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LANDFILLING OF WASTE CONTAINING NANOMATERIALS AND NANOWASTE

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DEFINITIONS

The following definitions are taken or modified from ISO/TS 27687; 2008 and ISO/TS 80004-4:2011

Nanoscale – size range from approximately 1 to 100 nm.

Nano-object – A material with one, two or three dimensions in the nanoscale.

Nanoparticle – A nano-object with all three dimensions in the nanoscale.

Nanoscale material – A material having one or more external dimensions in the nanoscale or a material that is nano-structured.

Nano-structured material – A material with an internal or surface structure in the nanoscale.

Nanomaterial – A material with any external dimension in the nanoscale or having internal structure or surface structure in the nanoscale. This generic term is inclusive of nano-object and nanostructured material.

Nano-enabled product/Nanoproduct- Any product in which engineered nanoscale material is intentionally added or attached, or a product embedded with nanotechnology and/or Engineered Nanomaterials (ENMs).

Engineered Nanomaterial (ENM)- A nanoscale object or material that has been intentionally produced in a manufacturing process to have specific properties or specific composition.

Nanowaste* – 1) incidental (nanomaterial generated as an unintentional by-product of a process) nanomaterial (ISO/TS 80004-1:2010) and 2) non-functional or irrecoverable by-product, product or nanoscale debris, comprising, containing or bound to nanostructured material or its discarded residues.

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* The term nanowaste was used generally to include both waste from nanomaterial manufacturing and commercial or post-consumer waste containing ENM (end-of-life nanoproducts/waste containing nanomaterials) in several of the studies quoted and in some cases has remained in the text so as to not alter the original intent of the word used by the authors.

LANDFILLING OF WASTE CONTAINING NANOMATERIALS AND NANOWASTE

1. Introduction

The nanotechnology industry is rapidly generating new forms of waste streams due to the production and use of engineered nanomaterials (ENMs) and their use in nanoproducts; however there is limited literature on the fate, behavior and impacts of these waste streams on the environment and human health. This growing industry, increasing in both production rates and diversity of products, will lead to an increase of ENMs in waste management facilities through the disposal of end-of-life consumer and commercial products (waste containing nanomaterials). Several studies have indicated that a significant proportion of ENMs may be disposed in landfills and have suggested that priority attention should be paid to improving the understanding of these waste streams, the associated environmental risks and the effectiveness of current waste management practices and technologies. This is required in order to prevent potential pollution by nanomaterials (Asmatulu *et al.*, 2012, Bolyard *et al.*, 2013, Boldrin *et al.* 2014, Bystrzejewska-Piotrowska *et al.*, 2009, Keller A.A. *et al.*, 2013, Holden *et al.*, 2014, Lin *et al.* 2010, Lozano and Berge, 2012, Mueller and Nowack, 2008, Musee 2010, Nowack *et al.*, 2013, Yang *et al.*, 2013).

The purpose of this paper is to provide an initial scoping review of readily available scientific information about the source of ENMs in landfills, their fate and behavior in landfills, and the effectiveness of treatment technologies. As with other potential pathways of ENM release to the environment, there are many complex factors to consider. This is an area of emerging scientific research with on-going investigation and debate within the field of nanotoxicology. This includes defining the characteristics of ENMs and their potential toxicity which can vary as a function of both their chemical composition and other characteristics including shape, size, and structure. Additionally, it is also quite likely that a large fraction of ENMs will transform once released, which needs to be taken into consideration (Keller A.A. *et al.*, 2013). Although all ENMs may not be considered to be hazardous (RCEP, 2008), the scientific literature consistently discussed risks associated with ENM disposal in landfills from a context of precaution. In presenting their findings, this paper included those precautionary views, accordingly which may be validated or disproved as additional scientific studies are made available. Finally, the paper intends to provide a basis for discussion by summarising key points of concern and identifying knowledge gaps in order to improve decision-making concerning the management of ENMs in landfills.

2. Landfills and the Introduction of Nanomaterials in Waste

Waste disposal on land (dumping) and landfilling remain the most prominent waste management techniques used worldwide. The standards and practices for this type of waste disposal vary greatly ranging from uncontrolled sites to highly specialised and controlled engineered landfills. The potential release of contaminants through landfill gas and leachate is largely dependent on landfill design, site conditions and the sophistication of the control measures in place, including landfill gas recovery and leachate collection and treatment systems.

Modern engineered landfills use synthetic barriers, with few relying on natural barriers, to line the bottom of a landfill and incorporate collection systems for both leachate and landfill gas. The purpose of these collection systems is to capture and treat leachate and landfill gas; thereby preventing the migration of leachate into ground/surface water and the release of untreated landfill gases to the atmosphere. An un-engineered landfill would be considered an uncontrolled system due to the lack of environmental controls, potentially resulting in significant environmental exposure of contaminants.

Because of the widespread use of ENMs in a broad range of products, it is possible that some ENMs could be released through landfill gas; however this paper will primarily focus on ENMs that may be present in landfill leachate, as this is considered to be the primary means by which ENMs could be transported out of a landfill. Characterization of landfill gases to identify the presence of ENMs should be considered an important area for further research.

Landfill leachate is generated when rain passes through the waste mass and by the liquid generated due to the breakdown of waste within the landfill. The composition of leachate is extremely variable depending on the type of waste landfilled, the quantity of precipitation, the construction and operation of the landfill, the age of the landfill and other factors such as pH, temperature and microbial populations. The variability of leachate chemical composition is also influenced by the diversity of chemical substances contained in consumer products found in residential wastes from households and other wastes disposed in landfills. A variety of other wastes disposed in landfills can originate from light industrial, commercial and institutional activities and may include construction, renovation and demolition waste; contaminated soils; ash and sewage sludge, which may also be sources of ENMs (see section 2.1).

Landfills remain a topic of intensive research with international scientific studies (Kurniawan, 2006, Eggen *et al.*, 2010, Marcoux *et al.*, 2013) voicing concern about the potential environmental impacts of releases of contaminants from landfills. As part of a multi-year research program (2008-2013) in Canada, key macroscale[1] chemical substances were detected in leachate samples from a select number of large municipal solid waste landfills. Research findings demonstrated that conventional on-site treatment technologies and wastewater treatment technologies may not be effective in treating some substances found in landfill leachate under various conditions (Marcoux, *et al.*, 2013, Conestoga-Rovers & Associates, 2013). This study did not include ENMs, but demonstrates the variability of treatment efficacy. A recent study by Hennebert *et al.* (2013) determined the presence of ENMs in varying waste leachates, demonstrating that a significant amount of colloids (dispersed phase in the size range of 1nm-1µm) in leachate were found, different in elemental composition from natural ones.

While many of the substances detected in leachate are often not found in high concentrations, little is understood about the potential for synergistic effects of this multi-contaminant source of pollution nor have all possible substances been exhaustively analysed. The disposal of ENMs in landfills may add a level of unanticipated complexity, uncertainty and risk to waste management systems which are not designed to cope with all existing contaminants (Marcoux, *et al.*, 2013). Although effective in treating a variety of substances, conventional on-site leachate treatment systems may, in some cases, not be effective in removing certain chemical substances or ENMs under varying conditions. Therefore, it is pertinent that the risks of ENMs in landfills and potential for releases are identified, including downstream impacts on environmental and human health. This information is required to guide future waste disposal management decisions and the development of solutions.

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[1] Macroscale chemicals are those refered to in traditional chemistry where observations can be made by the human eye. Contrarily, microscale or nanoscale objects are in the range of several micrometers (µm) or several nanometers (nm) respectively in size where observations cannot be made by the unaided eye and require the use of magnification devices such as optical microscopes or powerful microscopes such as the electron microscope or the scanning tunneling microscope. Microscale is around the size of a single living cell whereas nanoscale are about the size of single atoms or molecules. www.cengage.com/resource_uploads/downloads/1439049300_222029.pdf, http://chem.sci.utsunomiya-u.ac.jp/v10n2/MashitaA/MashitaA_body.html

2.1 Source of nanomaterials in landfills

ENMs are used in a range of product innovations in the consumer, industrial and medical sectors and have been incorporated in cosmetics and personal care products, clothing and textiles, antibacterial agents, polishing cleaning and binding agents, solar cells, strong-lightweight plastics for the automotive and aircraft industries, preservatives, food processing and food packaging (Bolyard, 2011, Health Council of the Netherlands 2011, Musee, 2011). The Project on Emerging Nanotechnologies (2014) reported that 1628 nanoproducts were in use as of October 2013, with the largest category consisting of health and fitness products (48% of all nanoproducts) of which cosmetics and personal care products represent the largest proportion (37%) of this sub-group. It is beyond the scope of this paper to determine which nanoproducts (and/or key ENMs) are primarily disposed of in landfills, characterize their risk or quantify ENM flows to landfill. However, this work has been initiated by several researchers. The continuation of these investigations, including ENM classification and hazard identification, will serve to guide further research on which ENMs are found in landfills and also identify their potential risk.

The BSI (British Standards Institution) British Standards Guide PD 6699-2 identifies four main types of nanomaterial-related waste streams (solid and liquid):

- Pure nanomaterials.
- Items contaminated with nanomaterials, such as containers, wipes, disposable Personal Protective Equipment (PPE).
- Liquid suspensions containing nanomaterials.
- Solid matrices with nanomaterials that are friable (can easily crumble or pulverize) or have a nanostructure loosely attached to the surface, such that they can reasonably be expected to break free or leach out when in contact with air or water, or when subjected to reasonably foreseeable mechanical forces (BSI, 2007).

A key source of ENMs in municipal landfills is the disposal of ENMs present in consumer products at the end of their useful life (Asmatulu *et al.*, 2012, Boldrin *et al*. 2014, Ganzleben *et al.*, 2011, Keller A.A. *et al*., 2013, Reinhart *et al.*, 2010, Nowack et al, 2013). One life-cycle analysis estimated that over 50% of three commonly used ENMs produced by weight (nano-silver, nano-titanium dioxide and carbon nanotubes) will eventually end up in landfills (Mueller and Nowack, 2008). Another study by Keller A.A. *et al.* (2013) estimated that the majority (63-91%) of over 260,000-309,000 metric tons of global ENM production in 2010 will likely be disposed of in landfills. In terms of ENMs used by weight, the largest source of nanoproducts may be those used in plastic composites and building materials (Bottero, 2014, Keller A.A. *et al.*, 2013).

The disposal of nanowastes from industrial sources into regulated hazardous waste landfills and potentially municipal landfills should not be overlooked. For example, according to information obtained by the Royal Commission on Environmental Pollution (2008), it was stated that in one process of the manufacturing of fullerenes (carbon based ENMs), only about 10% of this material is usable and the rest are disposed of in landfills. Boldrin *et al.* (2014) also points to data indicating that the amounts of waste generated from the manufacturing processes are, in several cases, significantly larger than the amount of the final ENM product. However, this may not be indicative of other ENM manufacturing processes and is likely a worst case scenario considering the economic implications of discarding a high proportion of the product. Although not conclusive, this indicates that the handling of nanowaste streams from ENM manufacturing should also be considered a priority (Boldrin *et al*. 2014).

In addition to these sources, incinerators and wastewater treatment plants may also transfer ENMs to a landfill through the disposal of ash, slag or biosolids. Nanoparticles that are retained and or transformed during sludge stabilisation or incineration could then enter landfill leachate (DiSalvo *et al.*, 2008, Mueller *et al.*, 2012). Although it is possible to incinerate waste without releasing nanoparticles into the atmosphere, observations have shown that residues to which they bind are eventually disposed in landfills (Walser *et al.*, 2012). Mueller *et al.* (2012) estimated the flow of ENMs in waste streams in Switzerland and their modeling found that the major ENM-flow goes from the waste incineration plant as bottom ash to landfills. Biosolids could also be a significant source of ENMs to landfills. It is estimated that about ¾ of the total nano-titanium dioxide entering wastewater treatment plants would finally end up in landfills and that an average of 4.77 tons of nano-silver may be dumped into landfills per year (Mueller and Nowack, 2008). Another source of nanowaste requiring consideration is the use of ENMs in remediation, for the removal of pollutants from either aqueous effluents and/or gas. These generate another form of nanowaste needing to be disposed of properly, after they have been used for remedial purposes (Gao *et al.*, 2008).

In summary, ENMs contained in a large diversity of consumer nanoproducts, nanowastes from manufacturing and from remediation, as well as residual waste products from other waste management systems are disposed of in landfills. As the likely final destination of many ENMs (Keller A.A. *et al*., 2013, Kim, 2014), landfills require special attention. Further research is required to determine the extent to which landfills act as a final repository for ENMs or as a pathway of ENM exposure to the environment.

2.2 What factors contribute to the risk and complexity of disposing nanomaterials?

ENMs exhibit distinctive "footprints" as a result of their inherent chemical composition, shape, size and structure, resulting in unique behaviors in different environmental media even when fabricated from the same bulk parent material (Pal *et al.*, 2007). The risk to the environment is not soley based on quantity or mass (concentration) but also on the unique properties of nanomaterials and their behavior (Ganzleben *et al.*, 2011). These considerations, in addition to the following factors, require careful deliberation for landfill disposal of ENMs or products containing ENMs:

i. **The manufacturing of ENMs may generate "nano by-products" and other nanowaste streams with distinct toxicological characteristics requiring specialised disposal**

Templeton *et al.* (2006) studied the interactions of SWCTs (single-walled carbon tubes) on crustacean test species and found that, though the original purified SWCTs caused no detrimental effects in the test species, their by-products (a synthetic byproduct during arc-discharge synthesis) could potentially cause deleterious effects. The finding of significant toxicity from a nanomaterial manufacturing byproduct stresses the need for considering such materials in any assessment of environmental and health effects of these ENMs (Templeton *et al.*, 2006).

Additionally, the manufacturing of a single ENM may generate nanowaste streams of different forms with variant hazard levels. For example there are 10 major types of MWCTs (multi-walled carbon nanotubes), which can be produced using 5 different fabrication techniques (some types containing varying degrees of impurities), with varying nanostructure sizes using 3 different purification techniques and 10 possible surface coatings (used to maintain their nanoscale properties during their application) (Musee, 2010).

ii. **A given nanoproduct may pose a range of risk profiles upon disposal**

Risk is evaluated by identifying both the inherent hazard of an ENM and potential exposure to environmental or human receptors. For example, an ENM considered highly hazardous, but firmly embedded in a product matrix (with low or no possibility of exposure) will likely present a low risk. However, an ENM, loosely bound within a personal care product such as sunscreen, may present risks upon disposal ranging from low to high depending on the differing toxicity of the ENMs used in their production (nano- titanium dioxide, nano-zinc oxide or fullerenes) (Musee, 2011) and/or depending on their surface formulations (Botta *et al.*, 2011). Therefore ENMs must be examined in the context of the product matrix, formulations and their use and application in order to determine the most appropriate method for disposal.

iii. **ENMs may bond with pollutants enhancing their toxicity and may facilitate faster translocation of these pollutants through air, soil and water**

The sorption [2] of pollutants onto ENMs may increase the toxicity, transport (Farré *et al.* 2009) and in some cases increase the bioavailability [3] of pollutants. He *et al.* (2012) found that in addition to organic molecules, potentially toxic metal ions also have the ability to adsorb on the nanoparticle surface, increasing the transport and toxicity effects of metal atoms (prompting the use of ENMs in remediation of toxic metal pollutants). This finding was also reported by Gao *et al.* (2008), whose results found that mercury sorbed onto ENMs could become bioavailable and toxic if introduced into natural environments. Cheng *et al.* (2004) and Yang *et al.* (2006) also reported that organic compounds such as polycyclic aromatic hydrocarbons (PAHs) can be adsorbed onto carbon nanotubes causing an enhancement of PAH toxicity. However, there are also some instances where ENMs may decrease the toxicity of substances (Baun *et al*. 2008).

Because of their small size and slower rate of gravitational settling, some ENMs may remain suspended in air and water for longer periods. They may be readily transported over much greater distances than larger particles of the same material (Lin *et al.* 2010). Depending on the properties of the ENMs and soil, ENMs may be retained by soil particles or break through the soil matrix and reach groundwater (Lin *et al.* 2010). Soils with high clay content tend to stabilise ENMs and allow greater dispersal (EPA 2014). However, Lecoanet *et al.* (2004) reports that ENMs exhibit widely differing transport behaviors.

iv. **The increase in concentrations of ENMs in the environment may cause long-term chronic effects through different food chains**

Some ENMs can persist for a long time or be taken up by biological organisms and can act as an ecotoxicological hazard[4], undergo biodegradation or bioaccumulate in the food chain causing long-term chronic effects (Edouk *et al.*, 2013, Lin *et al.* 2010, SCENIHR, 2006). Toxicity to

[2] In this paper, the term "sorption" includes both processes of "absorption" and "adsorption" where a substance takes up another by the whole volume or by the surface respectively.

[3] Bioavailability (or biological availability) means the extent to which a substance is taken up by an organism and distributed to an area within the organism. It is dependent upon physical-chemical properties of the substance, anatomy and physiology of the organism, pharmacokinetics, and route of exposure. Availability is not a prerequisite for bioavailability (United Nations 2013). An alternative definition for bioavailability is the rate and extent to which a substance can be taken up by an organism and is available for metabolism or interaction with biologically significant receptors. Bioavailability (biological availability) involves both release from a medium (if present) and absorption by an organism (IPCS 2004).

[4] According to the Basel Convention, Annex III, the hazard characteristic H12 "Ecotoxic" is defined as: Substances or wastes which, if released, present or may present immediate or delayed adverse impacts to the environment by means of bioaccumulation and/or toxic effects upon biotic systems. The ecotoxicological impact of a chemical substance or waste depends on the ability of the chemical substance or waste to act toxically on organisms in the environment as well as on the exposure of these organisms. (UNEP 2003)

food web members have been reported for bacteria, plants and multicellular aquatic and terrestrial organisms (Holden *et al.*, 2014, Lui *et al*., 2014, Maurer-Jones *et al.*, 2013). In addition, the adsorptive capabilities of some ENMs and their ability to permeate across membranes raises concerns regarding the transport of toxic chemicals in tissues and cells (Musee, 2011). This is of interest because though certain ENMs may not be toxic, 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 cell (Limbach *et al.*, 2007). However, the quantity of ENMs which can act as a Trojan horse for other contaminants, after their transformation, will depend on competition between ENM surfaces and other surfaces (Auffan et al., 2012).

When disposing of various nanoproducts, nanowastes and by-products of ENM manufacturing, the unique physicochemical properties of ENMs found in a diversity of products with variant hazard levels, requires careful consideration. The potential for interactions between ENMs with other contaminants in leachate, which then could have an impact on the toxicity and dispersion of contaminants beyond the landfill, requires further investigation. These factors, in a worst case scenario, could contribute to potential widespread contamination of the environment. Failure to adequately address landfill waste disposal management concerns may allow the release of ENMs (to water, air, and soil), which may cause contamination of soils as well as surface and underground water resources (Musee, 2011), particularly from un-engineered landfills. This subject is currently being studied by the European Union (EU), the United States (US) and France-ANR (Agence Nationale de la Recherche).

3. Fate of Nanomaterials in Landfills

It is likely that changing in-situ landfill conditions will greatly influence ENM behavior and need to be considered when determining the fate of ENMs since as they age, their surface changes and reactivity is altered (Reinhart *et al.,* 2010). Landfills remain anaerobic over time; however other conditions such as pH generally increase in older landfills. Landfills also exert physical stressors to waste through abrasion and compaction of the waste to reduce its volume. Given this context, the release of ENMs incorporated in nanoproducts is probable within a landfill (Reinhart *et al.*, 2010, Lozano and Berge, 2012, Nowack *et al.*, 2013). The fate of ENMs will most likely be a function of the mobility of the nanoparticles, their degradability and the degradability of the host material (Hansen, 2009). Physicochemical and hydrological conditions in the landfill may affect both the matrix material and the transformation of ENMs themselves (Boldrin *et al.* 2014).

3.1 Are nanomaterials subject to degradation in landfills?

There is discussion in the scientific literature that indicates that some ENMs may be subject to degradation and/or that they may be released from a nanoproduct under landfill conditions, depending on the nature, location and quality of the ENM bonds. The potential ease of ENM release from a given product is a function of loci (placement) in the nanoproduct (Hansen *et al.*, 2008). However, this is to be verified through continued research. This is currently one aspect of research under *The NanoRelease Project*, based in the United States,[5] which aims to support the development of methods to understand the

[5] The NanoRelease project is anticipated to proceed in 4 phases, with the output of each phase determining scope and resources for subsequent phases. The first phase of the project consists mainly of a workshop sponsored/supported by the following organizations: US Environmental Protection Agency, Office of Research and Development, Environment Canada, Emerging Priorities Division, Health Canada, New Substances Assessment and Control Bureau, American Chemistry Council, Nanotechnology Panel, Society of Chemical Manufacturers & Affiliates, National Institute of Standards and Technology, The Adhesive and Sealant Council, American Cleaning Institute.

release of ENMs used in products and foster the safe development of ENMs. Other related research projects in Germany, include FRINano[6], CarboSafe[7], CarboSave and CarbonLifeCycle.[8]

Generally, ENMs firmly bound in a solid nanoproduct (such as in automobile parts, memory chips etc.) may exhibit no or a very low degree of exposure (to the environment or living organisms), as the ENMs typically remain within the product. However, even with a more firmly bound product, harsh environmental conditions within landfills, such as low pH and strongly reducing conditions (due to the anaerobic environment), will likely aid the release of ENMs bound in polymers (Reinhart *et al.*, 2010). Materials bound in plastics/plastic resins/polymers/metal products, such as those found in construction waste, may also be released into the leachate as a result of mechanical stress and abrasion during compaction (Mueller *et al.*, 2012, Nowack *et al.*, 2013) and/or contact with leachate of an aggressive nature (Lozano and Berge, 2012).

In a study of the potential release of carbon nanotubes (CNT) used in composites, Nowack *et al.* (2013) discuss the possibility that if CNT composites are landfilled, they could slowly breakdown depending on their degradability and potentially release ENMs to the leachate (or via dust from weathered composites). However, degradation of the polymer matrix, under conditions in engineered landfills, and release of CNTs is likely to be extremely slow. In contrast, the situation in an un-controlled landfill may lead to greater post-consumer and environmental releases of discarded CNT composites (Nowack *et al.*, 2013).

Conversely, ENMs freely bound or loosely bound in liquid suspensions, potentially will have a high to very high degree of exposure (Musee, 2011). For example, release of ENMs from discarded products such as cosmetics, sunscreens, hair products, wastewater biosolids and nanomaterial manufacturing wastes may occur. Once nanomaterials are released into the leachate, leachate composition will significantly influence material fate (Lozano and Berge, 2012). Boldrin *et al.* (2014), applied an exposure assessment framework for titanium dioxide (TiO_2) used in sunscreen and states that, considering the significant amounts of cosmetics containing ENMs which may be disposed of, potential exposure is defined qualitatively as ‘medium’. However, it is important to consider that many nanoparticles are subject to important speciation modifications (or transformation) as they are released from the initial products (Kaegi *et al.*, 2011). ENMs may aggregate and agglomerate to form larger particles losing their inherent nano properties.

ENMs embedded within a product matrix, on the surface of a product or freely suspended particles in a product, will affect the potential for nanoparticle release from a product. Landfill conditions (chemical and physical) could favor the release of nanoparticles from solid waste nanoproducts, although personal care products or other loosely bound ENMs in liquid form could potentially be more problematic and available to react with leachate and its chemical components (Lozano and Berge, 2012, Reinhart *et al.*,

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[6] FRINano Project: A project that establishes a hands-on measurement technique for the quantification and characterisation of pigment nanoparticles, which might be released from coatings or plastics upon weathering and/or exposure to mechanical stress. See: www.vdmi.de/englisch/topics/nano.html

[7] CarboSafe Project: An alliance initiative that develops reliable measuring technologies for unambiguously determining the release rates of nanoparticles in the lifecycle of CNT-based products. Furthermore, the project aims to identify the ecotoxicological potential of carbon nanotubes and to accurately estimate the risk potential with the aid of newly developed measuring technologies. See: www.nanopartikel.info/en/projects/completed-projects/innocnt-carbosafe

[8] CarboLifeCycle Project: A research project on nano-safety aspects with an enphasis on ecotoxicological consideration and development of measurement engineering, the advancement of measurement strategies and the measurement of potential exposure within the production, processing, utilisation and “end of life” of CNT’s or CNT containing products. See: www.nanopartikel.info/en/projects/completed-projects/carbolifecycle

2010). Further research and hazard experiments, are required to study ENMs and their potential transformation under different environmental conditions, including landfills to accurately predict their effects.

3.2 How will leachate characteristics influence nanomaterials and their transport?

Studies have reported that organic matter in leachate influences ENM stability, aggregation and transport, and other findings discuss the influence of pH and other factors on ENM solubility and aggregation. However, leachate (a colloidal system) is very complex, and this paper is not intended to provide an in-depth scientific analysis of the topic. The transformation of ENMs after their release in the environment is currently being undertaken by research programs such as the FP7 NMP (NanoMaterials Programme), NanoSUN (sustainable nanotechnologies) and NanoMILE (Engineered nanomaterial mechanisms of interactions with living systems and the environment: a universal framework for safe nanotechnology).

One study on ENMs and pH found that the stability of nanoparticles in water depends upon their chemical structure, water pH and temperature (DiSalvo *et al.*, 2008). The results demonstrated that with fullerenes (C_{60}) the more alkaline the water, the less aggregation occurred where the diameter of C_{60} aggregates decreases with an increase in pH. However in a study by Labille *et al.*, (2010) on the aging of TiO_2 nanocomposites (coated or encapsulated) used in sunscreen, depending on solution pH, ionic strength and natural organic matter (NOM) concentration, the colloids tend to aggregate and settle out of the water column (Labille *et al.*, 2010). Additionally, Gao *et al.* (2008) discuss how ENM adsorption to pollutants is dependent on pH. The adsorption onto a solid depends effectively on the pH, but in a complex medium such as leachate, there is competition for many other sorbents and pH is not the main factor (Bottero, 2014). At low pH values, metallic ENMs become positively charged (+), whereas at high pH the charge becomes negative (-). The pH at which the surface of the ENM becomes neutral is called the isoelectric point (IP) and particles are expected to agglomerate (Gomez-Rivera, 2011). Another factor to consider is ENMs are often coated with engineered organic substances, which act to keep particles evenly suspended in the product. This has several implications for aggregation behavior (Krammer *et al.*, 2014).

Several studies have reported on the interaction between organic matter in leachate and its influence on ENM transport. Organics typically found in mature landfill leachate, such as humic and fulvic acid, have been reported to stabilise ENMs (Hyung and Kim, 2008, Saleh *et al.*, 2010, Lin and Xing, 2008). This enhanced stabilisation reduces particle aggregation, generally correlating to greater material mobility (Petosa *et al.*, 2010). Jaisi *et al.* (2008) and Lozano and Berge (2012) reported that transport of SWCNTs (single-walled carbon nanotubes) is enhanced in the presence of humic acid. Similarly, Lin and Xing (2008) reported that tannic acid improves mobility of carbon nanotubes. Enhanced mobility of MWNTs (multi-walled carbon nanotubes) when in the presence of natural organic matter was also reported by Saleh *et al.* (2008). Research results at the University of Central Florida suggested that humic acid could mobilise ZnO nanoparticles in leachate, thus making them more susceptible to transport (Bolyard et al, 2012). The study conducted by Lozano and Berge (2012) concluded that even at high ionic strengths, humic acid creates a steric barrier to material aggregation/agglomeration, which likely aids the transport of the materials through the waste.

Generally, pH could be one factor, among others (such as ionic strength, temperature, NOM, specific ENM properties etc.), which can influence whether an ENM aggregates in solution, but may promote or inhibit aggregation under different conditions (in conjunction with other factors) (Liu *et al.*, 2014). In terms of the presence of humic acid or other organic matter specifically found in leachate, results indicate that the stabilisation of ENMs may occur, minimising aggregation and reducing precipitation. Conversely, humic acid or fulvic acid could limit the transport of ENMs if their affinity for the background is stronger than ENMs (Bottero, 2014, Lowry G.V., 2012). A reduction in the deposition rate of ENMs within landfills may increase the maximum travel distance of many different types of ENMs. However, this is not conclusive and requires further investigation.

3.3 Will nanomaterials influence microbial processes?

Generally, Holden *et al.* (2014) discuss the concern that ENMs can decrease bacterial diversity in the environment with potential negative impacts on both ecosystem and human health. A few studies have specifically looked at the antimicrobial or antibacterial properties of ENMs within landfills and other findings, used only for a basis of comparison, discuss how these antibacterial properties of ENMs potentially alter the functionality of micro-organisms used in treating wastewater, especially in biological treatment plants (Klaine *et al.*, 2008, Holden *et al.*, 2014). In some countries, landfill leachate is primarily treated by wastewater treatment plants and therefore ENMs in leachate could have an indirect impact on the effectiveness of the treatment process.

ENMs exert anti-microbial properties through different mechanisms such as the formation of reactive oxygen species (ROS) and disruption of physiological and metabolic processes (Edouk *et al.*, 2013). One specific study relating to the impact of ENMs, namely nano-silver (nAg), and its influence on the microbial process in landfills was reported by Yang *et al.* (2013). The study reported the inhibition of methanogenesis (generation of methane) and biogas production from municipal solid waste (MSW) due to the presence of nano-silver at a concentration of 10 mg/kg, although they found no impact for lower concentrations. Another study conducted at the University of Central Florida produced results suggesting that zinc oxide (ZnO) and titanium dioxide (TiO_2) nanoparticles did not have an inhibitory effect on anaerobic or aerobic processes when exposed to mature or middle aged leachate due to the low concentration of dissolved/soluble zinc (Bolyard *et al.*, 2012).

Other sources voice concern that the antibacterial properties of many metal ENMs may considerably affect the operation of wastewater treatment plants, allowing conventional chemical and biological contaminants to potentially pass untreated through after microbial functionalities have been compromised by the presence of ENMs (DiSalvo *et al.*, 2008, Health Council of the Netherlands 2011, Klaine *et al.*, 2008, Musee 2011). However, this may only occur with high concentrations of ENMs. Results from a study conducted by Hou *et al.* (2012) indicated nano-silver (referred to AgNPs in this study) at a concentration of up to 0.5mg L^{-1} would not dramatically impact the NH_4 (ammonium) removal efficiency of the activated sludge process. Yang *et al*. (2013) suggest that the release silver ions of (Ag^+) from nano-silver in wastewater may inhibit nitrification (conversion of ammonia (NH_3) to nitrate (NO_3) by bacteria) and that nano-zinc oxide (ZnO) and nano-titanium dioxide (TiO_2) could decrease nitrogen and phosphorus removal efficiencies at high concentrations. Nitrification is also an important component of treating leachate in on-site landfill biological treatment systems, which are used to eliminate soluble organic pollution using microorganisms (bacteria) (WSP Canada 2014).

Based on this information certain ENMs particularly with metallic and metal oxide nanoparticles, may have the potential to inhibit microbial treatment processes of landfill leachate treatment systems (and in wastewater) at high concentrations, although several variables exist that may influence whether or not microbial functions will be affected. This may include how the variable constituents of leachate interact with ENMs, their concentration, whether the conditions are aerobic or anaerobic and whether the ENMs exhibit antibacterial properties before and after transformation. This area will require further investigation.

3.4 Do nanomaterials penetrate landfill liners?

Landfill liners are synthetic membranes used in an engineered landfill to separate landfill contents from the environment. Compacted clay has also been used alone to provide a physical barrier and is still currently used today in conjunction with synthetic liners, to provide a secondary barrier. The potential of

ENMs to penetrate or migrate through landfill liners is currently being studied; at this time, there is a lack of conclusive findings (Ganzleben *et al.*, 2011). Academic bodies, such as the East Tennessee State University and the Environmental Research and Education Foundation (USA) are now undertaking this work.

Recent findings from Siddique (2013) suggest that properly designed and constructed landfills will be able to significantly limit nanoparticle transport to the environment for extended periods of time (approximately 100 years). In an experiment conducted by NanoHouse (Nanowaste Management), barrier properties of geomembranes were evaluated with suspensions of nanoparticles used in paints. It was found with this diffusion test that the nanoparticles did not cross the membrane, which corresponds to an effective efficiency of geomembranes over 12 years in real conditions.

However, another study proposes that ENMs placed near the bottom of MSW landfills are of concern, as they may transport or diffuse through liners, especially if they are near the bottom of the landfill (Lozano and Berge, 2012). Since leachate, which is a mobile aqueous phase, could be released to the surrounding environment, human health risks could result (Boylard *et al.*, 2013).

Synthetic membrane liners will likely contain ENMs and is currently being researched. However further research is needed, in particular to determine the potential risk of ENMs seeping through clay liners in older landfills or in situations where uncontrolled landfills depend on natural attenuation for treatment.

4. Nanomaterials and Leachate Treatment

Leachate treatment can incorporate one or a series of different systems such as aeration, sedimentation, settling lagoons, filtration, Ultra Violet (UV) treatment, and biological and/or chemical treatments. The purposes of these treatments are to settle out solids, adjust pH, increase oxygenation and break down or treat contaminants. The effectiveness of leachate treatment systems to adequately manage risks from ENMs will be influenced by the unique properties of ENMs and their behavior in landfill environments. Considerations include: 1) how ENMs interact with leachate and its potential to increase (or decrease) mobility and/or toxicity; 2) the integrity and nature of liners and their ability to contain ENMs and 3) the impact of ENMs on the effectiveness of the treatment technology itself.

4.1 Do current treatment technologies capture nanomaterials?

There is a lack of research specific to on-site landfill leachate treatment systems and their ability to contain and/or remove ENMs, although studies on the effectiveness of wastewater treatment technologies to remove ENMs have been reported. They are briefly mentioned here, to deduce the possible impact on landfill leachate treatment systems. Generally in studies of ENMs in wastewater treatment plants, nanoparticles bind with organic matter, which is ultimately settled out; some naturally aggregate with one another, thus improving settling; some bind with organic contaminants and some adhere to selective surfaces (DiSalvo *et al.*, 2008).

Researchers have found that conventional wastewater treatment plants can effectively remove ENMs such as nano-silver oxide, nano-zinc oxide, nano-cerium oxide, nano-titanium dioxide ($Ag°$, ZnO, CeO_2 and TiO_2) from wastewater; however, the ENMs typically accumulate (> 90%) in the waste sludge or biosolids (Westerhoff *et al.*, 2013). Additionally, with exception of nano-titanium dioxide (TiO_2), the initial mineralogy of silver, zinc and cerium (Ag, Zn and Ce) is transformed by oxidation, reduction and dissolution. This results in a transformation of the ENMs, whereby they do not exhibit the same properties as pristine ENMs (Bottero, 2014). Kaegi *et al.* (2011) found that nano-silver sorbs to wastewater biosolids and to a large extent and undergoes chemical transformation into silver sulfide (Ag_2S) which exhibits a much lower toxicity than other forms of silver (Ag). Kaegi *et al.* (2011) also indicated that further research is required to assess if other types of surface-coatings on ENMs may stabilise nano-silver or other ENMs in wastewater. Results from Nguyen M.D. (2013) indicated that nano-zinc oxide (ZnO) and nano-cerium oxide (CeO_2) impacted anaerobic digestion by inhibiting biogas production and found that the toxicity of the ENMs remained in biosolids, which could inhibit bacterial viability, seed germination and root growth of plants. However, Barton L. *et al.*, 2014 recently studied the affinity of ENMs for sludge bacteria flocs using an experimental approach. The initial ENMs were transformed into new materials such as Ce-oxalate or silver sulfide (Ag_2S) or zinc monohydrogen phosphate (ZnHPO4), which would not have the same biological activity as the initial ENMs (Barton L. *et al.*, 2014).

It is difficult to directly relate the efficiencies of ENM removal in wastewater treatment plants to landfill leachate, as leachate is primarily an aqueous effluent. However, it is suspected that ENMs would also bind to organic matter and bacteria in leachate. ENMs may be present in residual sludge as a result of the accumulation of settled solids during biological leachate treatment. Recent research has indicated the successful removal and sequestration of ENMs in biosolids and, in some cases, their transformation. However, ENMs remaining in the sludge could result in potential releases to the environment if the sludge is land applied or is sent to a landfill (DiSalvo *et al.*, 2008, Lui *et al.*, 2014, Westerhoff *et al.*, 2013). Identifying the risk biosolids (containing ENMs) may pose is necessary to determine the appropriate management of the biosolids (further treatment as a waste or disposal). This requires consideration and further research; particularly the impact of disposing of biosolids containing ENMs in landfills.

4.2 What Best Available Technology is able to treat nanomaterials?

Best available technology treatment (BAT) technologies for ENMs have yet to be identified for on-site landfill treatment however, potential technologies are emerging. Although not all ENMs are toxic nor would they all require specialised treatment, it is necessary to prevent the release of ENMs deemed hazardous. This would begin by identifying optimal treatment by classifying these ENMs by hazard class, on a case-by-case basis. An approach to the treatment of nanowaste requires understanding of all its properties- not only chemical, but also physical and biological (Bystrzejewska-Piotrowska *et al.*, 2009). Approaches to disposing of ENMs have been proposed and treatment systems for industrial effluents containing ENMs are also currently being studied. This may provide some useful information on technologies that could be effectively applied, adapted or combined with on-site landfill treatment systems.

A recent ANR (Agence Nationale de la Recherche) project NANOSEP (France) has shown that treatment technologies such as coagulation-flocculation, membrane filtration and flotation are very efficient in removing ENMs. This project has shown that the combination of flocculation and membrane separation to be very efficient. Lui *et al.* (2014) also identified and evaluated several treatment technologies that showed variations of success in removing ENMs in wastewaters including: 1) Coagulation and Electrocoagulation (EC) Process; 2) Flotation process; 3) Filtration process; 4) Biological process, and 5) other processes for ENM separation. Lui *et al.* (2014) also states that it may be difficult for one type of method to treat the complex matrix containing ENMs and different techniques are usually required in conjunction with one another to achieve better removal efficiency. Westerhoff *et al.* (2013) discuss the findings and effectiveness of 1) Separation of nanomaterials using membranes; 2) Biological transformation of nanomaterials during biological treatment and 3) the Removal of nanomaterials across continuous-flow wastewater treatment systems. DiSalvo *et al.* (2008) suggest, the removal of nanoparticles in aqueous streams (or effluents), such as leachate, could be accomplished with nanofiltration or reverse osmosis.

The European NANOFLOC project is currently looking at the development of new technology based on nano-suspension destabilisation and agglomeration of charged nanoparticles using electroflocculation. NANOFLOC is also exploring other possible methods including coagulation and sedimentation, flotation, magnetic separation (only for magnetic particles) or zero valent iron applications. None of these individual options are universally applicable or effective on their own at this time.

For the treatment of hazardous solid nanowastes to be effective, they should either be effective in strongly binding the ENMs in a solid matrix, or firmly securing them in a rigid impermeable container (Harford *et al.*, 2007). Other methods such as vitrification for immobilising highly hazardous wastes, have been extensively studied for nuclear and industrial waste forms (Kavouras *et al.*, 2003) and such an approach could be explored for highly hazardous nanowaste (Allan *et al.*, 2009). Bystrzejewska-Piotrowska *et al.* (2009) suggest nanoparticle-containing waste should be stored in a way that prevents interaction of nanoparticles with water (possibly to diminish mobility). In the case of existing nanoparticle contamination in soil or water, novel bio-remediation techniques are also emerging, such as the use of mycoextraction (using fungi for the removal of contaminants) (Jakubiak *et al.*, 2014).

Best available technologies, can be effective if accompanied by best management practices such as hazard classification, labelling and segregation for the appropriate end-of-life disposal management of ENMs deemed hazardous. For the treatment of ENMs in an aqueous phase, such as leachate (which may contain non-hazardous and hazardous ENMs) a suite of technologies show potential to effectively remove ENMs in wastewaters. Approaches currently being tested for industrial (or other) purposes may be applicable to the waste sector, although may require a combination of advanced treatment systems to remove ENMs from leachate.

5. Regulations and Management of Nanomaterials in Waste

In 2013 the OECD adopted a recommendation on the safety testing and assessment of manufactured nanomaterials (OECD, 2013). This recognises "that the approaches for the testing and assessment of traditional chemicals are in general appropriate for assessing the safety of nanomaterials, but may have to be adapted to the specificities of nanomaterials" (OECD, 2013). Hence, regulations such as the European REACH legislation may be adequate in addressing the potential hazards of ENMs in many cases, especially once adapted to nanomaterials. Similarly, Breggin and Pendergrass (2007) have suggested that existing US regulations can cover ENMs. However, the literature also suggests that for some ENMs the current system of expressing toxicity may find limited application, requiring adjustments to existing control regimes and approaches for waste management. To date, the focus of environmental legislation and regulations has been on macroscale chemicals whereby risk is a function of exposure and hazard or toxicity as expressed in the form of mass per volume. Studies have suggested that the toxicity of some ENMs is a function of shape, size, surface reactivity and surface area (Breggin and Pendergrass, 2007, Musee, 2011, RCEP, 2008).

Knowledge gaps may limit the effective application of existing regulatory management controls. Key gaps include a lack of ENM hazard characterization, understanding ENM behavior in landfill environments and knowledge of quantitative data on toxicity. For example, it is possible that manufacturing waste by-products in the nanoscale size range could require more stringent disposal requirements than for the parent products. There are risks that toxic by-products generated during nanotechnology manufacturing may be handled inadequately due to insufficient quantitative toxicity data, lack of transmission of information or available appropriate treatment techniques (Musee, 2011). It is important that certain ENMs are recognized as hazardous materials and the labelling or tagging of such nanoproducts be introduced to facilitate their separation and appropriate recovery in order to prevent them from entering municipal landfills (Bystrzejewska-Piotrowska et al., 2009). However, there is need for an official definition and appropriate classification regime of nanomaterials if product labelling is to be effective.

For consumer nanoproducts that may exhibit hazards upon disposal, labelling (or product information inserts) and proper disposal options could assist the appropriate management of these end-of-life products.

Common consumer nanoproducts requiring special disposal could then be managed similarly to other household hazardous wastes. A nanoproduct, such as sunscreen, may not present a risk to the consumer, but may present varying hazards upon disposal (Musee, 2011) due to potential degradation of the product or potential interactions with other materials in the waste stream or the landfill environment. This is an area that requires further research and consideration.

Without knowing how companies plan to use and store recycled and non-recyclable ENMs, development of appropriate controls, regulations or other waste management protocols may be challenging. In order to adequately assess the potential risk posed by the use of ENMs, companies could be required to provide basic information on the quantities and characteristics of ENMs produced, used and discarded as well as estimated life-expectancy of the products containing nanoparticles (Powell *et al.*, 2008). Although, generators of nanowastes may have insufficient information to provide to owners or operators of treatment, storage and disposal facilities to enable them to manage such wastes appropriately (Breggin and Pendergrass, 2007).

To reduce the potential risk of releases of ENMs to the environment from landfills, a combination of improvement in segregation and recovery/recycling efforts, adequate landfill design and operation, effective leachate treatment technologies and access to specialised facilities when required may be necessary. Identification, classification and labelling will support the implementation of improved and appropriate waste management approaches and the application of appropriate technologies to manage potential risks posed by certain ENMs. Adapting and clarifying existing legislative frameworks and current waste management approaches may be needed to restrict the flow of hazardous ENMs entering municipal waste landfills.

6. Conclusions and Knowledge Gaps

It is recognized that scientific knowledge of ENMs, their fate and behaviour in landfills is progressing and needs to be understood further to guide effective waste management approaches for the varied waste streams containing nanomaterials. However, recent research in this area raises complex issues to consider. There is evidence that some ENMs are released in landfill environments from products containing nanomaterials and from other nanowaste sources. Therefore it can reasonably be asserted that landfills currently contain ENMs and can be a pathway into the environment if ENMs are able to cross landfill liners (particularly from uncontrolled landfills) and pass through leachate treatment. Secondary pathways to be investigated include migration via landfill gases.

Landfills will increasingly receive greater amounts of ENMs over time, in conjunction with the growth of the nanotechnology industry and the broad use of these materials. The release of ENMs from products is likely under typical landfill conditions, particularly from liquid wastes containing ENMs or other waste products containing freely suspended nanoparticles. Landfills are unique and complex environments and ENM behavior and their potential release is influenced by pH, anaerobic conditions, leachate composition and many other factors. For example, organic matter in leachate may enhance the mobility of ENMs, by preventing aggregation and precipitation. Physical stressors such as abrasion and compaction, may also aid in the release of ENMs in landfills.

ENMs are unlike any other known contaminant due to their unique physicochemical properties and characteristics such as size, shape, surface area and chemical reactivity. Nanowaste streams of different forms will vary from benign to extremely hazardous. Due to the binding and adsorptive properties of some ENMs, they may also enhance the toxicity and mobility of other pollutants. These unique properties could be highly problematic when combined with landfill leachate. In a worst case scenario, leachate, which already contains a variety of pollutants, may become more toxic, more bioavailable and mobilise other pollutants beyond landfills transporting them to distant ecosystems. However, ENMs may undergo transformations in landfills and the environment where they may no longer retain their original characteristics. These transformations will in turn affect the transport, fate and toxicity of ENMs in the environment.

The anti-microbial effects of ENMs in landfills have not been well researched; however ENMs could compromise the effectiveness of leachate treatment at high concentrations, where bacterial populations are used to break down pollutants. It is inconclusive as to whether ENMs can penetrate landfill liners, although this topic is currently being researched. The major concern remains with ENMs in collected leachate, when it leaves the landfill to be treated by wastewater treatment processes or is released directly to the environment with or without on-site treatment.

Although no specific information was found on best available technologies to remove ENMs in landfill leachate treatments systems, there are technologies used or being studied in industrial applications demonstrating various levels of success in removing certain ENMs in wastewaters that could potentially be adapted to leachate treatment technologies, where necessary.

The unique properties of ENMs may challenge the ability of existing management systems and regulations to adequately identify and address ENMs; specifically the variable risks they may pose which differ from their bulk forms. ENMs may be handled under existing regulations; however clarification and adaptions may be required to adequately provide clear guidance to industry and regulators to avoid significant long-term liabilities for the public, businesses, insurers and investors.

6.1 Summary of Knowledge Gaps and Areas of Further Research

While recent scientific knowledge has shed some light on the issue of ENMs in landfills, further research in the following areas is needed to improve our understanding of the problem and develop practical solutions:

a) *Development of analytical chemistry test methods to identify ENMs in environmental media, and distinguish them from normal scale chemicals they may contain.*

b) *Characterisation and quantification of the issue and understanding of the chemical and environmental processes in landfills:*

   i. Identify the types and quantities of ENMs and their individual level of hazard and potential exposure to evaluate the risk of products containing ENMs upon disposal and in nanowastes;

   ii. Identify and apply modern analytical methods available in other matrices (e.g., water, wastewater, gas) and investigate their applicability in studying ENM concentrations in leachate and landfill gas, as well as ENM fate and transport in landfills.

   iii. Understand the synergistic impacts of ENMs and typical contaminants in landfill leachate; specifically looking at key contaminants in leachate and studying the impact of ENMs on toxicity, bioavailability and transport of these contaminants;

   iv. Understand the process of ENM degradation and transformation in a landfill environment (in leachate) and the impact of degradation products; impact or release of ENMs from nanoproducts and nanowastes.

   v. Determine if there are ENM releases to air at the landfill surface or through landfill gas.

c) *Understanding the effectiveness and constraints of current landfill methods and technologies*

i. Understand the impacts of microbial properties of ENMs on on-site landfill treatment systems and other potential impacts that ENMs may have on leachate treatment systems;

ii. Identify what key ENMs cross landfill liners and pass through leachate treatment systems and determine to what degree they are "treated" (similar to studies of ENMs in Waste Water Treatment Plants) by conventional methods or other technologies;

iii. Determine the applicability of current BAT technologies, used in other wastewater treatment applications, to treat or remove ENMs in landfill leachate;

iv. Develop effective methods of diverting hazardous ENMs from municipal landfills and treating waste containing hazardous ENMs (i.e. adequately handling residual waste containing ENMs such as biosolids or ash and not simply transferring them to landfills).

d) Understanding the applicability of a future ENM classification system for waste management.

i. Examine the potential usefulness of classifying, labelling and segregating hazardous nanowastes and wastes containing hazardous ENMs, to effectively manage disposal through specialised hazardous waste landfills (or other treatment processes) as appropriate, to ensure adequate and safe disposal.

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