI increases the conversion rate by a factor of 30 [Xu, 2007].

Modern catalytic systems allow the conversion of phenols to carbon dioxide and water *via* a wide range of intermediaries, some with very low reactivity. Pt NPs imbedded in hyper-crosslinked polystyrene provides an excellent catalyst that remains stable and allows almost complete phenol oxidation [Doluda, 2007].

Iron oxide NPs (Fe_2O_3) show excellent catalytic properties for use in advanced oxidation processes (AOP) for the mineralisation of toxic organic pollutants to CO_2 and H_2O. Important requirements of such a catalyst include efficient catalytic properties, immobilisation of the catalyst on inert surfaces (without loss of activity) to avoid loss and additional pollution and efficient regeneration of both adsorbent and nanocatalyst. Fenton-like organic material degradation was found to be efficient in the presence of hydrogen peroxide but in the absence of UV radiation. The NPs showed no aging effects after 90 days. Phenol destruction with this iron NPs as catalyst was shown to be 35 times higher than related Fenton-like oxidation processes [Zelmanov, 2008].

Zero-valent iron (nZVI) nanotechnology is dependent on particle morphology, reactivity and mobility [Tratnyek, 2006]. *In situ* treatment of ecological contamination using nZVI NPs appears to be less hazardous than expected. Several factors prevent these NPs from exhibiting ecological toxicity and uncontrolled mobility once introduced into the environment at a specific polluted site. These particles are expected to form very large aggregates, approaching micron-sized dimensions and will therefore not exhibit many of the highly reactive surface characteristics expected of real nano-materials. These aggregates will tend to act more like the well known colloidal systems. High reactivity of these particles appears to be based on its large surface area and not surface reactivity. High reactivity indicates low specificity, associated with short reactive life-span in the environment. This could be beneficial for "*in situ*" applications. Collisions between NPs and a porous environment are controlled by Brownian motion for particles < 400 nm while sedimentation due to gravitation becomes more important for larger particles. The mobility of NPs in a porous environment like soil are therefore predicted to be no more than a few meters. This is a good example that NP dependent environmental treatment technologies should be judged in an application dependent manner.

Iron NPs have also been used for the successful *in situ* treatment of sites containing hazardous wastes with organic contaminants like dioxins, PCB's and chlorinated hydrocarbons [Hoyt, 2008]. Palladium-doped iron nanoparticles have been demonstrated to remove these contaminants from groundwater at experimental scale while magnetite and non-valent iron nanoparticles are showing promising results regarding the removal of arsenic from drinking water [Smith, 2006].

Nanostructured mixed metal oxides have been shown to destroy biological toxins in water through photocatalysis and oxidation (TiO_2 is the popular material of choice in this field) [National Science and Technology Council, 2007]. TiO_2 is a photo catalyst that can generate ROS at particle surfaces when exposed to UV light. ROS diffuses rapidly and catalyzes the degradation of airborne and aqueous chemicals like hormones that is especially difficult to treat in aqueous media. TiO_2 particles tend to aggregate at neutral pH values but the use of carrier polyelectrolytes help to keep these NPs in suspension. The combination of TiO_2 NPs and specific anti-bodies for biological and medical applications help to target specific molecules for maximum benefit from ROS generation [Ogino, 2007]. TiO_2 NPs are also used for phosphate removal through adsorption [Smith].

Conventional water purification technology includes iodination, ozonation, UV-purification and membrane filtration. The addition of excessive amounts of chemicals may be carcinogenic or react with NOM to form the carcinogenic TCM's and both UV and membrane filtration technologies are expensive and not always effective when used in isolation. The use of silver catalysts, although an ancient method for water purification, has recently been investigated with renewed enthusiasm due to its bactericidal properties. Despite its long use no reported or anecdotal evidence exists to indicate detrimental effects to human health. Ag(III) is reported to be 240 times more effective than Ag(I) while silver ions are also effective in both bacterial control as well as the removal of iodine from water. Many industrial processes use H_2 to reduce metal catalysts for use in hydrogenation and other reactions. Shashikala et al describes a method for the preparation of a silver catalyst for water purification without the use of H_2, an important economic factor due to the use of H_2 in the enrgy sector. This method prepares silver NPs electrochemically deposited over carbon covered alumina support structures. Alumina provides structural integrity while the carbon protects the alumina layer from interaction with the water and reduces alumina acidity by > 90% [Shashhikala et al, 2007].

10.4 Organic NM

Natural organic matter (NOM) represents a major complication in water purification forming carcinogenic trihalomethanes during chlorination and enhancing bacterial regrowth and biofilm formation if not removed efficiently. Activated carbon adsorption is used as the conventional treatment option but overloading and carbon bed adsorption capacity (regeneration and replacement costs) represents limitations. CNTs heat treated to increase its hydrophobicity, proves superior to activated carbon filtration for NOM adsorption and even increases adsorption efficiency with increasing NOM concentrations and in high ionic strength solutions. This treatment option is less effective at low pH values which might affect cost effectiveness [Lu, 2007].

Removal of polycyclic hydrocarbons from aqueous media using carbon based NPs like fullerenes, SWCNT and MWCNT may provide a powerful technique for the future treatment of effluent from the petrochemical industry [Yang, 2008].

There is also research underway to attempt the development of NT providing rapid detection and identification of pollutants like metals, bio-toxins, pathogens and organic compounds [Smith, 2006; Nowack, 2007].

11. Possible negative effects of NPs on waste disposal technology

From the available literature it is clear that nanosized metal and metal oxide particles are associated with bactericidal actions. This represents only one example of why the increasing use of metal NPs by industry can be expected (see tables 1 & 2 for more examples of NPs in consumer products and other industry sectors). Increased concentrations of these metals will therefore occur in waste water. Especially silver NPs from PCP and other household goods, appliances and textiles can be expected to enter waste water in increasing concentrations due to its wide spread use. CuO, TiO_2 and other metal NPs can also be expected to occur in increasing concentrations in waste water. This indicates steadily increasing concentrations of metal NPs in water treatment facilities in future. Although the potential bacterial toxicity of silver NPs may be mitigated due to its high affinity to aggregate and precipitate as Ag_2S with reduced sulphur components from waste and natural water sources, this process need to be investigated as silver toxicity to nitrifying bacteria could severely disrupt biological waste water treatment systems. At best, the precipitation of Ag_2S also means that Ag, a rare metal, is lost and that NT based on silver may not be sustainable. Processes for the recovery of silver once released as NPs into the environment needs to be investigated and/or developed if economically viable. Other NPs released *via* this route may not precipitate as easily as silver and their effects regarding biological waste treatment, release into the environment and consequently their removal in water purification plants must still be researched.

The reported possibility that both inorganic and organic NPs may associate with organic material, especially with the increasing levels of xenobiotics in waste water may drastically affect their environmental toxicity potential. Increasing levels of TiO_2 and CuO as well as the unknown effects of organic NPs may also affect waste treatment and scientific investigations regarding the possible disruptions of existing water treatment technologies will have to be initiated sooner rather than later.

A significant fraction of NPs may be removed in waste water systems *via* aggregation and sedimentation as well as uptake by micro-organisms probably accumulating in the sludge of WWTW's. NPs may accumulate in biological waste treatment systems due to re-solubilisation from aggregates and sludge with changes in the immediate environment (for instance pH changes) as well as release following natural or induced cell death. A similar situation exists for the removal of phosphates *via* sludge wastage but the potential accumulation of NPs in biological waste treatment systems must be investigated. One possibility is that NPs will leave the waste treatment facility as part of the final treated effluent which opens up even more scenarios for potential environmental pollution. Not only must regulators take into account the potential adverse effects of nanopollutants released after final treatment but also the possibility of NP modification that may occur during the biological treatment process itself. NPs are prone to modification when in contact with other organic or inorganic dissolved or colloidal species, as well as cellular metabolic processes. Chlorination of the final treated effluent of WWTW's is standard procedure and this may lead to enhanced toxicity of the NPs leaving the treatment system.

Disposal of possible NP containing sludge by landfill may severely affect the microbial processes normally responsible for the waste degradation and wide spread contamination of soil and water bodies *via* leaching holds further danger.

Incineration of waste sludge, especially if the NP content is unknown, simply displaces the potential pollution into the atmosphere. At best, it will have a financial impact on the incineration process due to special air filters (limited efficiency) required to remove NPs from the exhaust gases. The worst scenario will be that exhaust gases where inorganic NPs may be mixed with organic NPs like BC, an easily aerosol distributed mixture of potentially lethal toxicity to the environment. As the dominant exposure of humans to NP pollution occurs *via* inhalation, this scenario is truly disturbing.

It is inevitable that the concentrations of free NPs in the environment are set to increase, resulting in increased contact with humans and other organic life forms. The irresponsible use of NT, in view of the uncertain metabolic fate and lack of cradle-to-grave life cycle information of many types of NPs, may contribute to the pressure against the survival of the current, already heavily polluted environment.

12. Conclusions

Nobody will argue against the potential of nanotechnology to assist in the mitigation and elimination of many of the industry-related environmental pollution problems currently faced by modern society. Cleaner production processes, more economic manufacturing and fewer waste products are all promises made by the supporters of NT. Direct intervention in current polluted environments has been demonstrated. Future increase in life quality and even life expectancy due to medical NT intervention for a larger fraction of the human population are factors in favour of the development of NT. However, in dealing with such a large unknown quantities regarding the risks involved in NT, regulators as well as future consumers of NT must not lose focus regarding the potential of NT to destroy or severely impact on the sustainability of biological life. Unless each and every NP used in manufacturing, with the potential of environmental release, is scientifically proven to be non-environmentally disruptive, it should not be allowed the opportunity of environmental release. Future research should be aimed at data collection to enable a "cradle to grave" risk assessment of all potential toxic NPs including scenarios from normal exposure to catastrophic as well as for both organic and inorganic NP [Reijnders, 2006]. Such investigations and the development of accurate screening procedures for the different types of NPs and its environmental effects throughout its entire predicted life-cycle must be considered to be the highest priority.

13. References

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Table 1: Nanoparticles used in industry [Nanoshop.com]

Type of NP	Description	Industry
Carbon Nanotubes (CNT)	Single walled CNT	Chemical processing, electronics, biology, medicine, transportation, and energy management. 5 Times stronger than steel but only 1/4 of the mass. Used in sports equipment, rotor blades for wind turbines. Conducts electricity as well as copper
	Multi-walled CNT	Building blocks for innovative technologies
	Functionalized CNT	Medical industry
Carbon Nanofibers	Carbon Nanofibers	Used in the automotive industry, electronic industry, for sports equipment and the aviation industry. Additional uses of NF include filtration products, high performance structures, barrier fabrics, and biomedical devices. Thermal insulation, energy storage devices and lightweight structural composites can benefit from incorporating these nano fibres. Nanofiber membranes are a paper-like thin product made up of randomly laid nanofibers. Membrane characteristics include; high porosity, large pore volume, high moisture vapour transport, small fibre diameter, high surface area, high absorbency, and the ability to be functionalized with large numbers of chemically active groups.
Titanium Oxides		Nano photocatalyst
Nanocrystalline Powders	TiO_2, Y_2O_3, ZrO_2, CeO_2, NiO, Fe_2O_3, SnO_2, In_2O_3	Coatings, UV Protection
Nanostructured Powders	Tungsten carbide, cobalt, chromium, graphite, diamonds, silicon	Mechanical, Metallurgical, Chemical, Biochemical, Electronic, Optical, Magnetic, and Energy-source industries. Also used in thermal spraying
Other Nanoparticles	Polystyrene	
	Silica	

	Nano ceramic particles	Natural colouring
	Luminescent nanoparticles	
	Polymer nanocomposites	NP's incorporated into a polymer matrix
	Nano metal composites	
	Nanocrystals	LED lights, solar cells, biolabels
	Ultrananocrystalline Diamonds	Friction and wear resistant coatings for biomedical implants and electron discharge devices
Metal Nanoparticles	Silver Nanoparticles	Anti-microbial, inks, dietary supplements, catalysts
	Gold Nanoparticles	One of the most widely used classes of nanomaterials for chemical, bioanalytical, biomedical, optical and nanotechnological applications as well as catalysts and inks
	Pt	
	Cu	Inks
	ZnO	Sunscreens
	TiO_2	Sunscreens, Photocatalytic and used in remediating and degradation of volatile organic compounds in aqueous media and air. Food packaging
	SnO	

Table 2: Applications of Nanotechnology

Other industries	Type of NP	Application
Building products	Inorganic NP's incorporated into organic polymer particles.	Binders (crystalline NP) in paint products
	Colloidally dissolved hydrolysates and partial condensates, mainly of silicon alkoxides	Nano-paints
	Copper inserted into CNT and blended into	Deflects interfering radio signals

	paint for cellular phones	UV protection
	TiO_2 used in protective coatings	Used to increase hygiene levels in hospitals
	Silver nanoparticles with anti-bacterial, fungicidal and mildew preventative properties mixed into paint	
		Wooden floor protection
	Cross linked nanoparticles	Water repellent and UV protection
	Mixture of NP's to protect outdoor wooden surfaces	Penetrate and protect wood against microbial activity
	Copper oxide containing coatings	
		Glass, Perspex, ceramics, metals
	Hydrophobic or hydrophilic NP coatings as surface scratch and anti-glare protection as well as photocatalytic properties to break down organic material (TiO_2) and has bactericidal properties	
		Concrete and stone
	Hydrophobic NP coatings	
		Maintenance products for cleaner, more hygienic surfaces.
	TiO_2 and Titaniumphophate photocatalytic NP spray	Outdoor metal protection against corrosion and weathering
	Metal, ceramic NP coatings	Roof protection
	NP based roof coatings that provides anti-biological and organic removal protection	Provide quick durable repair for mortar
		Easily cleaned surfaces
	Nanocrete and	

	Fibre cement with hydrophilic properties Silica binders with different NP’s like; Tin Oxide Iodine and silver NP’s Swela nano clean fabric coatings NT used in the production of aerogels for isolation Silver NP containing products with bactericidal properties	Hydrophilic surface coatings Hydrophilic and reduces static electricity Provide anti-bacterial protection Self cleaning Fabrics superior thermal, fire and acoustic barriers Medical appliances, personal care products, consumer product surfaces
Automotive products	Scratch resistant polymers made from polystyrene and polypropylene blends only possible due to the use of a NT dependent filler material Metal nanoclusters, metal nanocolloids (organosols and hydrosols), metal nanopowders, metal nanoparticles, and magnetic fluids Nanotitanate batteries Surface protection using TiO_2 NT Air treatment systems in cars containing	Reduce/eliminate the need for painting interior surfaces Used in automotive parts Quick charging for ultimate use in electric cars NT to protect metal, plastic, glass and painted car surfaces Photocatalytic and decomposes VOC’s Anti-bacterial

	TiO_2 Silver NP Nano Carbon particles Nanolubricants based on carbon nanosphere chains Nanofilling material Nanosized particles enhances heat transfer properties of liquids nanoparticulate metal oxides	Adsorbes odour producing organic material Increased lubrication for engine protection Gasket sealers Coolants Improve diesel fuel consumption and exhaust gases
Manufacturing processes	Ceramic powders Plantic, a biodegradable nano-composite material made from corn Colloidal antimony pentoxide Colloidal silica Nano coating $BaNd_2Ti_3O_{10}$	Filtration devices, coatings Synthetic fibres, packaging materials, Flame retardants Translucency, transparency, , abrasion resistance Coating to prevent blackening of silver (Ag_2S) Coatings with extremely low thermal conductivity

	Cobalt alloy coatings Colloidal silica; Zirconium dioxide; Ceria and mixed rare earth metal oxides	Replacing chrome finishing on metal plates Surface polishing to angstrom level
Water and air treatment technologies		Air filters (adsorption onto TiO_2, silver air filters also available), air refresheners, dust collection filters, gas turbine air filtration, filter catridges, membrane dependent nano-filtration
Sustainable technology	TiO_2 and Iodide/Tri-Iodide	Energy generation from sunlight Soil enhancing, frying oil reforming, photovoltaic processes, biodegradable packaging material (Plantic), water soluble films
Agriculture		Boosters for nutrition uptake by plants GeoHumus for improved plant performance due to water retention and nutrient availability
Cleaning solutions	Silver NP's, TiO_2 and carbon	Microemulsions for environmental clean-up Cleaning solutions that eliminates organic material, odours, bacteria
Personal care products	Gold Hydroxyapatite Liposomes and silver NP's	Skin hydration, Anti ageing Calcium replenishment Cosmetics (skin penetrating delivery systems) Soap & shampoo, toothpaste

	Silver NP's Nanosomes as phytoestrogen delivery systems Charcoal fibres of Bamboo	Breast enlargement Face masks
Health products and medical applications	Phytosterols Micelles or nano-sized droplets	Combat heart disease and high cholesterol Nanotechnology delivery systems for vitamins Silver nanoparticles as immune booster, nano-milled tea, food functionalization, drug delivery systems. Medical implants including scaffolds for tissue regeneration, cancer treatment, tissue illumination, tissue healing and wound care, peptide controlled homeostasis through self-assembly,
UV protection	Sol-gel process to encapsulate active UV blocking chemicals in nanospheres and silica matrices to avoid direct contact with the skin. Al_2O_3, TiO_2 ZnO	UV pearls by Merck KGaA and EMD Chemicals Inc Eusolex, UV absorber (BASF, OPTISOL), Skin Rx Solutions NanoGard, NuCelle, ZinClear™, Skin Rx Solutions
Consumer and Household products	Nano Diamondcrystals Surface area and composition Nano-silver containing products	Non-stick cookware coatings Hydrophobic coatings Wet-wipes, toothpaste, porcelaine powder, rubber gloves, textile and fabric

		softener, brushes for baby-bottle cleaning, clothing, dishwashing liquid, bottles and mugs for babies, anti-microbial kitchen and tableware, toothbrushes, bedding material and fibres, insulation material, pillows, toilets, food storage containers, (LG, Samsung, Daewoo) vacuum cleaners, fridges, washing machines, shoe sanitizing and deodorizer
Personal protection		Chemical detection systems, UV blocking materials, IR blocking materials
Tools and technology	CNT's are the enabling component of these devices	Chemical force sensors, gas detectors, field emission displays, molecular wires, diodes, FEDs, and single-electron transistors Optical measurement systems, sensor systems, image technology, atomic force microscopy, semiconductors, nanorobotics, particle size analysis, nanomanipulation systems, self assembly of NP's in electronic manufacturing and transparent, conductive coatings Also used in cleaning solutions without acids and other chemicals, reducing hazardous waste. Used in capacitors for electricity storage
Hobbies and sport	Carbon nanotube re-inforcement	Golf equipment and variable hardness waxes for skiing. Tennis rackets of composite materials, longer lasting tennis balls Lighter and flexible horseshoes Nanocoated (polyimide) fishing lures with photo-activated colour changing properties Fog eliminating sprays for sunglasses and goggles Increased strength of carbon weight bars and icehockey sticks

	Carbon nanotubes re-inforcement	