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NANOMATERIALS ENVIRONMENTAL RISKS AND RECYCLING – ACTUAL ISSUES

EKOLOŠKI RIZICI I RECIKLAŽA NANOMATERIJALA – AKTUELNA PITANJA

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IZVOD – Nanotehnologije se smatraju pokretačkom snagom nove industrijske revolucije. Nanonauka je tokom poslednje decenije značajno evoluirala od nauke koja se isključivo razvijala u laboratorijskim uslovima, do njene aplikacije u primenjenim tehnologijama. Trenutno, nanomaterijali se koriste u širokom spektru komercijalnih proizvoda kao što su elektronske komponente, sportska oprema, kreme za sunčanje i u biomedicinske svrhe. Veličina nanočestica omogućava im snažnu interakciju sa biološkim strukturama, tako da nanočestice predstavljaju potencijalni rizik po životnu sredinu i zdravlje ljudi. Nanometar kao veličina takođe predstavlja problem za separaciju, reciklažu i ponovno korišćenje nanočestica.

Dakle, proizvodnja nanomaterijala u industrijskim razmerama i njihova primena mogli bi imati značajan uticaj na zdravlje ljudi i životnu sredinu ili stvorili probleme pri reciklaži. Sveobuhvatni termin "nanotehnologija" nije dovoljno precizan kada se radi o upravljanju rizicima. Procena mogućih rizika zavisi od razmatranja životnog ciklusa materijala koji se proizvodi, a koji uključuje razumevanje procesa i materijala koji se koriste u proizvodnji, verovatne interakcije između proizvoda i pojedinaca ili životne sredine tokom proizvodnje nanomaterijala i njegovog životnog ciklusa, kao i metoda koje se koriste za njihovo konačno odlaganje. Sa stanovišta kontrole rizika, neophodno je identifikovati kritične faze, koje je neophodno detaljno istražiti. Pregled aktuelnih trendova ekoloških rizika i reciklaži nanomaterijala prezentovan je u ovom radu.

Ključne reči: nanomaterijali, okolina, separacija, reciklaža, rizik

ABSTRACT - *Nanotechnologies are being spoken of as the driving force behind a new industrial revolution. Nanoscience has matured significantly during the last decade as it has transitioned from bench top science to applied technology. Presently, nanomaterials are used in a wide variety of commercial products such as electronic components, sports equipment, sun creams and biomedical applications. The size of nanoparticles allows them to interact strongly with biological structures, so they present potential human and environmental health risk. Nanometer size presents also a problem for separation, recovery, and reuse of the particulate matter.*

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Therefore, industrial-scale manufacturing and use of nanomaterials could have strong impact on human health and the environment or the problematic of nanomaterials recycling. The catch-all term "nanotechnology" is not sufficiently precise for risk governance and risk management purposes. The estimation of possible risks depends on a consideration of the life cycle of the material being produced, which involves understanding the processes and materials used in manufacture, the likely interactions between the product and individuals or the environment during its manufacture and useful life, and the methods used in its eventual disposal. From a risk-control point of view it will be necessary to systematically identify those critical issues, which should be looked at in more detail. Brief review of actual trends in nanomaterials environmental risks and recycling is given in this paper.

Key words: *nanomaterials, environment, separation, recycling, risk*

INTRODUCTION

The Greek word "nano" (meaning dwarf) refers to a reduction of size, or time, 10^{-9} fold, which is one thousand times smaller than a micron. One nanometer (nm) is one billionth of a meter, and it is also equivalent to ten Angstroms. As such, a nanometer is 10^{-9} meter, and it is 10 000 times smaller than the diameter of a human hair. A human hair diameter is about 50 micron (i.e., 50×10^{-6} meter) in size, meaning that a 50 nanometer object is about 1/1000th of the thickness of a hair. One cubic nanometer (nm^3) is roughly 20 times the volume of an individual atom. A nanoelement compares to a basketball like a basketball compares to the size of the earth [1].

Modern industrial nanotechnology had its origins during 1930s, in processes used to create silver coatings for photographic film; and chemists have been making polymers – large molecules made up of nanoscale sub-units, for many decades. However, the earliest known use of nanoparticles was in the ninth century during the Abbasid dynasty. Arab potters used nanoparticles in their glazes so that objects would change colour depending on the viewing angle (the so-called polychrome lustre) [2].

Nanotechnology represents the design and manipulation of materials at the nanometer scale such

that novel or enhanced properties emerge. It is a developing area of knowledge that promises amazing array of opportunities in the areas as manufacturing, energy, health care, waste treatment, etc. [3-5]. Nanotechnologies are booming business. It is now evident that nanotechnologies are becoming a substantial part of society and indeed already a multitude of nanotechnology products, or at least products with a nano-based claim, are commercially available. [6] Nanotechnologies include the development and production of nanosized engineered particles, fibres, coatings, etc., collectively referred to as nanomaterials (in further text: NMs). Similar to other chemical substances, society, governments and industry alike want to assure that these new products can be used safely. In case risk assessments indicate the unacceptable probability of adverse effects, risk management measures should be taken to protect the environment and human health [7].

Considering the enormous commercial and societal benefits that may potentially come from this technology, it is likely that NMs, and the products and other applications containing them, will be widely produced and used [8-12]. According to Cientifica Ltd. [13] the total government funding for nanotechnology research worldwide will be \$65 billion by the end of 2011, rising to \$100 billion by 2014 (Fig.1).

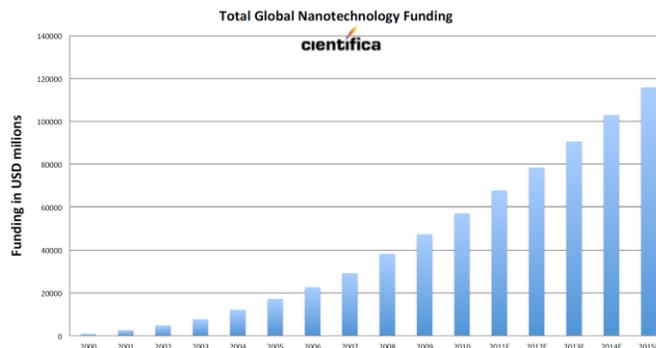


Figure 1. Cumulative global funding of nanotechnologies [13]

Risks of conventional chemicals are regulated in existing national and international regulatory frameworks. NMs are often praised for their “new and unique” properties. However, because of these new properties, NMs are also likely to differ from their conventional chemical equivalents with respect to their behaviour in the environment and their kinetic and toxic properties. This raises concerns in connection to their widespread use, as this leads to an increase of exposure to these NMs for humans as well as the environment. More, the understanding of the effects of long-term exposure to nanoparticles is very limited. This is a great concern, and many research groups around the world are working to better understand how ubiquitous low concentrations of nanoparticles will affect humans and ecosystems - particularly aquatic ecosystems, therefore it is especially important to understand and minimize the potential risks [14-20].

NANOMATERIALS DEFINITION AND LEGISLATION

In case regulatory risk assessment procedures are adapted for NMs, it is required that nanomaterials can be clearly and unambiguously identified. Some countries outside of Europe already have published definitions, not necessarily in a regulatory framework but as working definition [21] or presented as a general description in guidance [22]. The Scientific Committee on Emerging and Newly Identified Health Risks (SCENIHR) of the European Commission has published the scientific basis for the definition of the term nanomaterial [23]. In October 2011 the definition of a nanomaterial by the European Commission was published [24].

The European Commission based its recommended definition mainly on a reference report by the European Commission Joint Research Centre (JRC) [25] a scientific opinion by the SCENIHR. Inevitably, the final wording and especially the thresholds comprise political compromises as well. In its Recommendation (EU, 2011a) the European Commission states that: ‘Nanomaterial’ means a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm–100 nm. In specific cases and where warranted by concerns for the environment, health, safety or competitiveness the

number size distribution threshold of 50% may be replaced by a threshold between 1% and 50%. Alternatively, it is stated that a material should be considered as falling under the definition where the specific surface area by volume of the material is greater than 60 m²/cm³. The Recommendation also includes definitions for ‘particle’, ‘agglomerate’ and ‘aggregate’. The Commission foresees a review of the definition by December 2014, particularly focusing on the appropriateness of the 50% limit.

The definition of nanomaterial is intended to identify nanosized materials. It is explicitly stated in the definition that a nanomaterial is not inherently classified as a hazardous material (EU, 2011a). Yet, the identification of nanomaterials is useful for regulatory frameworks in order to cope with potential environmental and health related risks, for example by requesting further information on the nanomaterial. Although obvious, it is important to note that materials that are not classified as nanomaterial by the present definition, may still exhibit nano-related risks.

According to EU recommendation for a definition of a nanomaterial in 2009, the European Parliament urged the European Commission (EC) to review all relevant legislation to ensure safety for all applications of NMs in products with potential health, environmental or safety impacts over their life-cycle and to adopt a science-based common definition of the term ‘nanomaterial’ to be used in all European Union (EU) legislation [26].

NANOMATERIALS RECYCLING

Given the high value of specially manufactured NMs (e.g. nano-scale metals), there is a strong interest among the manufacturers and users in recovering certain NMs for reuse or recharge of products. However, due to a lack of information on NMs, they may be declared or treated as hazardous waste, which could lead to a loss of valuable materials [27]. NMs could be presented in the waste stream recycling process [23], including:

- Pure manufactured NMs (e.g. carbon nanotubes)
- Nano byproducts
- Liquid suspensions containing NMs
- Items contaminated with NMs (e.g. wipes)
- Solid matrices with integrated NMs.

The potential to separate nanoparticles from the waste stream in order to recycle them was also investigated [28]. The majority of the tested processes are conventional separation techniques, like

centrifugation or solvent evaporation, with high energy demand. Alternative methods such as the application of magnetic fields, pH and thermo responsive materials, molecular antisolvents, or nanostructured colloidal solvents, provide effective and efficient methodologies for recycling nanoparticles without significant costs, time consumption, or energy demand [24]. However, in order to set up efficient recycling for NMs, further studies on their intrinsic recyclability properties - such as thermal, mechanical, and chemical properties - are needed. Information on how these characteristics are changed once NMs are mixed with other products is also needed, as well as guidelines regarding the take back, disassembling and reuse in such cases. A reflection on how a proper product design could improve the disassembling of these materials would also help identify appropriate reuse and recycling options.

A lot of technological solutions for NMs recycling have been applied nowadays – i.e., the use of magnetically recoverable supports for the immobilization of gold nanoparticle catalysts, which guarantees facile, clean, fast and efficient separation of the catalyst at the end of the reaction cycle [29]. The OECD Chemicals Committee has established the Working Party on Manufactured Nanomaterials to address the issue of recycling and to study the practices of OECD member countries in regards to nanomaterial safety.

NANOWASTE ECOTOXICOLOGY AND TREATMENT

Communities are reluctant to embrace new technologies where there is inadequate disclosure about the potential impacts on health or safety. Molecular genetics and nanotechnology are two examples of such technologies which have generated extensive debate regarding potential public and environmental health impacts. For nanotechnology, given the potential for toxicity and lack of characterisation data, the management of nanowaste will need to be addressed before community acceptance of the potential benefits of nanotechnology can occur.

Many authors [30-32] have described the human and ecosystem impacts of anthropogenic waste and pollution. There are few published studies investigating the impact on the aquatic ecosystem, limited primarily to C60, nanotubes and titanium dioxide, with crustacean *Daphnia magna* the main test species [33]. There are many new questions about NMs that needs the answers: how can exposure to NMs be measured, what are the

potential health effects of NMs, what are the potential environmental effects of NMs, how well can we assess the risks from NMs, what do we still need to know. The answers to these questions are a faithful summary of the scientific opinion produced in 2006 by the Scientific Committee on Emerging and Newly Identified Health Risks SCENIHR [34] "modified opinion (after public consultation) on the appropriateness of existing methodologies to assess the potential risks associated with engineered and adventitious products of nanotechnologies" [34]. The SCENIHR also concluded that NMs may have different (eco-) toxicological properties than the substances in bulk form and therefore their risks need to be assessed on a case by case basis. Main risks and benefits of the nanomaterials [14] are shown in Table 1.

NMs waste was also considered recently. In the frame of separation and recovery concepts of safe nanomaterials management, there are three broad origins of waste from nanomaterials, with categorisation similar to conventional waste [36]:

- Waste generated during the production of nanomaterials or nanotechnology derived products,
- Waste generated during the usage of nanomaterials or nanotechnology derived products (e.g. abrasion, degradation etc), and
- Waste generated during the end-of-life activities (e.g. recycling, incineration, landfill etc.).

So far, The European Commission has launched thematic studies exploring nanomaterials and the EU environmental legislation in 2011, a report published in accordance with the Coherence of Waste Legislation in the EU [37]. Consumer participation during the early stages of nanoprodukt design may help to address information needs concerning product lifecycle requirements. Ratings of nanoprodukt could be introduced which exhibit varying degrees of end-of-product life practices and information provided for local government recycling depots. Nanomanufacturers could engage consumers throughout the product lifecycle in order to learn about their experiences, including the potential for product misuse whether deliberate or unintentional.

Current guidance suggests nanowaste should be classified as hazardous waste, and as a minimum, double bagged, enclosed in a rigid impermeable container and preferably bound within a solid matrix [38]. In the first instance however, nano-object capture and containment must be considered as an over-arching priority for effective nanowaste management. Where atmospheric dispersion of nano-objects occurs, nano-object

translocation to distant ecosystems may result, as well as deposition within and surrounding research and nanomanufacturing facilities. In order to avoid potential ecosystem impacts, parameters such as nano-object size, configuration and solubility will require assessment for each phase of the nanoproduct lifecycle before routine disposal methods can be considered [39]. Unless

securely enclosed in an impermeable container or bound within a solid matrix, contaminant runoff and atmospheric dispersion remain potential environmental exposure pathways. Groundwater contamination is also possible due to contaminants leaching from inadequately bound or secured containment methods [40].

Table 1. NMs Risks and Benefits [35]

Application	Risk	Benefit
Nanocrystals harvest light in photovoltaic devices.	Light pollution in rural areas, opportunity cost to fossil fuel economies.	Green, renewable energy, new self-lighting displays for electronic devices.
Antimicrobial wound dressings contain nanocrystalline silver.	Release of antimicrobials into the environment, hazard to natural microbial systems.	Improved healing in wounds and reduced risk of infection.
Sunscreens containing titanium dioxide NMs are extremely effective at absorbing ultraviolet light.	Titanium hazard to intertidal organisms and sandy shore ecosystems.	Consumer preference for transparent but effective sun creams. Potential decrease in skin cancer due to increased sunscreen use.
Metal nanomaterial supplements to increase the burn efficiency of fuels.	Respiratory exposure to NMs in fuel exhausts. Long range transport of particles in the atmosphere.	Less soot from diesel vehicles and urban air pollution. Burn efficient aviation fuels. Economic saving for transport infrastructure on fuel costs. Reduced greenhouse gases.
Medical applications of hydroxyapatite and nano-silica applications in bone reconstruction.	Durability-particles eroded from the surface may cause pathology in other internal organs in the long term.	Structural repairs to teeth and bone using a natural material already in the body (no adverse immune response).
NMs in food packaging	Unintended transfer of nanomaterial from the packaging to the food. Uncertain lifetime oral exposure risk.	Stronger lighter packaging to protect soft foods, antibacterial packing to improve shelf life. Increased food safety.
Use of carbon nanotubes to improve strength and flexibility of sports equipment.	Life cycle analysis, what happens to the materials in landfill at the end of their use?	Better product that lasts longer for the consumer. Reduced sports-related injuries.
Use of NMs as catalyst in industrial processes such as coal liquefaction and producing gas.	Inadvertent incorporation of toxic catalysts in consumer products, waste disposal of catalytic converters to landfill.	Improved efficiency and economy of industrial processes. Less industrial waste/ton of production.
Use of NMs in water filtration and purification.	Unintended waterborne exposure to wildlife of engineered NMs.	New sources of portable, safe drinking water in poor regions of Africa/Asia. More efficient purification systems for the water. Reduced exposure to waterborne pathogenic organisms and toxins.

Vitrification methods for immobilising high-level wastes have been extensively studied for nuclear, urban and industrial waste forms, particularly substances with

high potential for leaching [41]. It is feasible that such an approach could be explored for nanowaste using the SYNROC ceramic waste form, as this is

thermodynamically stable and very resistant to chemical weathering [42]. Efforts are increasingly being taken to reclaim precious materials from nanowaste using techniques such as phytomining. Parameters used to measure revenue generation include: volume of generated nanowaste; concentrations of precious materials; monetary value of materials recovered; and amount of effort required to recover materials.

NANOMATERIALS VISION FOR 2020

Nanotechnology R&D is expected to accelerate the succession of science and innovation breakthroughs toward nanosystems by design, and to lead to many additional and qualitatively new applications by 2020, guided by societal needs. Nanotechnology will be translated from the research labs to consumer use, motivated by responsiveness to societal challenges such as sustainability; energy generation, conservation, storage, and conversion; and improved healthcare that is lower-cost and more accessible. During the first decade, the main drive force was scientific discovery accruing from curiosity-driven research. During the next decade, application-driven research will produce new scientific discoveries and economic optimization leading to new technologies and industries. Such translation will benefit society but will require new approaches in accountable, anticipatory, and participatory governance, and real-time technology assessment. Key points of the consensus vision for nanotechnology R&D over the next decade are noted below.

Investment policy and expected outcomes:

- Major continued investment in basic research in nanotechnology is needed, but additional emphasis in going forward should also be placed on innovation and commercialization, on job creation, and on societal “returns on investment,” with measures to insure safety and public participation. With each new generation of nanotechnology products, there is improved focus on economic and societal outcomes.
- The frontiers of nanotechnology research will be transformed in areas such as: multiscale self-assembly of materials from the molecular or nanostructure level upwards, efficient energy harvesting, conversion, and storage with low-cost, benign materials artificial organs, including the use of fluid networks and nanoscale architectures for tissue regeneration, etc.

- Nanotechnology is expected to be in widespread use by 2020. There is potential to incorporate nanotechnology-enabled products and services into almost all industrial sectors and medical fields. Resulting benefits will include increased productivity, more sustainable development, and new jobs.
- Nanotechnology governance in research, education, manufacturing, and medicine programs will be institutionalized for optimum societal benefits.

CONCLUSIONS

In seeking to prevent the harmful effects of nanomaterials used in packaging or recycling, the prevention mechanism and reduced pollution rely on evidence of harm and can be connected with reduction of weight, recyclability, safety, better performance and engine efficiency (fuel saving), as well as the question about aesthetics and longer service life.

Increasing numbers of studies indicate the potential for nano-objects to adversely affect ecosystems. At the same time, nanotechnology is exhibiting useful application in the treatment of industrial wastes. Serious improvement in corporate transparency surrounding the treatment of industrial waste is required if acceptance of nanomaterials and consumer nanoproducts with unknown toxicity is to occur. The applicability of existing waste treatment methods to nanowaste is conjectural given the uncertainty of nano-object properties and behaviour.

Regulatory guidance on nanowaste management is minimal and the application of industrial waste treatment methods are problematic, due to incomplete physicochemical definition of nanoobjects. In the absence of definitive whole-of-lifecycle data for nano-objects, the twin dilemmas facing policy-makers are whether to tolerate the risk of potential ecosystem impacts and whether to accept that risk once definitive toxicological data becomes available.

Having in mind significant financials funds in nanomaterials research and development, the period to come will give more detailed information and correct answers to numerous questions still awaiting in this field. Also, it can be expected that more and different technologies for recovery, reuse and recycling of nanomaterials will be given and presented to scientific public in the near future.

Nanotechnology is still in an early phase of development, and fundamental understanding and tools are still in the pipeline of new ideas and innovations. It

will be vital over the next decade to focus on four distinct aspects of progress in nanotechnology: (1) how nanoscale science and engineering can improve understanding of nature, protect life, generate breakthrough discoveries and innovation, predict matter behavior, and build materials and systems by nanoscale design—knowledge progress; (2) how nanotechnology can generate medical and economic value—material progress; (3) how nanotechnology can promote safety in society, sustainable development, and international collaboration—global progress; (4) how responsible governance of nanotechnology can enhance quality of life and social equity—moral progress. There is speculation that a possible future convergence of nanotechnologies with biotechnology, information and cognitive sciences could be used for radical human enhancement. If these possibilities were ever realised they would raise profound ethical questions.

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