



# Nanowastes and the environment: Potential new waste management paradigm

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## ABSTRACT

Recent exponential growth in the development of nanomaterials (NMs) and nanoproducts is premised on the provision of novel benefits to the society—through the exploitation of their unique industrial and biomedical applications like medical imaging, fabrics in textiles, tissue engineering, nanocomposites, bioremediation, and biomedicine. These NMs and nanoproducts have increased in quantity and volume from few kilograms to thousands of tonnes over the last fifteen to twenty years, and their uncontrolled release into the environment is anticipated to grow dramatically in future. However, their potential impacts to the biological systems are unknown. Among the key present challenges in the waste management sector include the emergence of nanowastes; however, the effectiveness and the capability of the current systems to handle them are yet to be established. Because of limited studies on nanowastes management, in this paper, three-fold objectives are pursued, namely; (i) to raise concerns related to the alarming increases of uncontrolled releases of NMs into the environment through nanowastes, (ii) examine the unique challenges nanowastes pose to the waste management systems—both from technological and legislative perspectives, and (iii) summarize results of the first nanowastes classification formalism in order to elucidate the potential challenges of waste streams containing nanoscale dimension materials to the present waste management paradigm. Finally, the article closes by summarizing several proactive steps of enhancing effective long-term and responsible management of nanowastes.

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## 1. Introduction

Society is now firmly embedded in the nanotechnology age and the past two decades have been characterized by rapid emergence of nanotechnologically-enabled particles, materials, or products in the marketplace (Feynman, 1991; Ball, 2001). Some of these materials have uncontrollably entered into the biological systems and the environment though there is limited scientific data on fate, behaviour, and the interactions of nanomaterials (NMs) in such systems (Moore, 2006). Current scientific findings (Colvin, 2003; Hoet et al., 2004; Oberdörster et al., 2005; Moore, 2006; Helland et al., 2007; Kahru and Dubourguier, 2010) show that NMs are not as benign to either humans or other natural biological systems as previously presumed. Examples of the novel applications of NMs include: nanoelectronics, molecular assemblies, tissue engineering, biomedicine, and nanocomposites (Biswas and Wu, 2005; Aitken et al., 2006; Woodrow Wilson International Centre for Scholars, 2008; Nanowerk Nanomaterial Database Inventory, 2009), and the breadth of their uses is yet to be fully exploited.

It is likely that, just as the NMs and nanoproducts have reshaped many facets of modern science and engineering, similarly, they will potentially exert increasing effects on society through unanticipated health and environmental impacts. Moreover, these novel materials could pose new forms of challenges to the current waste management approaches either by rendering them inadequate or inappropriate. This raises a fundamental question; is nanotechnology likely to cause a disruptive paradigm in terms of technologies and approaches required for handling and treating waste streams containing NMs?

The large surface area, large quantum effects, biological reactivity, shape and size, deformability, durability, tendency to aggregate, optical sensitivity, and hydrophobicity among other surface characteristics of NMs (Shelley, 2005; Maynard and Aitken, 2007) may aid faster bonding with pollutants (e.g. cadmium and organics). Consequently, this may facilitate faster translocation of these pollutants through air, soil and water. NMs are known to move with high velocities through aquifers and soils (Colvin, 2002; Lecoanet et al., 2004), and may act as suitable carriers for rapid and long-range transportation of hazardous chemicals dispersing them widely throughout the environment (Kleiner and Hogan, 2003). For example, organic compounds such as polycyclic aromatic hydrocarbons (PAH) (Cheng et al., 2004; Yang et al., 2006) can be adsorbed by carbon nanotubes causing an enhancement of the PAH toxicity, and in addition, NMs have been shown to exert effects on the fate, transformation, and transportation of chemical compounds in the environment (Gao et al., 2008). The unusual properties of NMs render

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them ideal candidates for possible interactions with biological systems and the environment with the potential to generate undesirable effects (e.g. to generate toxicity) (Nel et al., 2006).

Lecoanet et al. (2004) demonstrated that different NMs exhibit diverse transport behaviors in the environment—contrary to assertions that nanoscale materials present monolithic risks to the environment. The findings suggest that, each nanowaste may require a unique waste management approach in addressing its potential environmental risks. This is unsurprising as each form of NM is unique as a functionality of; the fabrication method (Brant et al., 2006), crystal morphologies (Long et al., 2006; Warheit et al., 2007), adopted toxicity testing procedures (Tiede et al., 2009), and the abiotic factors at the point of entry into the environment (Handy et al., 2008). This allows NMs to exhibit distinctive “footprint” as a result of their inherent chemical composition, shape, and structure—which leads to resultant unique behaviors in different environmental media even in a case where they are fabricated from the same bulk parent material (Pal et al., 2007). As such, one of the key elements of reducing the potential long-term liabilities of nanotechnology is to establish sound waste management protocols and practices to limit uncontrolled and widespread dispersion of NMs into the environment.

The novelty and revolutionary character of nanotechnologies has resulted in dramatic growth of NM production globally (Woodrow Wilson International Centre for Scholars, 2008; Li et al., 2007; Nanowerk Nanomaterial Database Inventory, 2009). Consequently, these technological advancements have evoked great interest among stakeholders such as governments (Singer, 2004; Meridian Institute, 2005), academia (Cientifica, 2004a), pressure groups (ETC, 2003a,b), non-governmental organizations (Balbus et al., 2007), media (Wolfe et al., 2003), investors (Wolfe et al., 2003; Paull et al., 2003; Mazzolla, 2003), and industry (e.g. manufacturing and insurance (Mazzolla, 2003; Munich Re, 2002; Swiss Re, 2004; Allianz Group, 2005; Robichaud et al., 2005). The exceptional interest shown by the insurance industry in nanotechnology appears to be based on the lessons learned from previous cases of asbestos, genetically modified (GM) foods, benzene, chlorofluorocarbons (CFCs), etc. (European Environment Agency Report, 2001). This means that, any form of indecisive action in dealing with nanowastes may cause consequences thereof of similar magnitude and global scope as those of fourteen case studies recently explored in the European Environment Agency Report (2001).

Nanotechnology has ushered in a new era of miniaturization at industrial scale production. However, this has triggered the emergent of new unique forms of waste streams – containing residue NMs – which potentially may pose challenges to the current waste management practices and technologies. In the context of this paper, these new forms of waste streams are generically referred herein as nanowastes. For the purposes of consistency, a nanowaste refers to waste stream(s) containing NMs, or synthetic by-products of nanoscale dimensions, generated either during production, storage and distribution, or, waste stream(s) resulting from the end of lifespan of formerly nanotechnologically-enabled materials and products, or items contaminated by NMs such as pipes, personal protection equipment, etc. In light of this definition and the BSI British Standards Guide PD 6699-2, nanowastes can exist in four forms. These include: pure NMs at the point of production, materials and surfaces contaminated with NMs (containers, disposable personal protection equipment, etc.), liquid suspensions containing NMs, and solid matrixes containing NMs (e.g. in the bulk, surface, or as a coating on the surface). Based on the nanowastes types and classification discussed in Section 6, these forms of waste streams poses varied levels of threat to the environment and challenges in managing them.

In the current scientific literature, numerous aspects of NMs related to ecotoxicity (Colvin, 2003; Moore, 2006) toxicological and health effects (Hoet et al., 2004; Oberdörster et al., 2005; Nel et al., 2006), their fate and behaviour in the environment (Biswas and Wu,

2005; Wiesner et al., 2006; Holbrook et al., 2008) as well as occurrence, fate and effects on the environment (Nowack and Bucheli, 2007) have been studied, yet, the question of waste management regarding nanowaste streams remains largely unaddressed. Therefore, the objectives of this paper are three-fold, namely; (1) to examine the increasingly uncontrolled releases of NMs into the environment through nanowaste streams; (2) provide a summary of the potential challenges of nanowastes they are likely to poses to the waste management systems—with reference to handling, treatment technologies, and the legislative framework, and (3) illustrate through the use of nanowastes classification formalism the potential challenges of nanowastes, and thereafter discuss the recommendations on how to address these challenges.

## 2. Issues, concerns, and challenges of nanowastes management

### 2.1. Examples of nanowastes sources

In recent years, numerous publications and proceeding articles have highlighted the exponential growth in global nanotechnology research activity (Colvin, 2003; Biswas and Wu, 2005; Maynard, 2006; Ke and Qiao, 2007). Yet, these publications contain little scientific data on feasible approaches of dealing with nanowaste streams generated at various phases of the nanotechnology-based products and materials life cycle. Due to these data and knowledge gaps imply that the nanotechnology industry is likely to address such concerns reactively rather than proactively as the window of opportunity is rapidly diminishing. The lack of scientific publications to address the management of nanowaste streams is evidence of limited or no funding, or limited concerted effort by researchers in this field. However, nanowastes are potentially the most single pathway of introducing NMs into the environmental systems.

Failure to address these concerns leaves continued uncontrolled release of NMs into the environment (e.g. water, air, and soil)—which may cause contamination of soils as well as surface and underground water resources. In the long-term, this not only threatens the security of water resources, but, may prove to be impossible to remediate because of: the sheer size of the problems owing to wide geographical NMs dispersion in the environment, high clean up costs, and lack of suitable technologies for remediation and monitoring tools to identify the contaminated areas. For example, there is growing global demand on fuel additives, lubricants, and catalysts because of their enhanced performance achieved through the infusion of nanoscale cerium oxide particles. Generally, these nanotechnologically fuel additives, lubricants and catalysts are likely to be emitted through various waste streams into the air, water or soil systems. Ultimately they will end up into the aquatic and terrestrial environments through surface-runoffs, spillages during use, and leakages from vehicles, or via sewage drainage systems. This raises serious concerns of dealing with nanowastes from both point and non-point sources.

Another example is the cosmetics and personal care sector which constitute the largest number of nanoproducts (> 50%) currently available in the global market (Woodrow Wilson International Centre for Scholars, 2008). Over the last few years the use of NMs in cosmetics and personal care products has increased dramatically for several reasons, namely: ability to absorb and reflect UV light while they remain transparent (e.g. titanium oxide), a better antioxidant than vitamin E (e.g. C<sub>60</sub> fullerene), antibacterial properties (e.g. nano-silver), and anti-aging skin properties (e.g. nanosomes and gold particles).

On the other hand, the increased production and use of cosmetics will introduce waste streams containing NMs directly to the aquatic environments at application phase – through processes such as bathing and swimming – or indirectly through the sewage systems as a result of showering and washing processes. This is because of the high concentrations of NMs in cosmetic products in comparison to

other nanoproducts (Boxall et al., 2007), and taking into account Mueller and Nowack (2008) estimations that 95% of these nanoscale materials are most likely to end up in water treatment plants through releases of run-off during initial application or abrasion and liquid entrapment during use. Such data points to potential long-term unanticipated adverse impacts of nanowaste streams in the environment.

## 2.2. Potential nanowaste risk concerns

Currently since the introduction of nanowastes from nanoproducts it has been assumed that the existing waste management technologies have the capability to remove NMs from the solid and liquid waste streams effectively and efficiently. Yet, there are no hard data available to validate such an assumption as this largely remains unknown—with potentially far-reaching ramifications for the promotion of sound waste management practices. Results of Leppard et al. (2003) showed that standard wastewater treatment technologies are poorly suited to remove NMs from effluents, with non-manufactured nanoparticles being detected in discharges from wastewater treatment plants—possibly providing an escape route for dissolved chemicals. Recently, the laboratory-scale findings of Westerhoff et al. (2008) illustrated the wastewater treatment systems' inability to remove NMs from drinking water because of low removal efficiencies ranging between 0 and 40% as a function of the NM under question. Such data implies the potential presence of NMs in portable drinking water, and may pose an exposure pathway to humans (Westerhoff et al., 2008).

In addition, Zhang et al. (2008) investigated the dispersion and stability of metal oxide NMs in water as well as their removal through use of potable water treatment processes. The findings showed that after 24 h of fast aggregation, nanoparticles did not settle out of water efficiently, for example, 20–60% of the initial concentration of 10 mg/l still remained in the settled water. Thus, in an aqueous environment containing small concentrations of electrolytes, nanoparticles may be present for a relatively longer time even if they are in an aggregated state (Zhang et al., 2008). This means that even though nanowastes are not regarded as potential risk threat to the environment, current water facilities may face the challenge of removing NMs as the quantities increases in the foreseeable future. For instance, results showed that alum coagulation – a conventional water treatment process – removed less than 80% of the total mass of nanoparticles, and the addition of 0.45 mm membrane filtration as the final process improved the removal efficiency to slightly above 90%. Evidently, these findings are important for developing water treatment technologies to remove NMs from drinking water as well as the effluents—and are in agreement with results of Limbach et al. (2008) which showed that a significant fraction of the NMs escaped the wastewater plant's clearing system, and up to 6 wt.% of the model compound cerium oxide ( $\text{CeO}_2$ ) was found in the exit stream of the model plant.

On the other hand, earlier results of Wiesner et al. (2006) suggested that current wastewater treatment techniques are likely to remove NMs, based on the assessment of nanoscale materials behaviour and fate in porous media (Lecoanet et al., 2004). However, no data were published to support these assertions. Because research on the efficacy of removing NMs from wastewater systems has just begun, and the available data is fragmentary—it is early to draw generic conclusions on the effectiveness of the current waste management systems suitability of dealing with new pollutants containing nanoscale structures.

As a result, NMs are likely to pose new forms of challenges to the current waste treatment technologies such as reducing their operational efficacies due to the surface coatings. Ironically, the coating is important as it renders NMs inert; therefore, from a toxicological or ecotoxicological standpoint it limits their adverse effects while they

reside in the environment, as long as the coating lasts. This only holds if the coating is benign. Thus, owing to potential unintended effects of surface coating on the treatment technologies as opposed to its importance in protecting potential receptors of nanoparticles in the environment—future design and development of NMs must address this problem. Examples of the effect of the coated NMs in the wastewater will be presented in Section 5. Also, an illustration of the possible behaviour and fate of NMs in wastewater has been discussed to provide insights on the possible outcomes when released in wastewater treatment systems (see Section 5).

## 2.3. Nanowaste challenges to the current regulatory frameworks

Several publications have comprehensively addressed the challenges NMs are likely to pose to the current legislative frameworks (Bell et al., 2006; Davies, 2006; Breggin and Pendergrass, 2006; Franco et al., 2007; Powell et al., 2008), and only few salient aspects are treated here. The rapid developments in nanotechnology have started to challenge established waste management practices and technologies in addressing the potential nanowastes specifically with respect to the suitability of the current legislations. This is because of several reasons. Firstly, this is attributable to data and knowledge gaps concerning risk assessment of NMs in different environmental compartments as discussed in Section 4. This makes it difficult to develop legislative and policy frameworks that can address potential new forms of waste streams, or find best fits of current regulations in dealing with them. For instance, experts agree that little is known about appropriate ways of cleaning up NM spills and disposing of NMs in an R&D environment, let alone at industrial scale (Moudgil, 2004).

Though Hallock et al. (2009) indicated several methods have been applied in the management of nanowastes in the Massachusetts Institute of Technology research laboratories; however, their effectiveness for protecting the workers and the environment during and post disposal phase remained scientifically unjustified. Such knowledge gap challenges long-term safe, responsible, and sustainable development of nanotechnology. On the other hand, nanowaste streams were never anticipated by the existing regulatory regime, and raises questions about the adequacy of current legislative frameworks that govern conventional waste management paradigm. The core of the debate centers on the issue of whether or not, the current form of laws governing waste management can provide meaningful guidelines in terms of handling, treating and disposing nanowastes. Davies (2006) argued that the present legislative framework is unable to deal with nanowastes and may potentially yield unintended consequences to human health and the environment if not amended to take into account the emerging increase of nanowaste streams.

Moreover, for an informed and evidence-driven legislative framework to be developed, credible data are central on a range of nanowaste properties. These include the behaviour of nanoparticles in the environment, their bioavailability and biopersistence, as well as potential toxicity to various biological systems. Nonetheless, presently little is known about these aspects for numerous types of nanoparticles. Breggin and Pendergrass (2006) and Franco et al. (2007) examined the current legislative frameworks in the USA and the EU, respectively, as they apply to the management of nanowastes. The authors demonstrated several inadequacies in the current laws concerning issues on handling, storing, transporting, treating and disposing of nanowastes.

In addition, Hester (2006) revealed numerous inadequacies of RCRA of USA in dealing with nanowastes based on the EPA definitions of novel waste streams, implementation of the exception provisions of certain waste streams from legislative rigor in reference to the generated volumes, and unexpected or qualitatively different properties of NMs in the environment. The regulatory-related challenges of nanowastes become even more profound in the context of developing countries (Musee, 2008)—many of which are presently struggling with

inadequate legislative instruments of dealing with conventional hazardous wastes (Musee, in press; Musee, submitted for publication).

Therefore, in the absence of regulatory framework that can address potential risks posed by NMs throughout their life cycle—prompted increasing calls to governments to develop legislative mechanisms of regulating NMs (Davies, 2006; Lin, 2007). Such regulatory mechanisms are envisaged to provide companies involved in fabricating, distributing, and marketing nanotechnology products and materials with incentives to conduct health and safety research to demonstrate as well as confirm the low risks of their materials.

### 3. Quantification of nanowaste volumes

Because of the diversity of NM applications, large variation in production quantities, as well as wide geographic areas of their uses are among the reasons to pay attention in developing effective and efficient tools of managing current and future anticipated nanowaste streams. Present and envisaged future applications of NMs are the most significant sources of large quantities of NMs into the waterways through waste streams (Powell et al., 2008). However, guidelines and protocols of handling and disposing nanowastes safely and responsibly are undeveloped. For illustrative purposes, in this section, the growing challenges associated with nanowaste management are presented, for now and future. This will be achieved indirectly using surrogate data through summarizing the emerging trends on the production of NMs, commercialization of nanoproducts, and quasi-exponential growth of intellectual properties (IP) held by companies and institutions working in the fields of nanotechnologies and nanosciences. The complex linkages of these parameters are likely

to trigger increasing quantities of nanowaste streams production and releases into the environment as illustrated in Fig. 1.

#### 3.1. NMs production

Conventionally risk assessment of chemicals' potential impact to different environmental compartments is a function of their intrinsic characteristics, namely: bioaccumulation, persistence, inherent toxicity, and long-range transport (LRT)—and are independent of the chemical's quantity. However, findings of Swanson et al., 1997; Mackay et al., 2001; Arnot et al., 2006; Musee et al. (2008a,b) suggest that in addition to the intrinsic characteristics the quantity of chemicals emitted into the environment also contributes in undertaking realistic risk assessment (Musee et al., 2008a,b).

Until now, there are no published statistics on the quantities of nanowastes generated from nanotechnology-related industrial processes, or post-consumer waste streams neither in the product category or industrial sector. This means, current and future quantities of nanowastes uncontrollably entering into the environment at best can be estimated based on the reported nanoparticle production volumes, and postulated increases due to commercialization of the nanoparticle products and NMs. Fig. 2 depicts the distribution of nanotechnology applications by 2007, and emphasizes the fact that owing to the diversity of NMs application, large variation in production quantities as well as wide geographic areas of applications merits the development of effective and efficient strategies of managing both current and anticipated future nanowastes.

The emergence of nanowastes can be traced back in the 1990s and early 2000s occasioned by global demand for miniaturized products as a result of technological advances. For example, by 2000, the global

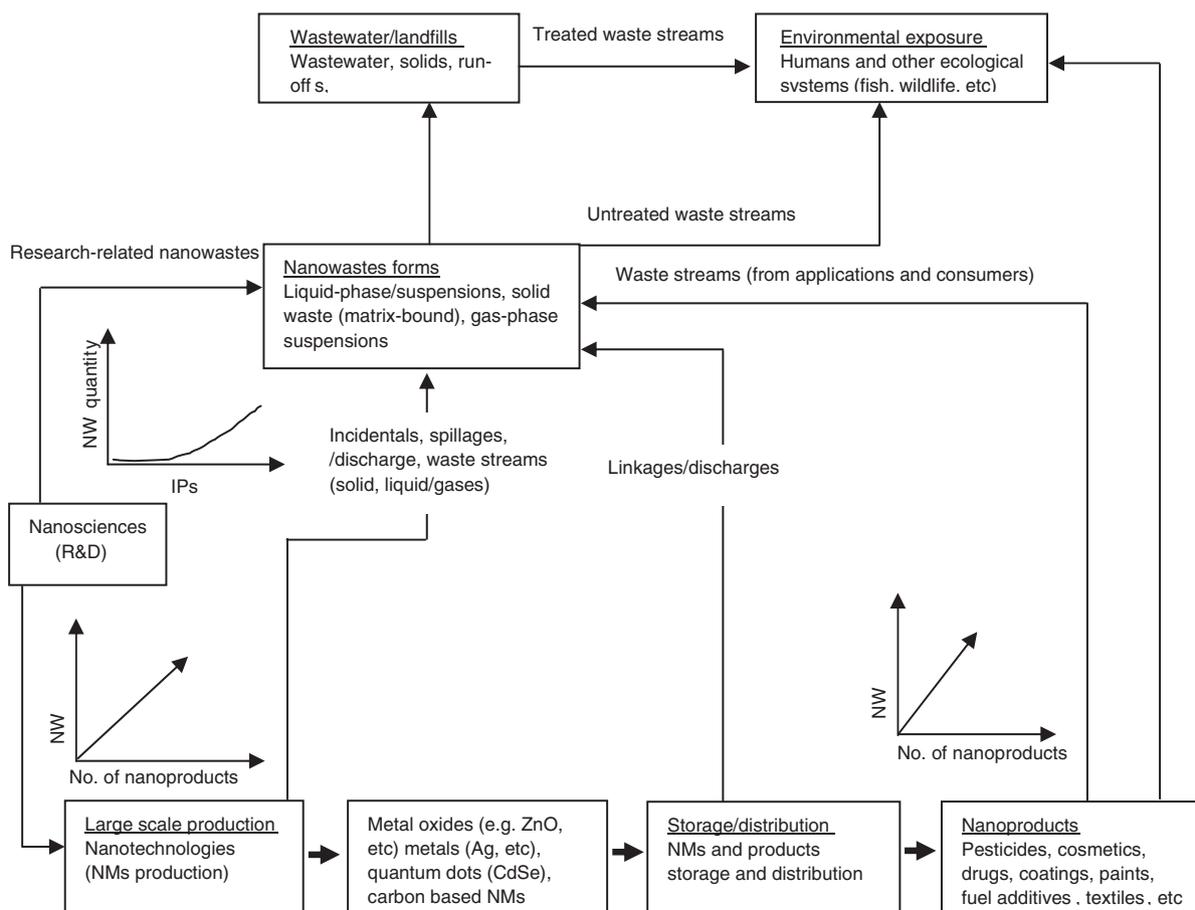


Fig. 1. Nanowastes generation and exposure pathways into ecological systems. NM: nanowastes, IP: intellectual property, R&D: research and development.

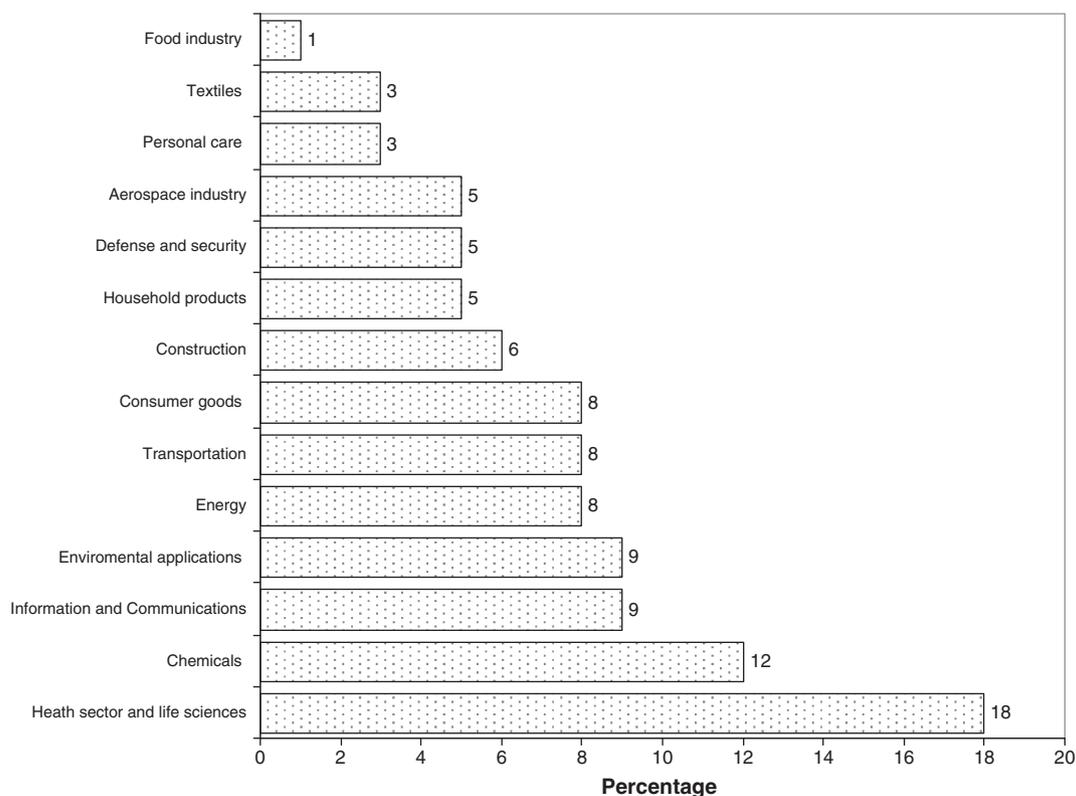


Fig. 2. Distribution of the main applications of nanotechnology sectors by 2007.

carbon nanotubes (CNT) production was estimated to have ranged from 1 to 5 kg according to Business Communications Co. (BCC) ([www.bccresearch.com](http://www.bccresearch.com))—and the production volumes have increased rapidly in the recent years due to advancement in manufacturing capabilities. From these activities and applications, the increases in NMs production concomitant to their incorporation into diverse products exacerbated releases into the air, soil or water with ultimate potential to cause contamination to food chains and soils (Reijnders, 2006; Holbrook et al., 2008).

In 2001, the projected global annual production of carbon-based NMs was in the order of a few hundred tonnes, and by 2003 the estimates were about 900 tonnes (Kleiner and Hogan, 2003). According to the Royal Society and Royal Academy of Engineering Report on Nanotechnology (2004) estimates the production of NMs was anticipated to increase from 1000 tonnes as of 2004 to 58,000 tonnes annually from 2011 to 2020 as shown in Table 1.

Cientifica (2005) survey on the CNTs production in 54 major global producers estimated that about 65 tonnes of nanotubes and fibers were fabricated in 2004. The commercial fabrication of fullerenes was expected to equal that of metal oxide nanoparticles as the Mitsubishi Company (in Japan) anticipated boasting the annual production by 1,500 tonnes of fullerenes ( $C_{60}$ ) by the year 2007 (Mitsubishi Company, Japan). Nonetheless, the latter figures have not been independently verified, and it is unclear how such high quantities of fullerenes will be used given the current limited market demand. This is true given the global production capacity for single walled carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT) was estimated to be approximately 100 tonnes in 2004 (Royal Society and Royal Academy of Engineering Report, 2004) had an anticipated increases of about 400% to 500 tonnes by the year 2008. The later estimates are in agreement with estimates of the Nanoroad SME research findings of 2006 as summarized in Table 2.

A survey on the use of NMs in Switzerland (Schmid and Riediker, 2008) was estimated as 2419 tonnes annually, a figure much higher

than the estimates of the Royal Society and Royal Academy of Engineering Report on Nanotechnology (2004) for the year 2010. Therefore, intuitively the true global production of NMs is likely to be in many orders of magnitude higher given Switzerland constitute about 0.0068% of the developed countries' population.

In summary, although the current production quantities of NMs are largely unknown, it is evident that the production rates will continue to increase dramatically in the coming years. This increase will be driven by improved production techniques, and growing demand for nanoproducts. Therefore, on the basis of the available limited production statistics of NMs four inferences can be deduced regarding nanowastes. Firstly, the available statistics provide insights into the potential corresponding rapid increases in the types and quantities of nanowastes generated from diverse nanoproducts

Table 1  
Estimated global production of nanoparticles and nanomaterials (Royal Society and Royal Academy of Engineering Report, 2004).

Application	Nanomaterials/device	Estimated global production (tonnes per year)		
		2003/4	2010	2020
Structural applications	Ceramics, catalysts, films and coatings, composite metals	10	$10^3$	$10^4$ – $10^5$
	Skincare products	$10^3$	$10^3$	$10^3$
ICT	SWNT, nanoelectronic, and optoelectronic materials (excluding CMP slurries), organic light emitters and electronics, nanophosphors	10	$10^2$	$>10^3$
Biotechnology	Nanocomposites, encapsulates, targeted drug delivery, diagnostic markers, biosensors	<1	1	10
Environmental	Nanofiltration, membranes	10	$10^2$	$10^3$ – $10^4$

**Table 2**  
Major types of nanoparticles with high commercial applications from 2006 to 2014.

Product	2006–2007	2008–2010	2011–2014
Nickel(carbon-coated) (Ni-C) powders	3500	7500	15,000
Poly(L-lactic acid) (PLLA) nanofilters	500	2500	5000
Yttrium oxide (Y <sub>2</sub> O <sub>3</sub> ) nanopowders	2500	7000	7500
Ceria (CeO <sub>2</sub> ) nanoparticles, coatings	N/A	10,000	N/A
Fullerenes	N/A	300	N/A
Graphite particles	1,000,000	N/A	N/A
Silica (SiO <sub>2</sub> ) nanoparticles, coatings	100,000	100,000	>100 000
Titania (TiO <sub>2</sub> ) nanopowders, thin layers	5000	5000	>10,000
Zinc oxide (ZnO) nanopowders, thin films	20	N/A	N/A

categories such as construction, cosmetics, personal care, chemicals, energy, among others. Such growth poses increased potential exposure of NMs to humans, and other ecological systems through waste streams.

Secondly, because the global statistics on the production of NMs are incomplete and contradictory, subsequently, both country specific and global quantities of nanowastes generated annually remain unknown. This scenario is likely to remain unchanged in the coming several years majorly because of commercial reasons. Consequently, this would hinder full assessment and quantification of nanowaste risks. Thirdly, while annual production quantities of NMs are relatively small in comparison to those of macroscale chemicals, however, their large surface area to mass ratio provides a large reactive area—making the current quantities though miniscule but of considerable concern given their potential hazards to humans and the environment. For example, the currently existing quantitative nanoecotoxicological data on single model organisms was applied and classified the NMs used in testing from “extremely toxic” to “harmful”, and none was found “not harmful” (Kahru and Dubourguier, 2010). This means, to date some of the NMs have proved to be as toxic or even more toxic than well known dangerous biocide pentachlorophenol (PCP) that has already been banned or severely restricted for health and/or environmental reasons in most countries (UNEP, 1996).

Finally, because the data available are only maximum estimated rates of NMs production and not the actual values – provides clear evidence that the growth of nanotechnology is attained faster – surpassing original expectations. From a waste management per-

spective, we posit that it should prompt urgent response aimed at safeguarding human health and the environment to avert unintended consequences related to poor nanowastes management.

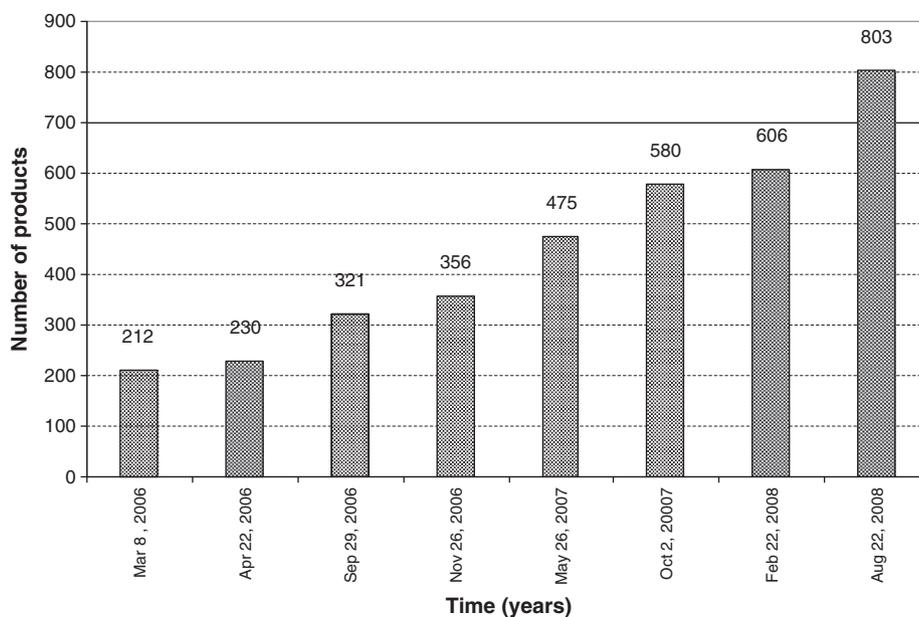
### 3.2. Growth of nanoproducts commercial activity

#### 3.2.1. Nanoproducts inventory

Quantification of nanowaste volumes can also be achieved through the use of the commercialization data of nanoproducts in the global market, and the filing of intellectual property (IPs) patents by companies and research institutions. Results of a nanoproducts inventory developed at the Woodrow Wilson International Centre for Scholars since 2006 (Woodrow Wilson International Centre for Scholars, 2008) show that the company-identified consumer nanoproducts fabricated using nanotechnologies increased from 212 in March 2006 to 580 in October 2007, and by August 2008 the figure had reached 803 (see Fig. 3).

The database developed by Nanowerk Nanomaterial Database Inventory (2009) contains higher numbers of nanocomponents with a total of 1979 products in August 2008, and the figures increased by 13.1% to 2238 in May 2009. A distribution of the nanoproducts by type from the Nanowerk database is shown in Fig. 4. The rapid increase in the number of products is consistent with dramatic commercialization of different nanoproducts over a short span of time—majorly fuelled by market competition and demand. In both inventories, the most common NMs in the products comprised of nanoparticles either of single metal (silver, zinc, titanium etc.), or binary compounds and fullerenes.

An analysis of the NMs mostly used in the nanoproducts reported by the Woodrow Wilson International Centre for Scholars (2008) is presented in Fig. 5. Therefore, present and near future nanowaste streams are most likely to contain the dominantly used NMs in the fabrication of nanoproducts in applications such as cosmetics, pharmaceuticals, pesticides, and sunscreens as per the databases of Woodrow Wilson International Centre for Scholars (2008) and Nanowerk Nanomaterial Database Inventory (2009). Notably, these statistics by no means are not the true numbers of nanoproducts commercially available globally (actual numbers are expected to be much higher), but illustrates the rapid uptake of nanotechnology into the commercial arena.



**Fig. 3.** Commercial nanoproducts growth from March 2006 to August 2008 (Woodrow Wilson International Centre for Scholars, 2008).

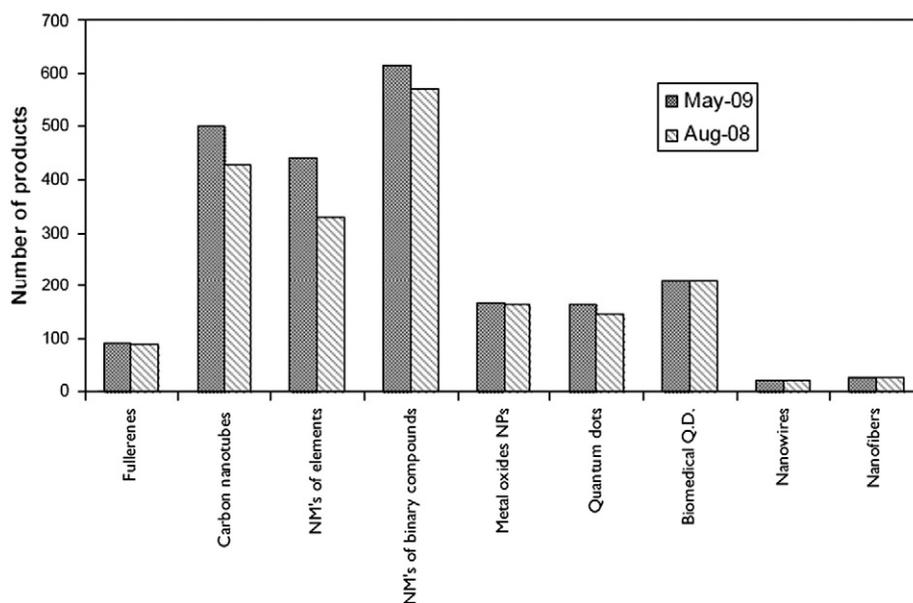


Fig. 4. The distribution of nanocomponents based on the Nanowerk Nanomaterial Database Inventory (2009).

Many of the NMs embedded into the products, and even the nanoproducts themselves are mostly fabricated in decentralized entities comprising of small start-up sized companies to global agglomerates (Pitkethly, 2003). The large number of production facilities, the diversity of NMs, wide regional and global distribution of these companies, and the sheer number of the nanoproducts makes it impossible to compile realistic statistics on the quantities of nanowastes presently at different phases of the nanoproducts life cycle. For example, the inventory at Woodrow Wilson International Centre for Scholars (2008) shows the distribution of the nanoproducts falls into different product categories (see the inset in Fig. 6). Secondly, the rate of growth of nanoproducts per category is very high, for instance, the product growth from February 2008 to August 2008 under just six months recorded growth rate under different product categories from 6% (goods for children) to 41% (appliances).

### 3.2.2. Patents inventory

The rapid growth of nanowaste streams since early 1990s is evidenced by dramatic increases in the registration of patents in the field of nanotechnology. An analysis on the repositories of patents data in the United States Patent and Trademark Office (USPTO), European Patent Office (EPO), and Japan Patent Office (JPO) on nanotechnology shows exponential growth of the nanotechnology industry since the 1990s particularly in USA and Europe (Li et al., 2007). The distribution of the patents among the three repositories is

shown in Fig. 7. For the period 1974–2004; USPTO, EPO and JPO held a total of 3087, 1732, and 1095 nanotechnology-related patents, respectively.

The distribution of the patents in each repository across different industries reveals that electronic- and personal care-related industries held the highest numbers of patents (Li et al., 2007). For instance, in the USPTO repository 55.7% of the total patents were held by electronics- and personal care-related industries in this period, each industry accounting for 35.8% and 19.9%, respectively. Similarly, in the EPO and JPO repositories, the same industries held 65.2% and 45.5% of the total patents, correspondingly. Because the purpose of companies in holding patents is to utilize them for fabricating products, it is clear from the patent analyses that, present and future nanowaste streams are likely to be generated from these two industries.

Therefore, a close examination of historical waste management practices in the electronics and personal care industries can provide some valuable lessons and insights in informing future policy formulation and development of waste management technologies to address nanowastes. The trends on the growth of patents are in agreement with the number of nanoproducts reported under the two databases discussed in Section 3.1.1. Other published patent statistics from the USPTO showed that the office issued for the first six months of 2005, 3818 patents with reference to nano, and 1777 applications had been submitted waiting for registration (Red Herring, 2005). Again, this shows the fast pace of nanotechnology industry growth will potentially trigger corresponding increases in the generation and release of NMs into the environment mostly through nanowaste streams.

## 4. Ecotoxicity of nanomaterials

Studies on the toxicity of NMs suggests that these nanoscale materials pose varied levels of potential risks to human health and the environment (Oberdörster et al., 1995; Dick et al., 2003; Donaldson and Golyasny, 2004; Lam et al., 2004; Oberdörster, 2004; Maynard and Kuempel, 2005; Oberdörster et al., 2005; Lam et al., 2006; Lovren and Klaper, 2006; Oberdörster et al., 2006; Roberts et al., 2007; Blaise et al., 2008). Most published toxicity studies have focused on understanding the NM potential risks in mammalian model systems, with limited investigations in other biological systems like invertebrates, fungi, plants, bacteria, reptiles, or amphibians.

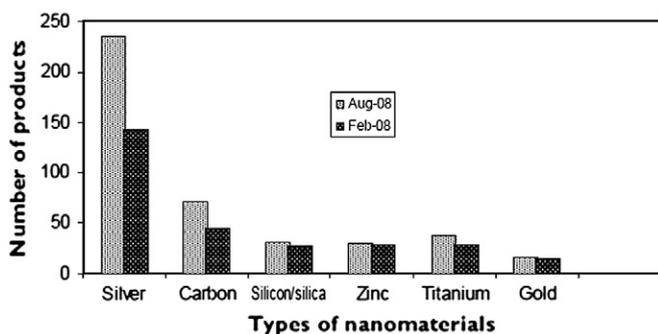


Fig. 5. Distribution of the NMs mostly used in the nanoproducts presented in Fig. 6 (Woodrow Wilson International Centre for Scholars, 2008).

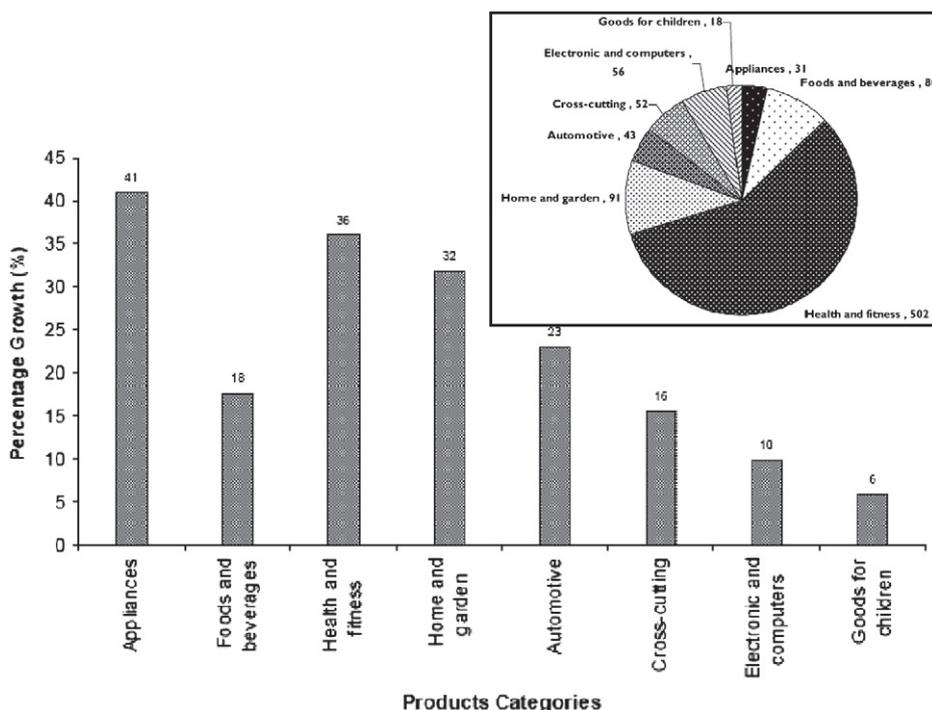


Fig. 6. Distribution of nanoproducts by application (inset), and the growth rate of each product type between February 2006 and August 2008 (Woodrow Wilson International Centre for Scholars, 2008).

Therefore, our understanding on the full extent of risk effects of NMs and nanoproducts are incomplete; for example, given the invertebrates constitute about 95–97% of entire fauna species. In addition, presently there are data gaps on the ecotoxicity of NMs in marine ecosystems. This means, current ecotoxicity data of NMs with respect to their interactions with freshwater aquatic organisms is limited or of no relevance in risk assessment in both estuarine and marine species. In this section, the limitations of the ecotoxicological reported data, and the available data are summarized in relation to how it limits and/or advances our knowledge in dealing with nanowastes. Finally, how the limitations of the available data impacts on the nanowaste classification paradigm presented in section 6.

4.1. Reported ecotoxicity data

Examples of the reported ecotoxicity data for NMs in different species are provided in supporting Table S1. The findings show that most quantitative studies on the toxicity of NMs are limited to fullerenes, carbon nanotubes (SWCNT and MWCNT), and a few metal

oxides (titanium oxide, zinc oxide, holmium oxide, etc.). However, data for ecotoxicity of quantum dots and polymer nanoparticles are limited. Secondly, there is paucity of data on the relationship between the physicochemical properties of NMs e.g. surface chemistry, particle physicochemical structure, aggregation and agglomeration potential, characteristics of the exposure environment (e.g. pH, presence or absence of oxidants, zeta potential, effects of organic macromolecules—Wiesner et al., 2008), association with bacteria (Lyon et al., 2005), and NMs preparation methods (Gharbi et al., 2005; Henry et al., 2007) in reference to: the observed toxicity, physiological, biochemical, growth and behavioral traits of the testing species (see Table S1). It is not the author’s intention to provide a comprehensive review of the published data on the ecotoxicity of the NMs. Rather, to illustrate how the reported data influences nanowaste classification of different NMs, and thereof propose ways towards achieving effective nanowaste management.

Thirdly, the diversity and complexity of NMs make it a laborious process of elucidating their possible levels of toxicity to different biological test species and end-points. This poses a challenge with respect to ascertaining which NM properties induce toxicity to the test species, as this is impractical owing to constraints such as; cost, complexity and feasibility of undertaking such testing because of unavailability of appropriate analytical techniques. Comprehensive reviews on the ecotoxicity of NMs in environmental systems have been presented by Nowack and Bucheli (2007) and Baun et al. (2008a), and only few examples are cited here. It is in this context that the complexity of NMs affects the nanowastes classification profiling—even for the material of the same bulk parent material.

Studies on the interactions of NMs with biological systems suggest that, though the original purified NMs may cause no detrimental effects in the test species, their by-products could potentially cause deleterious effects (Templeton et al., 2006). For example, exposures to aggregates of pure SWCNTs showed no chronic toxicity risk to sensitive meiobenthic estuarine copepod crustacean even at environmentally unrealistic high exposure concentrations of nearly 10 mg/l. However, an isolated soluble fraction of nanocarbon material—functionally distinct from SWCNTs produced as a synthetic by-

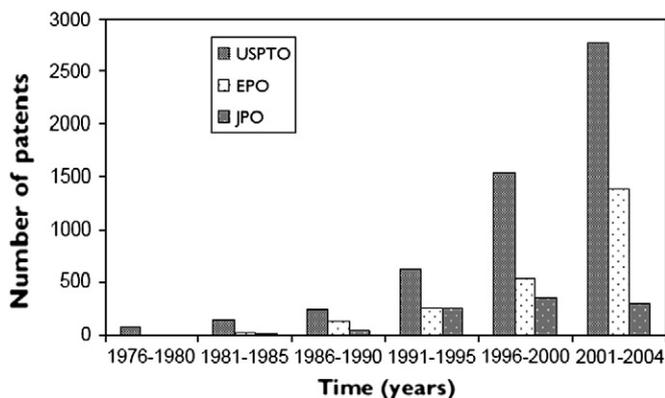


Fig. 7. Distribution of nanotechnology patents registered by USPTO, EPO, and JPO from 1974 to 2004 in bands of five years (Li et al., 2007).

product exerted chronic aquatic toxicity effects even at low concentrations of 0.58 mg/l (Templeton et al., 2006). These study findings presents several far-reaching implications from a waste management perspective. First, they demonstrate the need for adopting a holistic and integrated approach in managing products and by-product nanowastes streams generated during the production of NMs. Secondly, during manufacturing of NMs or nanoproducts there is a possibility of fabricating “nano by-products” with the potential to cause deleterious effects in the environment. This necessitates the development of a new paradigm of managing nanowastes due to the production of several derivatives of the same material depending on the manufacturing processes.

This raises the possibility of generating nanowastes of different physical–chemical properties (size, shape, composition, reactivity, etc.) of the same material which ultimately in turn exhibit a range of possible toxicological and ecotoxicity characteristics. For example, SWCNTs are fabricated at industrial scale using several different processes which yields materials (products) of different physical–chemical properties (Thomas and Sayre, 2005; Oberdörster et al., 2005). This implies that each product and its associated synthetic by-products may require a different waste management approach—a phenomenon that strikingly differs from the conventional large-scale management of macroscale chemical waste streams. This phenomenon will become clearer based on the results of nanowastes classification presented in Section 6.

Thirdly, it is plausible that the toxic by-products generated during nanotechnology manufacturing may have or will be handled inadequately owing to the paucity of their related quantitative toxicity data, and the treatment techniques are yet to be developed. Fourthly, it is likely that the waste by-products in the nanometer size range could evoke more stringent disposal requirements than the desirable parent products.

Kashiwada (2006) illustrated the NM-size effect on the accumulation of fluorescent nanoparticles in the *Oryzias latipes* (Japanese Medaka)—where smaller sized particles accumulated faster than those of larger dimensions. In addition, bioavailability and toxicity were influenced by multiple physicochemical properties and abiotic factors—with salinity as the dominant environmental factor in enhancing the observed adsorption, accumulation, bioavailability and toxic effects. Klaper et al. (2009) showed the effects of functionalization of NMs on the observed toxicity in *Daphnia magna*. Using glutathione-S-transferase (GST) and catalase (CAT) biomarkers, the researchers showed that although functionalization caused short-term toxicity and oxidative stress reduction in whole organism essays, however, the particles ( $C_{60}$ ,  $C_{60}H_x$ ,  $C_{70}H_x$ ,  $C_{60}(OH)_{24}$ , and  $TiO_2$ ) caused oxidative stress at lower concentrations as opposed to those measured in an acute toxicity. These results suggest the possibility of sub-lethal effects of NMs which may not be detected in the routine acute bioassay tests – which if not established in the near future may compromise long-term safe and responsible handling, treatment, and disposal of nanowastes.

Other studies have reported the Trojan horse effects of NMs owing to their large adsorption properties, and ability to transport other substances (environmental pollutants). Baun et al. (2008b) illustrated the carrier effect of NMs in invertebrates using *D. magna* species in the presence and absence of fullerenes. Baun et al.'s (2008b) findings established that toxicity of methyl parathion was not affected by the presence of fullerene aggregates, however, a 1.9 times decrease in the toxicity was observed for pentachlorophenol. For phenanthrene, an 85% sorption to the fullerenes aggregates increased its toxicity by 60%—attributed to the presence of fullerenes aggregates. These results illustrate that sorbed phenanthrene was made bioavailable to the test organisms (Baun et al., 2008b). Similarly, findings on the interactions and adsorption of environmental pollutants by NMs have been reported (Cheng et al., 2004; Yang et al., 2006; Gotovac et al., 2007; Gao et al., 2008; Hu

et al., 2008), and are likely to complicate nanowaste risk assessment in water and soil environments.

Moreover, the adsorptive capabilities of NMs and their ability to permeate across membranes raises concerns regarding the translocation of toxic bulk chemicals in tissues and cells which previously were unlikely to be affected by the macroscale chemicals. Therefore, this is of interest because even though certain NMs may not be toxic, however, if the nanowaste mixes/interacts with other conventional waste streams containing toxic chemicals, the former may act as a Trojan horse to transport the latter into the cells (Limbach et al., 2007). This raises questions on the effectiveness of current waste management systems in handling nanowastes. Other studies have shown that the sorption of pollutants into NMs (Yang et al., 2006; Knauer et al., 2007; Sun et al., 2007) is mainly due to the large surface area of these materials. Presently, these aspects have not been fully addressed particularly with respect to their potential implications to the nanowaste management, and these case studies are too few to offer a compelling case to generalize the fate and behaviour of NMs in the environment.

#### 4.2. Limitations of reported NM ecotoxicity data

While the volume of ecotoxicity data is increasing rapidly over the last few years (see reviews by Moore, 2006; Handy et al., 2008; Klaine et al., 2008; Tiede et al., 2009; Kahru and Dubourguier, 2010) the data is characterized by limitations that presents both direct and indirect implications in achieving effective nanowaste management. Significant adverse effects of nanowastes are likely to be experienced during post-disposal phase of the nanoproducts and materials. First, there are limited studies on the NM accumulation from lower trophic organisms to higher consumers (Holbrook et al., 2008). This is because numerous studies on toxicity of NM focus is mostly on the materials interactions with organisms at cellular or sub-cellular systems. Secondly, the mechanisms in which NMs causes the observed toxicity are not fully established. As such, despite the increasing numbers of data and information on ecotoxicity in the scientific literature, it is unclear if the reported observed effects are due to similar or different mechanisms as to those of the macroscale chemicals.

Thirdly, because of the multiplicity of factors that influences the ecotoxicity of NMs like the physicochemical properties (size, shape, surface chemistry, etc.), and abiotic factors (salinity, pH, water hardness, presence of dissolved organic matter, state of aggregation, etc.) (Handy et al., 2008); the reported toxicity data used in this study do not provide a holistic risk assessment of NMs with specific reference to the disposal phase. Consequently, NMs of the same material but with different size, shape or crystal structure exhibit different behaviour, uptake and effects (Pal et al., 2007; Warheit, 2008; Handy et al., 2008; Tiede et al., 2009). For instance, Pal et al. (2007) illustrated that triangular-shaped silver nanoparticles exhibited higher antibacterial activity to *Escherichia coli* in comparison to spherical- or rod-shaped ones.

Fourthly, present quantities of NMs being released in form of different nanowaste streams into different environmental compartment (air, water, and soil) – in addition on how their behaviour (influence of the abiotic factors) and fate (complexation, adsorption, mobility, etc.) will mirror the laboratory-scale controlled studies – is largely unknown (see Section 3). Fifthly, the modes of dispersing the NMs during bioassay experiments have been shown to exert direct impact on the findings derived from a given study. For example, studies on the effects of fullerenes ( $C_{60}$ ) on *D. magna* by Lovern and Klaper (2006) showed the use of tetrahydrofuran (THF) as the dispersion media in place of sonication technique resulted in observed elevated acute toxicity (48 h  $EC_{50}$ ) where in former being one order higher in comparison to that of the latter dispersion agent.

Similarly, the results of Oberdörster et al. (2006) for the same materials and physicochemical properties – where the stirring of

Milli-Q water method of suspension was used as the dispersion media – resulted to different toxicity effects on the *D. magna*, where concentrations of up to 5 mg/l were found as too low for the evaluation of LC<sub>50</sub> values. This complicates the interpretation of the ecotoxicity data due to limitations related to the dispersion methods used (stirring, sonication, use of chemical dispersant, or when used in combination, etc.). Previously, concerns on the toxicity of solvents used or the methods of dispersions in preparation methods in toxicity testing of NMs have been raised (Fortner et al., 2005; Zhu et al., 2006; Smith et al., 2007; Crane et al., 2008). Nonetheless, in many scientific papers this form of toxicity due to impurities is not discussed, and is impossible to isolate their impact on the reported data. The limitations of current reported data on ecotoxicity of NMs have been reported elsewhere (Gharbi et al., 2005; Henry et al., 2007; Handy et al., 2008; Tiede et al., 2009), and will not be repeated here.

In our study, these challenges were taken into account in addition to the lack of standardization of the experimental results due to the absence of agreed reference materials. As a result, this may introduce a high degree of uncertainties regarding risk evaluation of NMs in actual environmental conditions through nanowastes. However, the available data has been applied in conceptualizing a framework of classifying nanowaste streams in order to improve their management at various phases (generation, handling, transportation, and disposal).

## 5. Nanowaste streams treatment and disposal

Only recently scientific studies on the treatment of nanowastes in water, and sludge environmental compartments, or the behaviour of NMs in wastewater systems have begun to emerge. However, the available data and knowledge are insufficient to outline the general requirements for the identification of candidate streams meriting treatment before release into the environment. This can be attributed to lack of universally acceptable nanowastes classification essential in expressing their degree of hazardousness, or due to limited appreciation of the large volumes of nanowastes generated because partly nanotechnology is largely viewed as a green technology. In this section, available findings on the treatment, behaviour and fate of NMs in water and solid waste streams are summarized.

### 5.1. Removal of NMs in wastewater treatment plants

For example, according to the Royal Commission on Environmental Pollution (2008), during the manufacturing processes of fullerenes – only about 10% of the materials are usable – and the rest are disposed of in landfills. This is one example on the introduction of NMs into the landfills—yet the current methods for testing and detection are inadequate or were not designed to deal with wastes streams containing pollutants with nanoscale dimensions. In the following sections, we summarize findings on nanowaste treatment and/or behaviour of NMs in wastewater treatment plants (WWTP).

The removal of Ag NPs from wastewater was recently investigated by Benn and Westerhoff (2008). The leached out Ag NPs from the socks – and adsorbed into the WWTP biomass – was used in developing a model for predicting how a typical wastewater facility could treat effluent containing Ag NPs. The simulated model results suggested that WWTP have the capability to remove higher concentrations of Ag load from an influent stream than expected due to increased consumer nanoproducts containing Ag NPs. Whilst the removal of Ag NPs was found to be adequate, however, the concentration of Ag in the biosolids was found likely to exceed the recommended limit by the United States of America Environmental Protection Agency (USEPA). For example, the model results suggested that an influent with Ag concentration of 180 µg/l; the resultant Ag concentration in biosolids would exceed the 5 mg/l Toxicity Characteristic Leaching Procedure (TCLP) as prescribed by the USEPA.

Benn and Westerhoff (2008) findings suggest that the increasing use of Ag NPs may limit the utilization of the municipal biosolids for agricultural applications as compost or fertilizer. This is because of the inhibitory antibacterial property of Ag which is likely to cause adverse effects on useful microbial populations in the soil such as those required for nitrogen fixing bacteria. For example, Choi et al.'s (2008) results illustrated that autotrophic nitrifying bacteria essential for the nitrification process critical for the biological nutrient removal in wastewater were susceptible to inhibition (e.g. inhibited respiration by 86 ± 3%) by Ag NPs—and the accumulation of Ag NPs may cause detrimental effects in wastewater treatment. Musee (in press) illustrated through modeling how the WWTP efficiency removal of NMs from the influent influences the mode of introducing nanoscale pollutants into the environment. For instance, at higher efficiency regime, most NMs are removed from the influent but are adsorbed into the biosolids. Conversely, at low efficiency regime of the WWTP – most NMs passes through untreated – and introduced into the environment through the treated effluent. This implies that effective techniques for removing or neutralizing the NMs in the biosolids need to be developed to ensure continued use as fertilizer and/or compost.

Studies by Limbach et al. (2008) revealed that a large portion of the NPs can be removed from the WWTP through adhesion process to the clearing sludge. However, a significant percentage escaped the WWTP clearing systems. The findings showed that 6 wt.% of the cerium oxide NPs (CeO<sub>2</sub>) escaped from the model WWTP system. The quantities of the NPs that escaped depended on the surface charge and the addition of the stabilization surfactants—similar to those used in manufacturing nanoproducts. The presence of the CeO<sub>2</sub> in the effluent was associated with low tendency of NPs to aggregate with the bacteria in the sludge. However, these findings contrast earlier results of Limbach et al. (2005) because most oxide NP dispersions are unstable in the presence of high ion concentrations or complex organic solutions. Therefore, the results of Limbach et al. (2008) suggest that the current biological treatment steps in the WWTP are limited in removing oxide-based NPs from wastewater adequately. Because in the actual WWTP systems the oxide NPs are anticipated to be at much lower concentrations – such a scenario will disfavor the agglomeration mechanism – and motivates focused research to elucidate the role of sedimentation and other physical treatment methods for the removal of NPs from the wastewater.

Jarvie et al. (2009) investigated the fate and behaviour of silica NPs (SiO<sub>2</sub>) using the small-angle neutron scattering technique in a wastewater treatment simulated conditions. The researchers investigated factors that controlled the colloidal stability of SiO<sub>2</sub> NPs, the composition of the aqueous matrix, influence of the large particles, and the effects of surface functionalization of the NPs. The study findings suggested that both functionalized (using a thin coating of non-ionic surfactant—Tween 20) and unfunctionalized (naked) SiO<sub>2</sub> NPs were stable in nanopure water, and their stability was observed for over 24 h after dosing. Therefore, it appeared flocculation process was most suitable for removing SiO<sub>2</sub> from the wastewater—within appreciable limits of relevant retention times in the primary settling tanks.

On the other hand, unfunctionalized NPs were found to be stable both in raw and screened wastewater—demonstrating that no sedimentation occurred over a period of 3 h. These results suggest that no interaction occurred between the unfunctionalized NPs and the wastewater constituents that induced SiO<sub>2</sub> NP flocculation within the time scales of typical wastewater transit through the WWTP (Holt et al., 1998). In addition, the results indicated that unfunctionalized NPs may pass untreated into the effluent stream, with the potential to cause adverse effects on the secondary treatment steps or to the aquatic organisms in the ecosystems. The Tween-coated SiO<sub>2</sub> NPs were less stable in raw and screened wastewater—and experienced rapid sedimentation and sewage particulates were observed over a few seconds despite the likelihood of Tween-coated SiO<sub>2</sub> NPs to have

been retained in the suspension for a longer period (Jarvie et al., 2009).

In summary, the study results suggested that unfunctionalized SiO<sub>2</sub> NPs did not flocculate in wastewater within the typical residence times for the primary treatment, and hence were unlikely to be removed through sedimentation process, and may enter into the environment through the treated effluent. On the other hand, functionalized (surface-coated) underwent rapid flocculation in wastewater which suggests they are likely to be removed from the wastewater through sedimentation to the sewage sludge. This implies that the concentrations of NMs should be closely monitored to ensure that they do not exceed the recycling allowed limits for the sludge applications as compost or fertilizers.

### 5.2. Treatment of solid nanowaste streams

Up to now, there are limited or no scientific studies on the detoxification of solid nanowastes. Solid nanowastes are disposed in landfills where they can potentially leach out NMs into the soil systems. This may result to widespread nanopollution to both underground water as well as the domestic water supplies. For the treatment techniques of solid nanowastes to be effective—they should either be effective in strongly binding the NMs in a solid matrix, or firmly securing them in an impermeable container, or facilitating the recovery of NMs. Alternatively, poorly treated or untreated solid nanowastes may aid in widespread of NMs exposure to the aquatic and terrestrial organisms. For example, methods such as vitrification previously applied in the immobilization of high-level waste streams such as nuclear, urban and industrial waste streams (Kavouras et al., 2003)—mostly characterized by leaching of pollutants into the environment should be considered as potential candidates for the treatment of solid nanowastes. Notably, it is proposed that before such methods are considered a multi-criterion decision support model consisting of evaluation criteria like; cost, effectiveness, ease of use, among others be considered at the initial phases of the treatment technology development.

Liu et al. (2008, 2010) proposed several techniques of treating and disposing Cr(IV)-adsorbed solid nanowastes generated from the traditional industrial sludge. The waste streams considered in the Liu and colleagues investigations contained Mg(OH)<sub>2</sub> NPs (with mean size of 20 nm) generated during the brine purification step of the sea-salt raw material in the chlor-alkaline and chlorate industries (Kent, 2003). The study findings showed that transforming Mg(OH)<sub>2</sub> NPs into bulk materials facilitated the release of the adsorbed Cr(IV) into solution—where the later compound was recovered and reused as additives in other applications such as: paints, flame-retardants, lubricants etc. The Cr(IV) was transformed into non-toxic product through; (i) the desorption of the Cr(IV) from the surface of NPs due to phase-transformation, and (ii) the efficient separation of the Cr(IV)-containing liquid from the solid growth due to rapid crystal growth of Mg(OH)<sub>2</sub> NPs into micrometer-size. The second phase enhanced the settling velocity of the solid Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>·4H<sub>2</sub>O microspheres in addition to the separation effect of the supernatant liquid.

Liu et al. (2010) further improved the treatment of Cr(IV)-containing nanowastes by considering the technique efficiency at both room and high temperatures. The results showed that the process can be optimized at higher temperatures where detoxification achieved a total Cr(IV) content of 51.6 mg kg<sup>-1</sup> and a Cr(IV) leaching concentration of approximately 0.218 mg/l which satisfied the standards for utilization with a corresponding removal efficiency of 97.8%. The proposed methods have the potential for treating industrial scale generated nanowastes. However, there is a need of undertaking further investigations in establishing the efficacy and other variants of the technique's capability of treating different

nanowastes particularly those containing intentionally engineered NMs, and also in certain cases are functionalized.

Thus, technologies that can adequately handle, treat, clean up, and dispose nanowastes still remain underdeveloped or are at the infancy phase of research and development. This implies that the challenges related to managing nanowastes will continue to grow unabated in the coming years.

## 6. Nanowaste classification

Bulk-based chemicals waste streams generated at different phases of materials and products life cycle are generically classified as benign to extremely hazardous. The classification is based on the inherent characteristics of constituent chemicals (or compounds), the expected exposure dose, and the waste stream quantity (Musee et al., 2008a,b). However, such classification is inadequate for waste streams containing nanoscale materials whose properties cannot be predicted from the current knowledge of the counterpart bulk parent chemical properties. Currently, there is no internationally agreed nanowastes classification system or paradigm that can support the waste management industry and regulators in developing precautionary and practical approaches of managing different classes of waste streams containing nanoscale materials.

To address part of this challenge, recently Musee (in press) proposed the first qualitative nanowastes classification paradigm that seeks to aid in managing various types of waste streams containing nanoscale materials. In this section, only the most salient features of the proposed classification paradigm are summarized to illustrate a number of unique aspects of the nanowastes management as opposed to the conventional waste streams. To date, there is lack of exposure potency data such as the biopersistence, bioaccumulation, and partition of NMs data in the environment—aspects which strongly controls the potential bioavailability of pollutants to the environmental receptor organisms. Therefore, the possible degree of NMs exposure can at best presently be estimated based on their loci in the nanoproducts (Hansen et al., 2007, 2008; Musee, in press).

For example, in real world scenario the potential exposure of NMs contained in a given nanoproduct to the receptor organisms in the environment is influenced by numerous factors. These factors, for instance, at the disposal life cycle phase include: (i) unknown exposure scenarios of a given product; (ii) presence or absence of the coating of the NMs in a given product; (iii) multiplicity of possible disposal pathways for a given nanowaste stream (e.g. through wastewater, landfills, recycling, or incineration); (iv) effect of the disposal media (air, soil or water); (v) bioavailability and persistence of the NMs in different media; (vi) the potential ease of NMs release from a given product as a function of loci in the nanoproduct; (vii) quantities of the nanowastes released into the environment; and, (viii) the presence or absence of other environmental contaminants that may lead to antagonistic or synergistic effects to a given set of NMs.

Taking into account the above factors, then the exposure of NMs from nanowastes can only be estimated based on their loci in a given nanoproduct presently (point vi) – as the data for the rest of the factors are yet to be determined. This is because the locus of NMs in a nanoproduct largely determines their ease of release, or not – for any form of exposure to occur. For example, NMs that are firmly bounded (sintered) in a solid nanoproduct (in automobile parts, memory chips, etc.) will exhibit *none* or *very low* potential degree of exposure. On the other hand, NMs which are freely bound or loosely bound in liquid suspensions – which constitute the highest class of NMs found in numerous nanoproducts (Hansen et al., 2008) – have *high* to *very high* degree of exposure. It is in this context that the loci of NMs in nanoproduct are argued presently to be the best predictor of the NMs exposure to the environmental organisms.

To fully characterize the risk posed by nanowastes, the degree of hazard also needs to be evaluated because risk is a function of both hazard and exposure. In this study, the hazard was derived from the ecotoxicity data of NMs currently published in the scientific literature (examples on some of the published data are provided in Table S1). Note that the reported data in certain cases may not be representative of the actual abiotic factors that NMs may encounter in real world environmental scenarios. Nonetheless, the reported ecotoxicity data to date was viewed as providing useful information to aid in understanding and appreciating the potential risk profiles of NMs after their release into the environment. In this paper, the available data was qualitatively ranked using the globally harmonized system (GHS, 2003; Silk, 2003), and the highest reported data value for a given NM was adopted for characterizing the hazard. Following this formalism, different NMs degree of hazard were ranked as follows: fullerenes (high), SWNCT (high), MWCNT (high), SiO<sub>2</sub> (low), silver (medium), TiO<sub>2</sub> (low), Al<sub>2</sub>O<sub>3</sub> (medium), etc.

The next step entailed identifying, characterizing and categorizing nanowastes into various classes. Nanowastes classifications has several benefits including: isolating waste-types that merits special operational management practices during production, handling, transportation, storage, treatment and disposal to mitigate against any form of adverse effects to the humans and the environment due to their degree of hazardousness. Secondly, it allows effective determination of appropriate modes of treating and disposing of various types of nanowastes. In the present study, the classification is based on the potential exposure potency at the disposal life cycle phase of the nanowastes. Using both the exposure and hazard data, nanowastes were broadly categorized into five probable classes as summarized in Table 3. Practically, it is impossible to accurately classify a certain nanowaste in a specific class as a result of the limitations described in section 4.2. The paucity of data to elucidate the relationship between each of these factors poses one of the greatest challenges of effectively classifying nanowaste streams—and is likely to dominate the research activity in this field for the next five to ten years as efficient classification underpins effective management and development of enforceable legislative instruments.

To illustrate how waste streams containing NMs are likely to fundamentally challenge the waste management practices as cur-

rently known—several risk profiles of different nanoproductions are presented. Conventionally, the risk profile of a given macroscale chemical remains unchanged as a function of the chemical's structure, and consequently, the management approach or technique of a given product waste stream at disposal phase remain relatively constant. Strikingly, because one nanoproductions-type, for instance sunscreens, poses a wide range of risk profiles at the disposal phase—as function of different NMs used (ZnO, TiO<sub>2</sub>, fullerenes, etc., see Table 4). Therefore, the risk profile of a given nanoproductions at disposal phase may vary from low to very high. Such a phenomenon is uncommon in the case of macroscale chemicals.

This implies that, waste streams of the same product after the post consumer use may range from Class I-type of nanowaste (most benign) to Class V-type of nanowaste (highly toxic and hazardous)—a phenomenon likely to trigger serious implications on nanowaste management in general. Consider the case of sunscreens. If a certain sunscreen nanowaste contains TiO<sub>2</sub> as the constituent NM—the resultant likely waste stream category is Class I-type nanowaste. On the other hand, if the constituent NM in the sunscreens is fullerenes, the resultant likely waste stream category is Class V-type nanowastes. These findings reveal that the same nanoproductions – but containing different NMs – may result to different classes of nanowaste streams with highly variant risk profiles as shown in Table 4 (the potential nanowastes individual class-type characteristics are discussed elsewhere (Musee, in press) and will not be repeated here). This is likely to trigger requirement of different waste management approaches as prescribed for different nanowaste classes presented in Table 3 of the same nanoproductions. On the other hand, such diversity of nanowaste streams of the same product is likely to pose new challenges in terms of developing legislations that governs waste streams containing NMs at the disposal phase. From this example (see Table 4 for other cases), it is clear that the current legislative framework did not anticipate such a scenario.

The complexity of dealing with a given nanoproductions-type variant waste streams is due to several factors. Firstly, it would be laborious, time consuming, and costly if not practically impossible to adequately segregate waste streams of the same product. As a result, nanowastes are likely to introduce new challenges of managing waste streams with respect to: classification, identification of appropriate handling

**Table 3**

Nanowaste classification as a function of constituent NMs toxicity and exposure potency as a function of NMs loci in the nanoproductions.

Nanowaste classes	Description	Comments/description	Examples of waste streams in terms of nanoproductions
Class I	<i>NM hazard:</i> non-toxic; <i>Exposure:</i> low to high	Concerns on waste management may only arise if the bulk parent materials (Trojan horse effects) can cause toxicity to humans and the environment through accumulation beyond a certain threshold concentration limit. Otherwise, nanowaste can be handled as benign/safe. No special disposal requirements. Risk profile: <i>none to very low</i> .	Display backplanes of television screens, solar panels, memory chips, polishing agents
Class II	<i>NM hazard:</i> harmful or toxic <i>Exposure:</i> low to medium.	Toxicity of NMs may warrant establishing potential acute or chronic effects to determine the most suitable and optimal management approach during handling, transportation or disposal processes. Risk profile: <i>low to medium</i>	Display backplane, memory chips, polishing agents, solar panels, paints and coatings
Class III	<i>NM hazard:</i> toxic to very toxic; <i>Exposure:</i> low to medium	Protocols appropriate for managing hazardous waste streams in the entire waste management chain are desirable/recommended. Need for research to determine if current waste management infrastructure is adequate to deal with hazardousness of waste streams due to nanoscale materials. Risk profile: <i>medium to high</i>	Food packaging, food additives, wastewater containing personal care products, polishing agents, pesticides
Class IV	<i>NM hazard:</i> toxic to very toxic; <i>Exposure:</i> medium to high	Waste streams should be disposed only in specialized hazardous wastes designated sites. Inadequate WM could lead to serious threats to humans and environmental systems. Risk profile: <i>high</i>	Paints and coatings, personal care products, pesticides, etc.
Class V	<i>NM hazard:</i> very toxic to extremely toxic; <i>Exposure:</i> medium to high	Dispose only in specialized hazardous waste streams designated sites. Poor waste management can cause extensive nanopollution to diverse ecological and water systems, which may prove to be costly, laborious, and time consuming to remediate. Immobilization and neutralization techniques among the most effective treatment techniques. Risk profile: <i>high to very high</i>	Pesticides, sunscreen lotions and food and beverages containing fullerenes in colloidal suspensions

Examples of nanowastes provided are based on the available data, and quantitative studies are essential to verify and enhance the transparency as well as the credibility of the proposed qualitative classification formalism proposed.

**Table 4**

Few examples of risk profiles of nanoproducts and/or applications containing different NMs at the disposal life cycle phase.

Application	NMs	Hazard	Exposure potency	Risk at disposal	Potential nanowaste class
Personal care pro.	Ag	Medium	High	Medium	Class II/Class III
	Fullerenes	High	High	High	Class IV/Class V
	Fe <sub>2</sub> O <sub>3</sub>	Medium	High	Medium	Class II/Class III
Food/beverages	TiO <sub>2</sub>	Low	High	Low	Class I
	TiO <sub>2</sub>	Low	Medium	Low	Class I
	ZnO	Medium	Medium	Medium	Class II/Class III
Sunscreens lotions	Fullerenes	High	Medium	High	Class IV/Class V
	Dendrimers	Medium	Medium	Medium	Class II/Class III
	ZnO	Medium	High	Medium	Class II/Class III
Automobile parts	TiO <sub>2</sub>	Low	High	Low	Class I
	Fullerenes	High	High	High	Class IV/Class V
	Dendrimers	Medium	High	Medium	Class II/Class III
Polishing agents	SWNCT	High	Medium	Medium	Class II/Class III
	MWNCT	High	Medium	Medium	Class II/Class III
	Nanoclays	Low	Medium	Low	Class I
	Fullerenes	High	Medium	Medium	Class II/Class III
	TiO <sub>2</sub>	Low	High	Low	Class I
	ZnO	Medium	High	Medium	Class II/Class III

Class I has lowest risk profile, Classes II and III exhibits moderate (medium) risk levels, and Classes IV and V have the highest degree of risk.

techniques, and the development of appropriate legislative frameworks to govern them. Secondly, the data and information has to be complimented by knowledge elucidated from waste management specialists and practitioners as means of identifying the most practical approach of dealing with potentially increasing quantities of nanowaste streams. These aspects are likely to remain of great concern in the nanowastes management domain in the coming years, and it is recommended that practical steps that can minimize the present uncertainty be sought before the quantities of nanowastes reach out of proportions (see examples of proactive steps of addressing some of these challenges in Section 7).

## 7. Discussion

In this paper, the most salient aspects and challenges related to rising quantities of nanowaste streams, and how potentially will dramatically cause waste management paradigm shift as currently known have been presented. We argue that while nanoproducts and NMs are increasingly becoming part of waste streams from factories, laboratories and end-of-life consumer products (Shadman, 2006; Luther, 2004)—there is lack of well documented evidence on their potential impacts on humans and the environment. In addition, even the available data is highly fragmented as well as limited to aid in deriving the appropriate strategies of managing nanowastes. Therefore, in the event of industry and government failures in taking proactive approach at present infancy phase of nanotechnology development in addressing the potential impacts of nanoproducts and NMs may result to long-term unintended consequences (Allianz Group, 2005; Cientifica, 2004b).

In the following sections, the most salient aspects of nanowaste management regarding: the quantification of nanowaste volumes, hazard evaluation of the actual toxicity of nanowaste streams, their potential impact to the present legislative frameworks, nanowaste classification as well as treatment technologies are summarized. Under each aspect, recommendations on how the current obstacles can be addressed are presented.

### 7.1. Legislative framework

Examining the current legislative frameworks shows that toxicity is expressed in form of mass per volume—yet studies have shown that

the toxicity of NMs are a function of shape, size, surface reactivity, and surface area. Therefore, the current system of expressing toxicity is likely to find limited application in expressing the actual environmental risk levels of NMs contained in the nanowastes. This implies that the traditional dose–response curves that have served as a single index – for the conventional macroscale chemicals waste streams – for expressing toxicity may not be a useful predictive parameter in the case of NMs. This is because the NM toxicity is not a function of a single factor such as size, surface area or rates of uptake and transportation among others (Sayes et al., 2005). It is therefore recommended that systematic risk identification of nanowastes through the development of useful indices of characterizing the toxicity of NMs in aquatic and terrestrial organisms be developed. This endeavor is envisaged to be successful if techniques that can easily detect and monitor nanowastes as well as measure different physicochemical properties of NMs (size, shape, surface area, chemical reactivity, etc.) easily in the actual environmental compartments are developed. Such tools are central in developing and enforcing policies and legislations in an attempt to limit widespread nanopollution.

Flowing from the first aspect, till now, the current legislative frameworks do not provide the “environmental allowable limits concentrations” of NMs—which may require to be expressed in a multiplicity of indices and units. This knowledge merits urgent attention through directed and focused research given the rising accumulation of NMs in different environmental compartments. On the other hand, there is need of verifying to what extent the current metrology of measuring pollutants in the actual environment applies within the context of NMs from nanowastes, and what forms of modifications are required.

### 7.2. Quantification of nanowaste stream volumes

Long-term effective management of nanowastes is closely intertwined with the ability of quantifying their volumes as it is highly improbable to manage unknown quantities. In other words, one cannot manage what is unquantifiable. In Section 3, surrogate data (number of consumer products, patents, etc.) were used to illustrate the increasing quantities of nanowaste streams. Because of the large uncertainties and unreliability of the surrogate data calls for the solicitation of more accurate data on the volumes of nanowastes. Such data would be useful in aiding effective decisions on how to manage nanowastes in the water and soil environments. It is therefore recommended that companies fabricating nanoproducts and NMs should provide data sheets on the likely expected volumes of nanowaste streams from a particular nanoproduct or industrial applications at different phases of the nanoscale materials life cycle. Such information would considerably improve the capability of evaluating and managing appropriately the increasing volumes of nanowaste streams.

Most importantly, the inventories of NMs and nanoproducts, economic as well as intellectual property data suggest that despite the lack of systematically reported nanowaste volumes presently in the scientific literature do not preclude their presence and rising entry into the environment. Thus, the information derived from these inventory databases should be viewed as an early warning system to the international community, governments, and industry to motivate the establishment of a collaborative initiative among these stakeholders. This would support coherent nanowaste management approaches and toxicity testing protocols towards achieving sustainable development and exploitation of nanotechnology capabilities for the societal benefits.

### 7.3. Toxicity evaluation of NMs

The challenge of evaluating and classifying nanowastes adequately is closely linked to the approaches adopted in establishing the NM

toxicity. In [Section 4.2](#), a number of limitations of the currently reported NMs ecotoxicity data were summarized. In addition to the suggestions proposed in addressing these challenges, it is recommended that studies on hazard evaluation should consider actual nanowaste streams. Such studies should be designed to take into account all the relevant biotic and abiotic factors in order to provide the most realistic threat of such nanowastes streams to organisms at different trophic levels either in the aquatic or terrestrial environments. For example, better data should be derived to elucidate the potential carrier capability of NMs to other environmental contaminants (Trojan horse effect), whether the observed toxicity is due to individual NMs or aggregated formations, and how actual environmental factors influences nanowastes risk factors. Secondly, such studies would aid in establishing realistic allowable environmental concentrations limits that may not cause any observable ecological effects to the receptor organisms.

Because risk assessment is a function of hazard and potential exposure scenarios for a given NM, it is prudent to ensure that the following aspects are effectively addressed. First, by ensuring that the reported toxicity data in the scientific literature is standardized possibly based on the values of universally agreed reference materials. Unfortunately the current available data lacks consistency; it is non-standardized, and consequently, compromises transparent classification of nanowaste streams. Thirdly, a protocol needs to be established outlining the minimum required variables for consideration in reporting the toxicity of NMs. Therefore, a set of minimum variables that needs to be examined and published for a given NM as basis for the reported toxicity are required. Owing to the diversity of physicochemical properties of NMs, and the general lack of findings linking the reported toxicity and the physicochemical properties inhibited standardizing the risk profiles reported in this paper.

On the other hand, it is essential for the manufacturers of NMs to provide data on the potential exposure pathways to the environment in relation to the application (or envisaged applications), and concentration of NMs in a given product. Lack of data on both aspects hinders effective risk assessment as this limits the determination of actual quantities of NMs in the environment that can trigger or cause adverse effects on the receptor organisms.

#### 7.4. Nanowaste treatment technologies

Based on the preliminary studies on the treatment of nanowastes in liquid and solid phases (see [Section 5](#)); it was noted that no single NMs removal technique from wastewater or portable water achieved 100% efficiency in dealing with emerging the nanoscale environmental pollutants. This means that a certain percentage of NM passes untreated, potentially can adversely impact on the aquatic, terrestrial, or human life forms. Conversely, high removal efficiency of WWTP was found to aid in the transfer of NMs from the liquid phase (influent) to the solid phase (biosolids). In addition, to date no single study on the treatment of NMs from commercial and industrial sources has been reported in the scientific literature. This implies a high possibility of the current WWTP allowing considerable volumes of NMs into the aquatic and terrestrial (e.g. through irrigation) environmental compartments. Thus, it is recommended that the treatment of nanowastes in WWTP be investigated to address the current data and knowledge gaps because the available results from laboratory simulated scale model results are too few, and are derived under highly controlled experimental settings that lacks credibility to provide sufficient evidence of real world industrial treatment plants.

Also, NMs have the potential to alter the functionality of the micro-organisms used in treating the waste streams especially in biological treatment plants as most of them have antibacterial properties (Klaine et al., 2008). This may imply that the conven-

tional chemical and biological contaminants treated at current plants may pass untreated including NMs after microbial functionalities have been compromised. Though, presently there are limited studies on the effects of NMs on the microbial communities in WWTP, the full extent this may have in actual plants is yet to be established. We therefore recommend an investigation on the extent to which the impact of NMs in nanowastes may exert onto actual treatment plants. Secondly, how NMs may affect the lifespan of current effluent and solid waste treatment plants—given they have been developed over the years using large sums of dollars from public and private investments.

#### 7.5. Nanowaste classification

One way of advancing our collective understanding on nanowaste management is through systematic classification of nanowaste streams. Musee (in press) proposed the first qualitative nanowaste streams. The results suggested that current waste management systems may be inadequate in dealing with these new forms of waste streams—as different waste streams of the same product were not anticipated in the context of current waste management paradigm. Secondly, it is likely that the development of comprehensive classification framework for nanowastes may be impeded for several years due to insufficient toxicological and epidemiological data, multiplicity of potential different waste streams of the same product, and the lack of exposure data.

However, several practical alternatives in addressing a number of these limitations have been proposed (see [Sections 7.1 to 7.4](#)), and this work lays a foundation in developing and advancing capabilities of dealing with emerging waste streams systematically. Moreover, the qualitative classification is viewed as a start, and it is recommended that data-driven quantitative nanowaste classification be developed based on the accumulative data on risk assessment of NMs at different phases of the materials life cycle. Such classification system will facilitate in the establishment of internationally accepted nanowastes classification system.

In summary, in this paper, we proposed several proactive approaches towards supporting responsible and sustainable nanowastes management. This is to provide a systematic approach on managing nanowastes as opposed to the knee-jerk reactive policy mechanisms as the case in numerous previous experiences after the emergent of new environment pollutants. However, if the status quo is maintained characterized by lack of data may lead to widespread contamination of surface and underground water resources by NMs from nanowastes. Such a scenario could pose potentially damaging and costly implications for authorities and industries as witnessed in numerous previous malevolent technologies development profiles documented by [European Environmental Agency \(2001\)](#).

## 8. Conclusions

Since the industrial revolution age—waste generation both in terms of quantities and nature (form) have continued to increase. Therefore, from the laboratory and industrial fabrication processes of NMs and/or nanoproducts has caused the generation of nanowastes. This, in the context of rapidly growing nanotechnology industry with corresponding increases in uncontrolled releases of NMs into the environment particularly through post-consumer nanowastes streams may cause expansive adverse effects to humans and the environment. For the nanotechnology to be sustainable, nanowaste streams must be effectively managed. In this paper, different aspects that potentially can improve nanowastes management have been discussed. These aspects include; the quantification of nanowastes volumes, hazard evaluation of the actual toxicity of nanowaste streams, examination of the potential impacts to the present legislative frameworks, nanowastes classification as well as treatment

technologies. The findings are that, nanowastes are likely of introducing a new paradigm to waste management as currently known.

In this paper, practical suggestions on how to address some of the identified data and knowledge gaps in dealing with nanowastes have been described to aid in developing; (i) a systematic risk assessment framework of NMs in actual waste streams, (ii) a well defined nanowastes classification protocol, (iii) industrial-driven and legislative initiatives, and (iv) appropriate technologies for handling and treating nanowaste streams. Under each focus area among others, a set of recommendations were made with the core emphasis leading to the development of widely agreed nanowastes classification within the international community. Finally, as the excitement generated by new applications of nanotechnology into nanoproducts has been witnessed in the last few years, an equal corresponding measure is fundamentally essential in parallel towards appreciating or understanding of NMs potential toxic effects in humans and the wider ecology.

Supplementary materials related to this article can be found online at doi:10.1016/j.envint.2010.08.005.

The following is the supplementary materials related to this article. Table S1. Examples of ecotoxicity data for several nanomaterials.

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