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Short Description (e.g. abstract, summary, table of contents, free text etc.)	D6.72 is analysing aspects related to accidental risks of ENMs starting with the definition of nanomaterial and its possible revision. An overview and evaluation relevant existing legislation is given highlighting difficulties in their implementation. The different types of nanomaterials currently on the market and their critical properties have been examined as well as their uses, the produced amount, the registration under REACH and the declared type of hazard. Scenarios of major accidents involving nanomaterials include production processes, transport and manufacturing and storage. Possible risks associated with an accidental explosion of nano-powders have been assessed and suggestions are given to reduce fire and explosive risks. Also the environmental fate of manufactured nanomaterials has to be taken into account when assessing human exposure and safety hazards due to accidental spills. Based on the available and analysed information, suggestions are given on emergency plans involving nano-powders.
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1. Abbreviations and acronyms

CMP -	Chemical-mechanical planarization
CLP -	Classification, Labelling and Packaging
CNC -	Condensation Nuclei Counter
CPC -	Condensation Particle Counter
ECHA -	European Chemicals Agency
ELPI -	Electrical Low Pressure Impactor
ENMs -	Engineered nanomaterials
GHS -	Globally Harmonized System of Classification and Labelling of Chemicals
KETs -	Key Enabling Technologies
MAPP -	Major-accident prevention policy
NSAM -	Nanoparticle Surface Aerosol Monitor
OEL -	Occupational Exposure Limits
PPE -	Personal Protective Equipment
QDs -	Quantum dots
REACH -	Registration, Evaluation, Authorisation and Restriction of Chemical substances
SCINIHR -	Scientific Committee on Emerging and Newly Identified Health Risks
SMPS -	Scanning Mobility Particle Sizer
SRI -	Strategy Research Institute
TEOM -	Tapered Element Oscillating Microbalance
VSSA -	volume-specific surface area

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2. Summary

In the European Union, the prevention of major accidents involving chemical substances is regulated by the Seveso III Directive (2012/18/EU). Art. 1 of this Directive lays down rules for the prevention of major accidents which involve dangerous substances, and the limitation of their consequences for human health and the environment, with a view to ensuring a high level of protection throughout the Union in a consistent and effective manner. With this report, we examine the monitoring specifications developed for accidental risks at industrial sites and/or during transport, and the evaluation of existing emergency plans for the release of nanomaterials. We also examine the requirements for the protection of the public and the environment from possible major accidents by taking into consideration regulations that have not been adopted for nanomaterials, in particular regulations concerning major industrial accidents.

3. Introduction

It is useful to remember the definition of nanomaterial recently adopted by the European Commission (2011) [1]. The core elements of the definition are laid down in articles 2 to 4:

- *"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 %.
- *By derogation from point 2, fullerenes, graphene flakes and single wall carbon nanotubes with one or more external dimensions below 1 nm should be considered as nanomaterials.*
- *For the purposes of point 2, "particle", "agglomerate" and "aggregate" are defined as follows:*

  a. "Particle" means a minute piece of matter with defined physical boundaries;

  b. "Agglomerate" means a collection of weakly bound particles or aggregates where the resulting external surface area is similar to the sum of the surface areas of the individual components;

  c. "Aggregate" means a particle comprising of strongly bound or fused particle".

Until 2013, JRC completed a series of three reports (Towards a review of the EC Recommendation for a definition of the term "nanomaterial") on the possible modification of the definition adopted in 2011. In particular, the third report (Part 3: Scientific-technical evaluation of options to clarify the definition and to facilitate its implementation – June 2015) lists available options [2]. The option not to change a specific element is always considered and the resulting consequences are discussed. Other options that imply a change of the definition are presented as well, together with possible technical or scientific consequences. In particular, the following items are deeply examined in Part 3 of the JRC report [2].

1. Scope in terms of origin of the materials (natural or manufactured)
2. Particulate matter and nanostructured materials (particulate materials or embedded nanomaterials)
3. Size as the only defining property and the selected size range (for instance to include properties other than the size as identifier of nanomaterials or to extend or reduce the size range)
4. A fraction of the number of particles as defining threshold (number-based size distributions are often not easy to measure, especially when there are particles with size in the 1 nm to 100 nm range. Indeed, particle number estimates derived from these mass- or volume-based mean diameters, often refer to particle aggregates or agglomerates)
5. What are constituent particles and how to measure their size? (number of the comments and criticisms to the EC definition refer to the analytical challenge of identifying the constituent particles and measuring their size inside aggregates) (for instance it should be possible to define "constituent particles are particles separable from larger particles")
6. Flexibility of the threshold value in the particle number based size distribution (Situations may arise where a specific material is considered a nanomaterial under one regulatory framework whereas the same material is not considered a nanomaterial in another regulatory framework covering a different sector)
7. The term "particle" (a discussion is ongoing about including or excluding, for example, single molecules, micelles and non-solid materials)
8. The terms "one or more external dimensions" (For instance, flat, flake- or platelet-like particles with only one external dimension in the nanoscale, but two larger, lateral dimensions (well) outside the nanoscale, could not be considered as nanomaterials.)
9. The word "containing" (The definition uses the term "containing particles", which seems to suggest that a nanomaterial can also contain other and even large fractions of matter that is not "particulate", e.g. a continuous solid matrix.)
10. The term "unbound" (The current definition refers to the "unbound state" of particles which is

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perceived by some as a term that is not precise enough)

11. The volume-specific surface area (VSSA) (there is some confusion about when VSSA can be used as a proxy method)
12. How to prove that a material is not a nanomaterial and how to avoid unintended inclusion of materials in the definition? (For a large number of materials it is possible to demonstrate that they meet the nanomaterial criteria of the current Recommendation. However, it can be extremely difficult to prove that a material is not a nanomaterial, but it is important to be able to confirm that a material does not fulfil the EC definition of nanomaterial. So, this observation should be duly considered.)
13. Materials explicitly included in the definition

Moreover, the report provides a Guidance to list additional information for helping to understand and implement the definition, thereby keeping the actual definition lean and placing detailed explanations and interpretations elsewhere.

Nanotechnology has been identified as one of the four Key Enabling Technologies (KETs) offering great potential for improving the competitiveness of Europe's industries. The nanotechnology is developing extremely rapidly both in the research field and in the application areas, creating new generation of smart and innovative products. Engineered nanomaterials (ENMs) are promoting research and applications in a large variety of fields: medicine, chemistry, electricity and electronics, electron microscopy, optics, mechanics, catalysis, sensor technology, cosmetics, etc. This is due to the unique physical properties exhibited by nanostructures that come from size reduction up to these dimensions. Thereby, the science of nanomaterials results very attractive due to the great potential in developing new materials and exploring innovative solutions in many fields.

On the other hand, while the properties of nanomaterials continue to be successfully explored, there is insufficient scientific research for an assessment of the risks from nanomaterials. Indeed, due to the rapid increase in production of nanomaterials to be employed in a wide range of products, it is thinkable that release of nanomaterials might diffuse into the environment according to the different sources. These ones include point sources, such as industrial installations, and diffuse source emissions, such as agricultural crops or, in general, products containing nanoparticles along their life cycle. It can be expected that the progressive use of ENMs in consumer products might increase the exposure of populations to ENMs through air, water and soil. Thereby, a tentative assessment of the risk to human health or in the ecosystem from nanomaterials must include an understanding of hazard and the quantification of exposure. This means that a new field of nanosafety has to be explored and new safety assessment methodologies need to be developed. The importance to investigate possible risks from nanotechnology is due to the fact that ENMs can exhibit different properties and reactivity with respect to larger size particles. Thereby, in principle, must be considered separately both in regard to concentration and to potential toxicity. For example, volume-based thresholds for certain chemicals, above which problematic effects may occur, cannot be simply transferred from these materials to the same at the nanoscale. The thresholds of ENMs which have been identified as potentially dangerous should therefore be allocated under the Seveso III Directive.

Health and safety aspects must include possible intrinsic hazards of the ENMs, exposure to workers, consumers and at the waste stage, as well as risk management measures.

Apart from the problem of the potential hazardous effects of ENMs on human health and on the environment and the need to implement the existing regulations in this field, we have to take into consideration the possibility of a major accident event. For this reason, and based on the work done within Task 6.4 on industrial risks and in WP4 on improving current risk and life cycle assessment schemes, the applicability of relevant current regulations to nanomaterials has been reassessed. Indeed, it is unknown how great would the risk of a major accident be, in which nanomaterials would be released (see also D6.70 and D6.71). Moreover, although these materials are already used extensively in industrial production processes, no satisfactory answers have yet been supplied to these questions.

4. Review of emergency legislation

The 2012 Communication on the Second Regulatory Review on Nanomaterials describes the

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Commission's plans to improve EU law and its application to ensure their safe use [3]. It is accompanied by a Staff Working Paper on nanomaterial types and uses, including safety aspects, which gives a detailed overview of available information on nanomaterials on the market, including their benefits and risks [4].

The main conclusions of the review is that nanomaterials are similar to normal chemicals/substances. Indeed, in the light of knowledge and opinions of the EU Scientific and Advisory Committees and independent risk assessors, nanomaterials are similar to normal chemicals/substances in that some may be toxic and some may not. Important challenges relate primarily to establishing validated methods and instrumentation for detection, characterization, and analysis, completing information on nanomaterial hazards and developing methods to assess exposure to nanomaterials (which was a major task of NanoValid). The following conclusions were drawn so far:

- Possible risks are related to specific nanomaterials and specific uses. Therefore, nanomaterials require a risk assessment, which should be performed on a case-by-case basis, using pertinent information. Current risk assessment methods are applicable, even if work on particular aspects of risk assessment is still required.
- Overall the Commission remains convinced that the Registration, Evaluation, Authorisation and Restriction of Chemical substances (REACH) Regulation is the best possible framework for the risk management of nanomaterials when they occur as substances or mixtures, but within this framework more specific requirements for nanomaterials have proven necessary.

4.1 REACH

REACH is a regulation of the European Union, adopted to improve the protection of human health and the environment from the risks that can be posed by chemicals, while enhancing the competitiveness of the EU chemicals industry. It also promotes alternative methods for the hazard assessment of substances in order to reduce the number of tests on animals.

In principle, REACH applies to all chemical substances; not only those used in industrial processes but also in our day-to-day lives, for example in cleaning products, paints as well as in articles such as clothes, furniture and electrical appliances. Therefore, the regulation has an impact on most companies across the EU.

Companies need to register their substances and to do this they need to work together with other companies who are registering the same substance.

The European Chemicals Agency (ECHA) receives and evaluates individual registrations for their compliance, and the EU Member States evaluate selected substances to clarify initial concerns for human health or for the environment. Authorities and ECHA's scientific committees assess whether the risks of substances can be managed.

Authorities can ban hazardous substances if their risks are unmanageable. They can also decide to restrict a use or make it subject to a prior authorisation.

4.2 Classification, Labelling and Packaging

Regulation (EC) No 1272/2008 on Classification, Labelling and Packaging (CLP) of dangerous substances and mixtures entered into force on 20 January 2009.

- CLP Article 9: Evaluation of hazard information for substances and mixtures
- "When evaluating the available information for the purposes of classification, the manufacturers, importers and downstream users shall consider the forms or physical states in which the substance or mixture is placed on the market and in which it can reasonably be expected to be used."
- Different forms/particle sizes may have different classifications
- Substances incl. nanomaterials classified as hazardous to be notified
- Classification & Labelling inventory includes nanoforms

In addition, the Scientific Committee on Emerging and Newly Identified Health Risks (SCENIHR)

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concluded that “while risk assessment methodologies for the evaluation of potential risks of substances and conventional materials to man and the environment are widely used and are generally applicable to nanomaterials, specific aspects related to nanomaterials still require further development. This will remain so until there is sufficient scientific information available to characterise the harmful effects of nanomaterials on humans and the environment.”

The different types of nanomaterials to which apply the review are those related to the definition of nanomaterials adopted in 2011. In particular, the Appendix 2 of the Staff Working Paper accompanying the second regulatory review gives a detailed overview of nanomaterials currently on the market, as well as their uses [4]. In the remaining sections of this chapter, an overview of these nanomaterials is given with a focus on those ENM properties that should be taken into consideration in accident scenarios and when adapting or modifying available emergency plans.

4.3 Inorganic Non-Metallic Nanomaterials

4.3.1 Synthetic amorphous silica (silicon dioxide, SiO2, EC Number 231-545-4)

There are various forms of synthetic amorphous silica placed on the market, including precipitated silica, silica gels, colloidal silica or silica sols and fumed or pyrogenic silica. Most forms are either used as stable dispersions of non-agglomerated SiO2 particles (colloidal silica) or as agglomerated or aggregated particles (other forms of silica).

Synthetic amorphous silica has been in use since the 1920ies. According to SRI (Strategy Research Institute), the global consumption of all types of synthetic amorphous silica was around 1.5 million tons in 2010, with a market value of around 2.7bn €.

Colloidal silica’s are stabilised dispersions of non-agglomerated, mostly spherical SiO2 particles. The main uses are in paper industry; chemical-mechanical planarization (CMP) slurries; coatings, paints, inks and adhesives; precision metal casting and refractory; food industry (e.g. as an aid for clarifying wine, beer, fruit juices etc.); bulk plastics and composites; photography; metal surface treatment; catalysis; textile; leather; and building industry (e.g. thermal and acoustic insulation).

Precipitated silica is made up of primary particles in the size range of around 5-100 nm which are aggregated and agglomerated in the final product. The biggest use of precipitated silica is for the reinforcement of elastomer products, primarily automotive tyres, footwear, rubber articles and cable sheathing. In tyres, formulations using precipitated silica reduce rolling resistance, improve traction under slippery conditions and improve fuel efficiency. Precipitated silica is also used in batteries; as anti-blocking agent in thermoplastic films; as carrier silica for liquids and semi-liquids and anti-caking agent in food powders, in health care products such as toothpastes, detergents and cosmetics; as matting agents in paints and varnishes; in the paper industry as advanced fillers in newsprint paper and in special coated papers for inkjet and direct thermal printing to enhance ink absorption; and in agricultural products.

Synthetic silica gels are products of the polymerisation process of fine colloidal silica. They are used in many food and health products, in food industry as an anticaking agent and as a carrier for vitamins and as a tableting aid in pharmaceuticals. They are also used in cosmetics such as face powders, as flow conditioner and for oil absorption. Silica gels also serve as drying agents, protecting a wide variety of products during shipment and storage. They are also used in paints, catalysts, paper coatings etc.

The substance silicon dioxide (synthetic amorphous silica) has been registered under REACH. Given the explanations in the registration dossier, referring to amorphous silica, fumed and precipitated silica, it seems however clear that the dossier mostly, if not exclusively relates to the nanoform. It has not been classified as hazardous by the registrant.

Synthetic amorphous silica (primary particles in the size range 1-100 nm) needs to be distinguished from respirable crystalline silica (primary particles mostly above 100 nm). Contrary to synthetic amorphous silica, crystalline silica is known to produce silicosis, a serious chronic lung disease observed in particular with workers who have inhaled particles of crystalline silica

Substances similar to synthetic amorphous silica. Examples are salts of silicic acid (e.g. silicic acid, calcium salt and silicic acid, aluminium sodium salt, other amorphous silica products), silica

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fume (by-product of thermal silicon production), fused silica and polymerised forms of biogenic silica (e.g. from diatomae).

4.3.2 Titanium dioxide (TiO2, EC Number 236-675-5)

In its bulk form, it has been used extensively for about 90 years as the principal white pigment (maximum reflectivity at around a particle size of 300 nanometres). Titanium dioxide is also an effective UV filter. The nanoform (around 50 nanometres) is transparent, which provides an aesthetic advantage for uses in sunscreens (mostly rutile). Nanoform TiO2 in the anatase modification also has specific electrical and photocatalytic as well as antimicrobial properties. The nanoform of anatase is reported to be more reactive than the bulk form

The substance titanium dioxide has been registered under REACH. According to industry, the registration covers all forms of titanium dioxide including the bulk and the nanoform but with no specific differentiation. The substance has not been classified as hazardous by the registrant.

Titanium dioxide has been in 2006 classified by the International Agency for Research on Cancer (IARC) as an IARC Group 2B carcinogen "possibly carcinogen to humans. US NIOSH recommended a lower exposure limit for ultrafine particles of titanium dioxide: 0.3 mg/m3 for TiO2 nanoparticles (<100 nm), versus 2.4 mg/m3 for fine particles (>100nm), based on the particle surface reactivity. Although it is established that TiO2 does not pass undamaged skin, there is an ongoing scientific debate on whether and to what degree TiO2 nanoparticles can penetrate damaged skin. The approval for use of TiO2 as a UV filter in sunscreens is currently being updated by SCCS (Scientific Committee on Consumer Safety)

According to SRI, the global market for nanoform TiO2 is estimated to be about 10 thousand tonnes per year. Around 5 thousand tonnes per year are used in the personal care industry, of which around 430 tonnes in sunscreens. Next to sunscreens, the UV filtering properties are also used in coatings for plastics and metals, varnishes for wood preservation, in textile fibres and in packaging films. Another main use is catalysts (e.g. decomposing NOx into nitrates or N2). The photocatalytic and antimicrobial properties are used in 'self-cleaning' products (e.g. windows, cement, tiles and textiles for use in hospitals) and air purification systems. Use in tribological coatings prevent deposits in engines and enhance fuel efficiency. TiO2 nanoparticles are also used to increase scratch-resistance of coatings and in the production of electronic components and dental impressions. TiO2 can also be used in dye-sensitized solar cells to produce electricity, though efficiency is currently lower than traditional silicon solar cells.

4.3.3 Zinc oxide (ZnO, EC Number 215-222-5)

Like titanium dioxide, zinc oxide powder exists in bulk and in nanoform. Its nanoform is colourless and an effective UV-filter with a different spectrum than titanium dioxide. It also has antimicrobial properties (though less strong than TiO2) and can be used as an active agent in self-cleaning products.

The substance zinc oxide has been registered under REACH. However, the registration is unspecific to the nanoform (although certain references could be interpreted as referring to the nanoform). It has been classified as hazardous (Aquatic Chronic 1) with the following Hazard Statement (GHS): H410: Very toxic to aquatic life with long lasting effects. SCCS currently assesses ZnO UV filters.

According to SRI, the global market for nanoform zinc oxide is several thousand tonnes per year. Major uses are as a UV-filter in cosmetics (where it competes with bulk zinc oxide but has the advantage of being transparent), in varnishes (as a UV-filter and self-cleaning agent), ceramics and electronics. Nanoform zinc oxide is also used in rubber, improving toughness, increasing abrasion resistance (e.g. reducing wear loss in tyres) and preventing UV and bacterial degradation. In this way, the life time of rubber products can be prolonged. An emerging use is zinc oxide nanowires for UV nanolasers. Uses are also reported in liquid crystal displays and solar cells.

4.3.4 Aluminium oxide (Al2O3, EC Number 215-691-6)

Aluminium oxide nanoparticles are widely used as fillers in polymers and tyres and to increase scratch- and abrasion-resistance in coatings. The substance aluminium oxide has been registered under REACH236. However, the registration is unspecific to the nanoform (although certain references could be interpreted as referring to the nanoform). It has not been classified as

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hazardous. Aluminium oxide nanoparticles show a low level of toxicity, although pulmonary inflammatory responses can be observed at very high doses.

According to SRI, the global market for nanoform alumina powders is estimated at 200 thousand tonnes, representing a market value of €750 million. Nanoform Al_2O_3 powders and dispersions are used inter alia in scratch- and abrasion resistant coatings, as abrasive particles in slurries for polishing semiconductor and precision optical components, in the coating of light bulbs and fluorescent tubes, as a flame retardant, as fillers for polymers and tyres, in coatings of high-quality inkjet papers, in catalysts including the support structure in automobile catalytic converters, in refractory materials and as ceramic filtration membranes. Nanoform alumina can also be used for the manufacture of transparent ceramic bodies for high-pressure lamps.

4.3.5 Aluminium hydroxides and aluminium oxo-hydroxides

There are also different aluminium hydroxide (e.g. bayerite and gibbsite) and aluminium oxohydroxide (e.g. boehmite and diaspore) particles in nanoform. Aluminium hydroxide $Al(OH)_3$ in powder form is used as a flame retardant and as filler in carpets, rubbers, plastics, and foamed plastics. Moreover, it is used in toothpaste and cosmetics. Aluminium (hydr)oxides are often used in the dye and plastics industries as thickeners and fillers and as agents that reduce adhesiveness and increase scratch resistance. Besides, they serve to enhance the colour saturation of paints and varnishes.

4.3.6 Iron oxides: Diiron trioxide (ferric oxide, hematite, Fe_2O_3, EC Number 215-168-2) and triiron tetraoxide (ferrous-ferric oxide, magnetite, Fe_3O_4, EC Number 215-277-5)

There are several types of nanoform iron oxides. According to SRI, the most common ones are nanoform hematite (ferric oxide or Fe_2O_3) and nanoform magnetite (ferrous-ferric oxide or Fe_3O_4).

The substance diiron trioxide has been registered under REACH. However, the registration is unspecific to the nanoform (although certain references could be interpreted as referring to the nanoform). It has not been classified as hazardous. The substance triiron tetraoxide has been registered under REACH. However, the registration is unspecific to the nanoform (although certain references could be interpreted as referring to the nanoform). It has been partly classified as hazardous with the following hazard statement (GHS): H251: Self-heating: may catch fire.

According to SRI, industry sources believe that the global market for iron oxide nanoparticles is currently about €20-40 million, which should correspond to roughly 100 tonnes.

4.3.7 Cerium dioxide (CeO_2, EC-Number 215-150-4)

Ceria (CeO_2) is a rare-earth oxide with specific optical properties. The substance cerium dioxide has been registered under REACH. The registrant has indicated that the substance has a nanoform and has provided separate information on the nanoform. Neither form has been classified as hazardous.

According to SRI, the global market for nanoform cerium oxide is around 10 thousand tonnes. Nanostructured CeO_{2-x} films are used in applications in optical, electro-optical, microelectronic and optoelectronic devices. Nanoform ceria is used inter alia as a polishing material for glass surfaces and silicon wafers, to finish photomasks and disk drives, as an anticorrosion material and in fuel cells. Another major application is as a catalytic diesel fuel additive, decreasing toxic diesel emissions and increasing fuel efficiency.

4.3.8 Zirconium dioxide (ZrO_2, EC-Number 215-227-2)

Ceramic materials made by sintering nanoform zirconia (ZrO_2) powder have a number of unique properties, including some forms with very high fracture toughness.

The substance zirconium dioxide has been registered under REACH. However, the registration is unspecific to the nanoform. It has not been classified as hazardous.

According to SRI, total consumption of nanoform zirconium dioxide is estimated to be in the range of 2,500-3,000 tonnes. The largest application, with about 50% is in optical connectors, followed by fuel cells, lithium-ion batteries, catalysts and ceramic membranes. Other developing applications are in structural and electronic ceramics, dental fillings, prostheses, fluorescent lighting and as polishing agent.

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4.3.9 Other oxide nanomaterials

Other oxide nanomaterials on the market include barium titanate, barium sulphate, strontium titanate, strontium carbonate, indium tin oxide (ITO) and antimony tin oxide (ATO). Barium titanate powders are the dominating raw material for the production of ceramic dielectric layers in low-temperature multilayer ceramic capacitors (MLCC). According to SRI, it is marketed in annual quantities of 15000 tonnes globally. Indium tin oxide is a semi-conducting material used as thin-film material for the production of transparent electrodes in liquid crystal displays, touch screens, organic LEDs, thin-film solar cells, semiconducting sensors etc. Due to its IR-radiation reflectivity it is often used as thermal insulation coating on window glass. Its anti-static properties make it additionally suitable e. g. for packing and storage of sensitive electronic components.

Among these materials, only the substances barium sulphate and strontium carbonate have been registered under REACH (both unspecific to nanomaterials). They have not been classified as hazardous.

4.3.10 Calcium Carbonate (CaCO3, EC-Number 207-439-9)

Most of the fine-ground calcium carbonate is generally in a particle size above 100 nm. There are however also nanoforms of this material, although it is difficult to get a full picture of the use of the nanoform. It seems that ultrafine calcium carbonate is used as an advanced filler in sealants and in plastic for window frames. Fine-ground calcium carbonates are widely used as fillers in paper, plastics, paints and coatings, and adhesive and sealants. They are also used as a food additive (E 170). In the latter cases, most of the material used seems however to be in a particle size above 100 nm.

The substance calcium carbonate has been registered under REACH. The registrant has indicated that the substance has a nanoform and has provided separate information on the nanoform. Calcium carbonate, including its nanoform, has not been classified as hazardous.

4.3.11 Other non-oxide inorganic non-metallic nanomaterials

Substances in this category which have nanomaterial forms include e.g. aluminium nitride, silicon nitride, titanium nitride, titanium carbonitride, tungsten carbide, tungsten sulphide. Among those substances, only the substance tungsten carbide has been registered under REACH. However, the registration is unspecific to the nanoform. It has not been classified as hazardous.

Aluminium nitride is used in the electronic industry in various particle sizes, including nanoparticles. Titanium nitride powders with a particle size from nano- to micrometres are used as additive in the production of wear-resistant sintered materials. Furthermore it is added to plastics, particularly to PET. TiN nanoparticles improve the thermal properties of the material and allow increasing the production output of PET bottles. The nanoform has been assessed by EFSA and authorised as a food contact material.

4.4 Metals and Metal Alloys

4.4.1 Gold (Au, EC-Number 231-165-9)

According to SRI, the global production of colloidal gold dispersions in 2010 corresponded to an equivalent to 3.5 kilograms of gold. Gold nanoparticles are mostly used in medical applications, in particular in in-vitro-diagnostics. Other applications include catalysts, optics, solar cells, and inks for printable electronics, sensors and surface coatings. Among the few available studies, results on toxicity of gold nanoparticles seem to be somewhat contradictory, but there are indications of inflammatory responses (in particular for smaller particle sizes). Gold nanoparticles can become systematically available following exposure and tend to accumulate in the liver (but to an extent also other organs).

4.4.2 Silver (Ag, EC-Number 231-131-3)

Nanosized silver was first produced in 1880. It was used for a long time in photographic film applications. Today, it is mostly used in antimicrobial applications where a high release of silver ions is needed (in other applications, bulk silver or silver salts are used).

The substance silver has been registered under REACH. Despite a number of references to tests

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relating to nanoforms, there is an explicit statement that the nanoform is not covered by the dossier. Silver powder has been classified as hazardous (Aquatic Chronic 1 and Aquatic Acute 1) with the following Hazard Statements (GHS): H410: Very toxic to aquatic life with long lasting effects and H400: Very toxic to aquatic life.

According to SRI, the global market for nanoform silver in antimicrobial uses is estimated at 22 tonnes (around 10% of total use of silver for antimicrobial use). Antimicrobial uses of nanoform silver include anti-microbial textiles for hospitals, wound plasters, and anti-odour sportswear, bed mattresses, socks or underwear. There are also reported uses in toys, household appliances such as refrigerators and washing machines, cosmetics, containers for contact lenses, etc. A much lower amount (in the range of 200 kg) went into non-textile antimicrobial coatings. Other uses of nanoform silver in small quantities include inks for inkjet printers and printable electronics, catalysts, photovoltaics, displays and fuel cells.

4.4.3 Other metallic nanoparticles

Platinum and palladium alloy nanoparticles are mostly used in electronics (production of multi-layer ceramic capacitors). According to SRI, quantities reported are in the range of 12 tonnes annually (including sizes above 100 nm). Other uses include catalysis (including combustion exhaust purification) and energy technologies. Uses in data storage and medical applications are being discussed.

Copper nanopowders (though mostly in sizes above 100 nm) are used in electronics and, to a small degree, in inks. Copper nanoparticles are highly toxic to the aquatic environment.

Iron nanoparticles are mostly used in magnetic recording tapes (needle shaped ferrite particles), though this use is declining.

Titanium nanoparticles are increasingly used as an alloy compound in lightweight materials within the aerospace and increasingly the automotive sector, and as a material for medical implants.

There are also other metal nanoparticles (e.g. nickel, cobalt, aluminium, zinc, manganese, molybdenum, tungsten, lanthanum, lithium) used in smaller quantities, e.g. in electronics, though it is not always clear to what degree the particles are below 100 nm. Rhodium nanoparticles are reported to be used in catalysts

4.5 Carbon-Based Nanomaterials

4.5.1 Fullerenes

Fullerenes are molecules consisting of an even number of 60 or more carbon atoms, which form a cage-like fused-ring polycyclic system with 12 5-membered rings and the rest 6- membered rings. The simplest molecule with 60 carbon atoms is spherical with a diameter of around 0.71 nm.

Despite substantial research and development activities, the current market for fullerenes and derivatives is supposed to be relatively small, including additives for polymers used in sports equipment such as tennis rackets and golf balls (strength), cosmetics (dark colour, anti-aging skin creams), in fuel cells, lithium battery anodes, solar cells component, protective eyewear etc. There is also significant research, e.g. into medical applications

4.5.2 Carbon nanotubes and carbon nanofibers

Carbon nanotubes are tubes consisting of one or more concentric sheets of carbon atoms arranged in the same way as the carbon atoms in ordinary graphite. In the case of single walled carbon nanotubes, the tube diameter is close to 1 nm. Multi-walled carbon nanotubes consist of several such tubes in each other (similar to a Russian doll but made out of tubes). Depending on the structure of the tube, they may exhibit very high thermal and electric conductivity and a high strength-to-weight ratio.

The substance multi-walled carbon nanotubes has been registered under REACH. The registrant has indicated that the substance is a nanomaterial. It has not been classified as hazardous. There is another registration of multi-walled carbon nanotubes under graphite. The registrant has indicated that the substance is a nanomaterial. It has been classified as hazardous with the following Hazard Statements (GHS): H319: Causes serious eye irritation; and H335: May cause

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respiratory irritation.

According to SRI, the market of carbon nanotubes (thinner than 20 nm) worldwide is estimated around 200-250 tonnes (€30-40 million, mostly multi-walled carbon nanotubes) in 2009. The largest use is as a product imparting electrical conductivity to plastic materials, e.g. in disk drive components or automotive plastic fuel lines and fenders (electrostatic coatings). Other uses include polymer additives, paints and coatings, fuel cells, electrodes, electrolytes and membranes in batteries, especially in miniature lithium batteries. There is a lot of research and development into new applications, including into “in-situ component use” which might in term complement and expand the use of silicon in electronics. According to SRI, the market for carbon nanofibres in the thickness range between 20 to several 100 nm is estimated at around 300-350 tonnes (€50-60 million) in 2009. There is a strong increase of use of nanofibres in lithium ion batteries which is by far the largest application. Other uses include fuel cells, fabrics for filtration or in plastic compounds for fuel lines.

4.5.3 Carbon black (EC number 215-609-9)

Carbon black is a black powder consisting of amorphous carbon to a degree of 80-95 %. It is manufactured by controlled incomplete combustion of hydrocarbons. There are various grades with different primary particle sizes, most of them between 1 nm and 100 nm (more than 95% of global production). However, there are also grades with primary particle sizes up to 500 nm. In industrial materials, the primary particles are normally aggregated or agglomerated.

The substance carbon black has been registered under REACH (identified in one of three registration dossiers as a nanomaterial using the relevant tick-box). In one of three registration dossiers, it has been classified as hazardous (Carc.2) with the following Hazard Statement (GHS): H351: Suspected of causing cancer; Route of exposure: Inhalation. In the other two dossiers, it has not been classified

According to SRI, total world consumption of carbon black was estimated in 2010 at 9.6 million tonnes, with a market value of around 10bn €. As filler material carbon black substantially increases the mechanical wear-resistance of rubber products. Around 73% of the world production goes into tyres, and another 19% into other rubber products. Further applications include pigments (toners, printer inks) and antistatic fillers for plastic packaging. There are also reported uses as mascara, flower soil, décor paper and fibres, and to manufacture electrodes and carbon brushes.

4.5.4 Graphene flakes

Graphene flakes consist of a single-layer graphite sheet. They became subject of significant research since 2004, when graphene flakes were isolated through new methods, for which Andre Geim and Konstantin Novoselov were attributed the Nobel Prize in Physics for 2010.

Graphene flakes are a semi-metal or zero-gap semiconductor. They have a very high electron mobility at room temperature, a high opacity and a number of other properties which makes them a promising material for a number of applications, even though market development is still at an early stage. Possible applications are sensors, graphene transistors, integrated circuits, electrochromic devices, transparent conducting electrodes, solar and fuel cells, antimicrobial materials, specific materials for aircraft (e.g. lightning strike protection, prevention of ice adhesion, radiation hardness) and the automotive industry (e.g. prevention of static build-up on fuel lines).

4.6 Nanopolymers and Dendrimers

There are many nanomaterials used as an ingredient in polymers. In addition, there are specific polymeric nanoparticles, nanotubes, nanofibres, nanofilms and nanostructures. Polymers are not subject to REACH registration. Dendrimers are a distinct group with specific polymeric structures. Most of these substances are at an early stage of market development described applications are often still at research and development stage.

Polymer nanoparticles are nanoscale polymeric units such as e. g. polyalcylbenzenepolydiene nanoparticles (PAB-PDM). They are used e.g. in drug delivery systems or as filler material in matrix composites.

Polymer nanotubes, nanowires and nanorods have potential applications in electronic, magnetic, optical, optoelectronic, and micromechanical devices.

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One of the promising polymeric nanotube types are polyaniline nanotubes (PANI) which show a good conductivity and may be used for e. g. conductive fabrics.

Polyglycidylmethacrylate (PGMA) fibres can be utilized to form fabrics and so called "smart fibres", which change their properties depending on the environmental conditions. Textiles based on PGMA fibres may switch e. g. between hydrophobic and hydrophilic, between conductive and non-conductive, between acidic and basic properties or may change colours etc.

Nanocellulose (fibrils and crystals) can be used as a reinforcement material in composites and for medical implants.

Nanostructured polymer-films are polymeric nanoscale thin films appearing mainly as polyalcylthiophene-films, polystyrene-polyethylene oxide (PS-PEO) films or as acrylic glass (Poly(methyl methacrylate) (PMMA)) films. They are used as coatings in the bio-medical sector and have the potential to be used also in other sectors

Polyacrylonitrile nanostructures (PAN) give rise for utilization in semiconductors, solar cells, sensors and membranes in filters. Their electrical properties are based on a variable and controllable bandgap for semiconductor use.

Dendrimers are tree-shaped molecular structures similar to polymers. They are characterised by a high specific surface and, when dispersed, by a non-linear mass-viscosity relation. They are relatively expensive and there is not much information about the current market size. Their major applications include pharmaceuticals, light-emitting diodes and lasers, catalyst carriers, cross-linking agents in radiation-curable surface coating resin, semi-permeable membranes, polymer additives and biotechnological applications.

4.7 Quantum Dots

Quantum dots are semiconductors whose electronic characteristics are closely related to the size and shape of the individual crystal. Typical dots are made of nanomaterials such as cadmium selenide, cadmium sulphide, indium arsenide and indium phosphide. They are applied in rather small quantities in computing, biological analysis, photovoltaic devices, light emitting devices and photodetector devices. The global market for quantum dots is estimated at around €55 m.

4.8 Nanoclays

Nanoclays are nanoparticles of layered mineral silicates such as montmorillonite, bentonite, kaolinite, hectorite, and halloysite. Nanoclays have uses e.g. as polymer nanocomposites, in paints, inks, greases, and cosmetics formulations, as a drug delivery vehicle, in waste water treatment and in tyres. The global market for nanoclays has been evaluated at around €150 m. Several substances which also exist as nanoclay have been registered under REACH. However, the registration dossiers are generally unspecific to nanoclays. Moreover, according to industry sources, some of the nanoclays occur in nature and thus are exempt from registration.

4.9 Nanocomposites

There are various types of composites of nano- and non-nanomaterials. These materials are not separately described here but mentioned as possible applications of the relevant substances mentioned above.

Due to the great importance of data about production amounts and product distribution for assessing possible risks to the environment, in the following it will be reported the data contained in [5]. The authors provided information on production amounts and product distribution of ten different ENM: TiO_2, ZnO, FeO_x, AlO_x, SiO_2, CeO_2, Ag, quantum dots (QDs), CNT, and fullerenes considered the most important either for production amount or, since certain materials are new, to be subject to the general trend of increasing production. The authors based their work on a survey carried out among experts in various companies and institutions within the nanomaterial industry sector. The survey comprised an inquiry about the estimates of global, national (Swiss), and regional production and utilization quantities of ENM as well as the allocation of this production to different product categories.

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5. ENM Production

Data about production and product distribution for assessing possible risks including accidental risks to man and the environment can be consulted in [5]. The reported data contained information on production amounts and product distribution of ten different ENM: TiO_2, ZnO, FeO_x, AlOx, SiO_2, CeO_2, Ag, quantum dots (QDs), CNT, and fullerenes are considered to be the most important either for production amount or, since certain materials are new, to be subject to the general trend of increasing production. The data has been obtained through a survey carried out among experts in various companies and institutions within the nanomaterial industry sector. The survey comprised an inquiry about the estimates of global, national (Swiss), and regional production and utilization quantities of ENM as well as the allocation of this production to different product categories.

Comparing these data with those reported above and contained in [3], it is immediate to observe the mismatch between the two statistics. A remarkable example is given by nano-ZnO. Indeed, in this paper it was reported an amount of 550t against several thousand tonnes per year. The case of TiO_2 is again different, but to a lesser degree. When it comes to SiO_2, also taking into account that in [3] not only nanoform is considered, the data are completely different. However, it is possible to quantify the amount of manufactured nanomaterials in several millions of tons per year. Indeed, three different main types of nanomaterials can be identified:

- Commodity materials (e.g. carbon black or synthetic amorphous silica) – more than 95% of market, used for decades, including in high exposure situations.
- Newly developed medium volume substances (e.g. nano-TiO_2, carbon nanotubes etc.) – some of them under discussion for safety aspects
- Newly developed low volume substances (a large variety of substances) – most of them used in technical applications such as catalysts, batteries, solar cells etc.

According to the second regulatory review, the annual production of nanomaterials is:

Table 1: The annual production of ENM

ENM	Tonnes per annum
Carbon black	9 600 000
Synthetic amorphous silica	1 500 000
Aluminium oxide	200 000
Titanium dioxide	10 000
Zinc oxide	8 000
Cerium oxide	10 000
Carbon nanotubes and nanofibres	Hundreds or a few thousand
Barium titanate	15 000
Nanosilver	20

In the light of what was reported above about the registration of nanomaterials in REACH and CLP, it has been observed that the information provided was either inadequate or insufficient. Often the dossier regarding nanomaterials lack of reliable information on the safe handling of the substances. It seems that the implementation of nanomaterials in the frame of the existing legislation hasn't been adequate and industry has performed poorly when submitting information on chemicals. On the other hand, it has been noted that there are obstacles in the text which make it very difficult to address these information gaps for the majority of nanomaterials on the market.

Thereby, not only is necessary to review all regulatory measures that allow exposure to nanomaterials for consumers, workers and the environment, but it is important to assess, for each nanosized substance, a separate determination of threshold values and criteria for evaluation. Indeed, it is not possible to prescient the different behaviour exhibited by ENMs from current

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knowledge on larger materials, with different properties and reactivity.

6. Major Accidents Prevention

In the European Union, the prevention of major accidents involving chemical substances is regulated by Seveso III Directive (2012/18/EU) [6], [7], [8] and [9]. The Art. 1 of this Directive lays down rules for the prevention of major accidents which involve dangerous substances, and the limitation of their consequences for human health and the environment, with a view to ensuring a high level of protection throughout the Union in a consistent and effective manner. The Annex 1 of the Directive enumerates the dangerous substances without any frame of reference The Art. 8 - Major-accident prevention policy states

Member States shall require the operator to draw up a document in writing setting out the major-accident prevention policy (MAPP) and to ensure that it is properly implemented. The MAPP shall be designed to ensure a high level of protection of human health and the environment. It shall be proportionate to the major-accident hazards. It shall include the operator's overall aims and principles of action, the role and responsibility of management, as well as the commitment towards continuously improving the control of major-accident hazards, and ensuring a high level of protection.

6.1 The potential of accidents

Major accidents occur whenever large amounts of potentially toxic or reactive substance are released in the environment. These can happen during production, manufacturing, storage and transport of these materials. Concerning ENM major accidents might occur during the interaction with substances or during site specific conditions i.e.:

- Form of ENM: suspended or as powder
- Presence of flammable or explosive substances (e.g., metallic ENM or organic solvents)
- Type of containment of ENMs
- Risk of accident during transport
- Safety measures.

In general, the potential for major accidents is higher when ENM are present as powder, because they are easier dispersible than suspended nanomaterials [12]. This is due to the fact that in the regulation of major accidents, only the first 30 min after the accident are of interest and the acute loss of lives or acute damage of the environment is calculated. The consequences on water and soil are secondary as these can be purified and major consequences in the long-term are not included in the regulatory measures. The velocity of dispensability of powders compared to pre-suspended ENM can also be of secondary importance in accidental considerations. However, the proximity of storage of ENM in flammable or explosive compounds increased the importance of accident potential during the specific site potential. Also, natural hazards such as lightning, earthquakes, or flooding need to be considered as triggers of major accidents, in addition to man-made disasters such as explosions in neighbouring factories or airplane crashes [13] and [14].

The following release scenarios should be considered as realistic for major accidents involving nanomaterials:

6.1.1 Accidents during production

ENM are produced in very diverse operations. In general, the mechanical-physical top-down, approaches can be distinguished from chemical-physical bottom-up approaches. In top-down approaches, ENM are made from larger materials through milling; in bottom-up approaches, ENM are synthesized from atoms, ions, or molecules in a chemical reaction. Milling operations are used for metallic or ceramic ENM with a relatively wide particle size distribution. Chemical-physical approaches have the advantage that the form and size of the particles can be better controlled.

Possible reactions are precipitation and flame-plasma-, or gas-phase synthesis. During milling, a major accident with consequences for the general population can practically be excluded, because in this process, only small amounts (around 100 kg) of ENM are used, mainly in aqueous dispersion and of metallic or ceramic ENM; hence, explosions can be excluded. If the process is carried out in organic solvents, then this process needs to be carried out in explosion-proof

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systems, but due to the small amounts (batch volume of around 100 L with max 10-kg ENM), no hazard for the population is to be expected. In gas-phase processes, a deflagration and, with easily flammable solvents, a fire hazard cannot be excluded. Nevertheless, a chain of different events is necessary so that release of ENM beyond the fabrication site is possible.

A possible scenario is the explosion of a distillation equipment with subsequent fire during which all ENM in the same fire compartment are released. Depending on the safety measures, amounts stored, and situation-specific conditions, larger amounts of ENM could be released into air or wastewater. We also need to consider that carbon-based ENM could be combusted while metallic ENM could be oxidized.

6.1.2 Manufacturing and Storage Accidents

During manufacturing or storage of ENM, fire is a possible hazard, which can result in the release of ENM into air (when stored as powder) as well as into water/wastewater (ENM dispersions). The cause for the accident can be internal (e.g., technical) as well as external factors. Deflagration is possible for metallic ENM, but they are usually stored in dispersion and/or under inert atmosphere. An example is nano-zero-valent iron for which also hydrogen production and the danger of hydrogen explosion need to be considered.

6.1.3 Accidents during transport

Transport of toxic substances is connected with a rather high risk because traffic accidents are quite common and because easily flammable substances can be released (e.g. fuel) (see results from case study 4 performed and reported in D6.71 simulating a traffic accident). However, the transported amounts of ENM are currently rather small, compared to the total amount of produced material in any size (compare 5 Mio t of produced TiO_2 of which only 17,000 t are nano-TiO_2 as shown at Table 1), and this is one of the nanomaterials with the highest production amounts). Although there is currently no nano-specific obligation to label, we propose that the containers for transport of ENM should be labelled as a hazardous material and that containers of the highest safety standards be used. An accident during transport could lead to the spilling of dispersions/powder or a fire through which ENM could reach air, soil, wastewater, or natural waters (Figure 1).


(a)


(b)

Figure 1: The Italian train explosion at Viareggio on 29 Jun 2009(a) and the Canadian train derailment on 10 mar 2015 (b).

6.2 Possible related measures

The following technical, organisational, preventive and construction measures can be taken for the mitigation of accidents related with ENM.

6.2.1 Technical measures

Various technical measures can prevent or restrict a major accident. These include sprinklers in storage rooms, pressure-controlled equipment, and disconnection of ventilation in case of accident. However, these tools are not nano-specific but target the accident prevention of easily flammable compounds, which are stored in the same room. If these conventional measures are adopted consistently, they are also effective for ENM.

6.2.3 Organizational measures

Simple but effective organizational measures are access restrictions and sound employee trainings. All employees working with ENM should get an appropriate training and should be able to have access to personal protective equipment. The plant fire department or the local fire brigade should be informed about the presence of ENM and should be trained in suitable firefighting procedures.

6.2.3 Preventive measures

In the prevention of a major accident, a special emphasis should be placed on safety measures. This is especially important with downstream users. Whereas high safety measures are normally standard at production sites, especially in the chemical industry, the handling of ENM in manufacturing of the final products is much less controlled and can result in a much higher possibility for release [15] and [16]. An important step in this context is the employee training. The safe handling of ENM does not require sustainably more action than needed for the handling of powders and conventional chemicals.

Production and manufacturing sites have to comply with existing high safety standards, which are determined by the chemicals (e.g., solvents) that are used during the process. Special emphasis has to be placed on those companies that have no experience in handling conventional chemicals but were founded as pure ‘nano’-company. A critical issue is the fact that downstream users of ENM do not have other information than those given in the MSDS, because these contain actually no nano-specific descriptions.

However, these companies are likely to store only small amounts of ENM on their site - due to the high reactivity of the materials and the normally low concentrations used in final products - thus, the relevance for major accidents is seldom given.

6.2.4 Constructional measures

Constructional measures are indispensable for a safe handling of ENM. However, the established safety procedures used in the chemical industry are deemed to be sufficient. The procedural methods should be distinguished according to the specific form of the ENM. During production, manufacturing, and storage of suspended ENM, a detention basin is needed. The rooms should also not have any direct connection to the sewer system, or the connection needs to be equipped with a possibility for closure during an accident. For ENM in powder form, the ventilation and the configuration of the building envelope are central because they determine if ENM are released through damaged windows/ceilings or through ventilation into the environment. In both cases, fire prevention measures such as fire doors, separate storage rooms for organic solvents, and separate fire compartments are key.

7. Human and environmental toxicity associated with major accident

As pointed out in WP4, Task 4.2 on the life cycle assessment of nanomaterials, a better understanding of the fate and behaviour, and of the life cycle of nanomaterial-embedded products

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is necessary to minimise potential hazards for consumers, workers and the environment as well as to develop proper risk management systems. In the 2009 report, SCENIHR reviewed the available data on the release on ENMs into the environment and the subsequent exposure to humans via the environment [17]. It was concluded that "currently available knowledge of these processes is insufficient to allow quantitative predictions of the environmental fate of nanomaterials". However, at the present day, many further studies have been carried out and the knowledge about the matter has been improved (see also results received from the other case studies in WP6).

Fig. 2 provides an overview of the different stages of a product life cycle at which ENMs could enter the environment [18] (see also D4.38 and D4.39). The yellow boxes represent the various stages of the life cycle of a product containing ENMs, from the synthesis of a specific ENM, its use in a product and the final disposal of this. The boxes in blue represent different waste options, including incineration, landfill, waste water treatment and recycling. The boxes in green represent possible emissions to the environment, including emissions to air, releases of treated waste water effluent and leachate from landfills [18]. Correspondingly, it is possible to assume that the population can be exposed to ENMs through different pathways, for example through contaminated air, drinking water and food, as highlighted in Fig.3 which gives an overview of possible sources of ENM released from nano products and their fate until exposure (see in particular also D4.38 and the case study on sunscreen in D4.39).

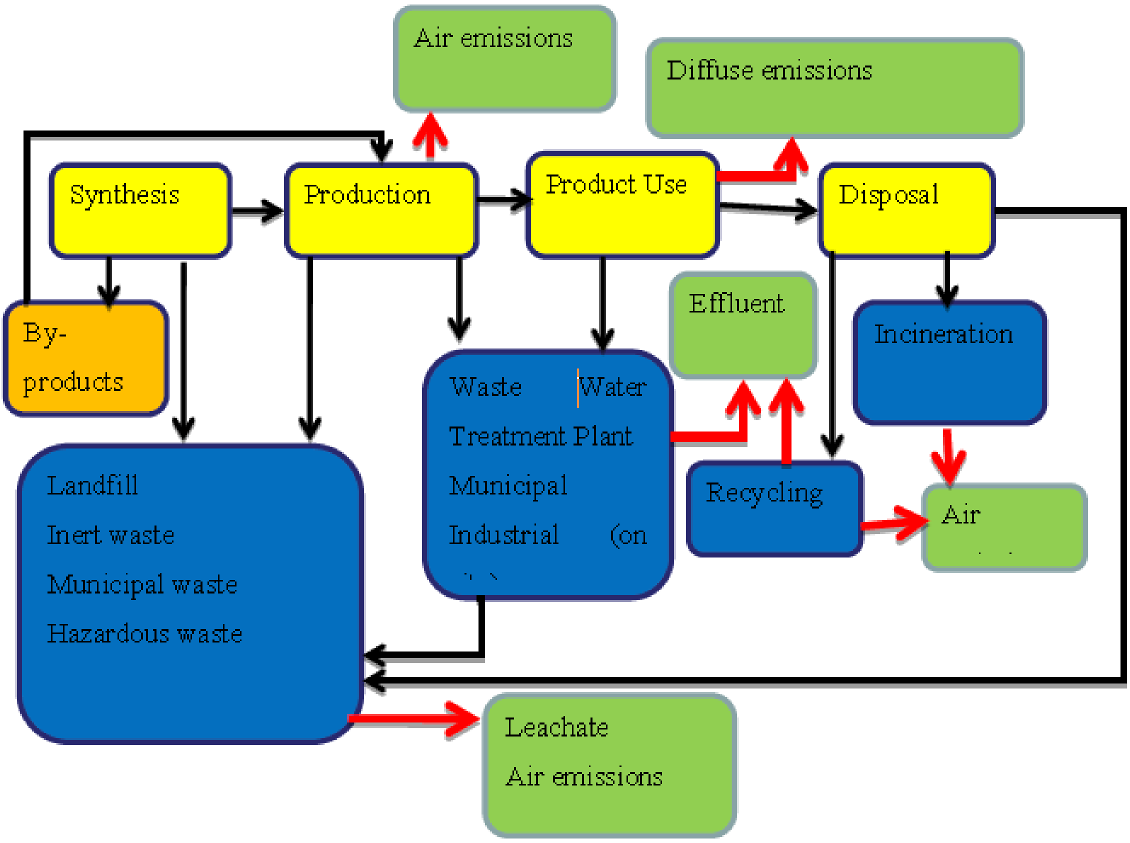

Figure 2: Potential exposure pathways for ENMs.

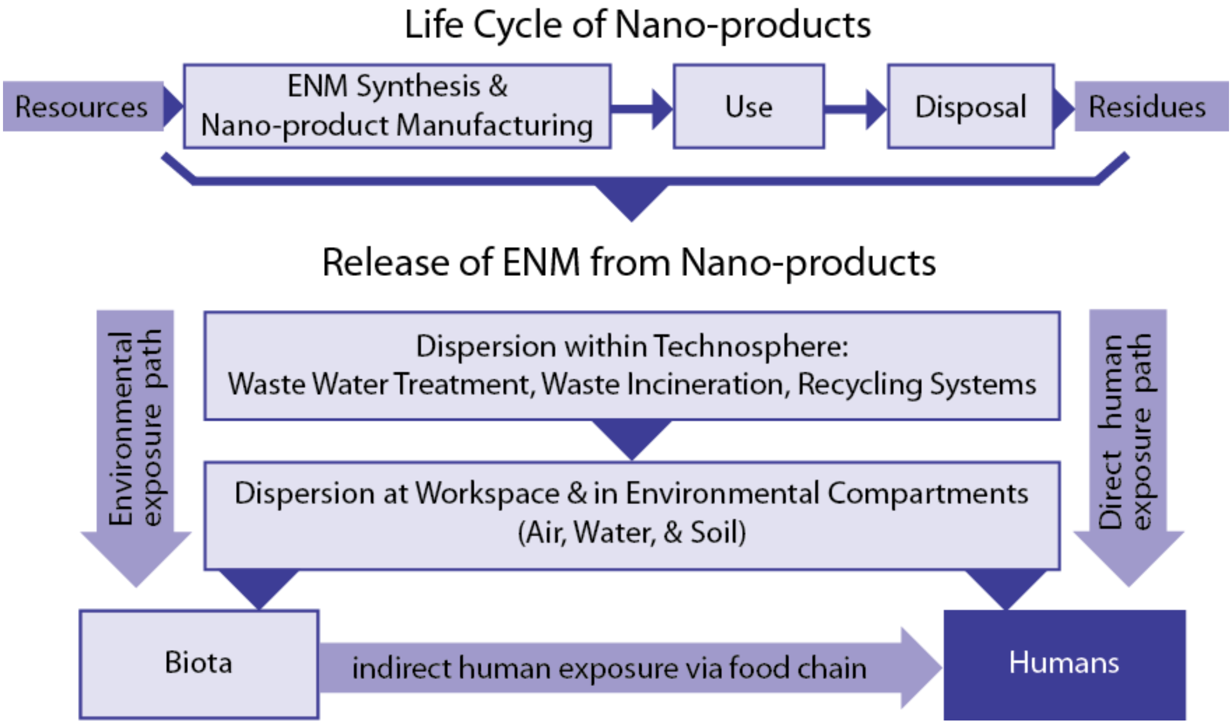

Figure 3: Exposure pathways from ENM release to human and environmental impacts.

The behaviour of ENMs in the environment is dependent both on the physicochemical properties of the ENMs, and those of the environment into which they are released. ENMs possess both intrinsic properties that affect fate and behaviour and others due to the association with other dissolved chemical substances in the environmental matrix and this fact limits the applicability of existing exposure models [19]. Thereby, the novel desirable physicochemical characteristics of ENMs, also present a difficulty in determining their interaction with the environment. At the same time, such interaction processes are crucial to understand the ENMs transformation and distribution in the environment. This knowledge is also fundamental for developing nano-tailored models, or model approaches, and hence to improve the estimation of ENMs concentrations in the environment [20].

To predict human exposure as well as the fate of ENMs in environment, it is crucial to link quantities of environmental release and concentrations able to have possible eco-toxicological effects. There are many studies related to effects, but a lack of quantitative knowledge and appropriate methods for detecting, characterizing and quantifying ENMs in environment. However, some results have been obtained both through in situ measurements and through modelling techniques. In particular, Gottschalk et al. [21] identifies the following methodologies to approach the problem:

- Analytical in situ methods
- Experimental/simulation studies in laboratories
- Modelling/estimation
- Exploratory chemo metric approaches, i.e. probabilistic mass flow analysis.

In the “Milieu report” [18], a wide review of papers related to the above four methodologies has been reported. However, current data still suffer limitations in comparability and breadth in covering the wide range of nanoforms, but it can be expected that the application of analytical techniques to a wider range of ENMs and emission scenarios will begin to generate more comprehensive and comparable datasets. In this context, Clark et al. [19] identified a set of minimum data requirements to know for studies reporting on ENM exposure.

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Table 2: The recommended minimum data requirement for studies on ENM exposure

Description of physical and chemical form of the ENMs used (i.e., at source)

- Chemical composition
- Size distribution (including dimensions for fibres)
- Whether MNM is bound in a matrix. If so, describe: The matrix itself (e.g., plastic, rubber, concrete, paint) Form of matrix (e.g., powder, liquid, solid, granules) Amount of MNMs used in the matrix

Description of physical and chemical form of released/detected particles

- Embedded in a matrix, agglomerated, single particle
- Elemental composition by EDX/EDS or chemical analysis

Potential other sources of ultrafine and other particles

Exposure characterized using a combination of metrics and measurements, which could include, but are not limited to, mass, particle number, and particle size distribution.

Information on process:
- Description of the process and all activities included in the process;
- Typical duration and frequency of these activities; and
- Type of enclosure of process: if enclosed, provide frequency and duration of opening for maintenance, quality control and/or other manual operations.

Description of site:
- Room size, windows and other features that may affect exposure.

Risk management measures (RMM):
- For occupational studies, standardized description of RMM types (e.g. ventilation) and personal protective equipment present;
- For consumer studies, product design that affects the release (e.g., maximum volume released from one use of a spray) and description of other types other RMM applied during the measurement; and
- Other measures (e.g., administrative controls, additional engineering controls).

Environmental release information:
- Total volume of MNMs used on site;
- Amounts and processes for disposal and/or recycling;
- Volume of air flow and MNM concentrations in outlet air (emission to air after filters); and
- Volume of waste water flow and MNM concentrations in effluent (after treatment) (emission to surface waters).

Sampling and data analysis strategy:
- Location of samples/measurements relative to source and receptor (e.g., workers);
- Number of samples/measurements taken;
- Description of activities associated with each sample/measurement;
- Qualitative assessment describing how representative the measurements are for personal exposure;
- Description of data analysis, including the difference between background and activity, and how this was calculated, whether and how peaks were addressed, whether and how data were averaged.

The worker exposure to ENMs might occur during their production, or their use in next processes or in the phase of incorporation into products or during treatment of ENMs-embedded products. ENMs follow three main routes to enter in the human body: inhalation into the pulmonary system, absorption through the dermal system and ingestion through the gastrointestinal system, being the inhalation exposure the most important with regard to the effects of ENMs on occupational health.

Due to the size effects, nanoparticles may diffuse fast in air and can enter into the respiratory tract. Moreover, nanoparticles can be hardly removed from the body because they cross mucus membranes. In the Fig. 4, many potential health effects together with the involved organs are pointed out [22].

As the walls of the capillaries and alveolar are approximately 0.5µm thick, airborne particles in the micro- and nano-scale easily inhale into the body. Exposure can be separated into three

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categories: more than 2.5µm, less than 2.5µm and less than 100 nm

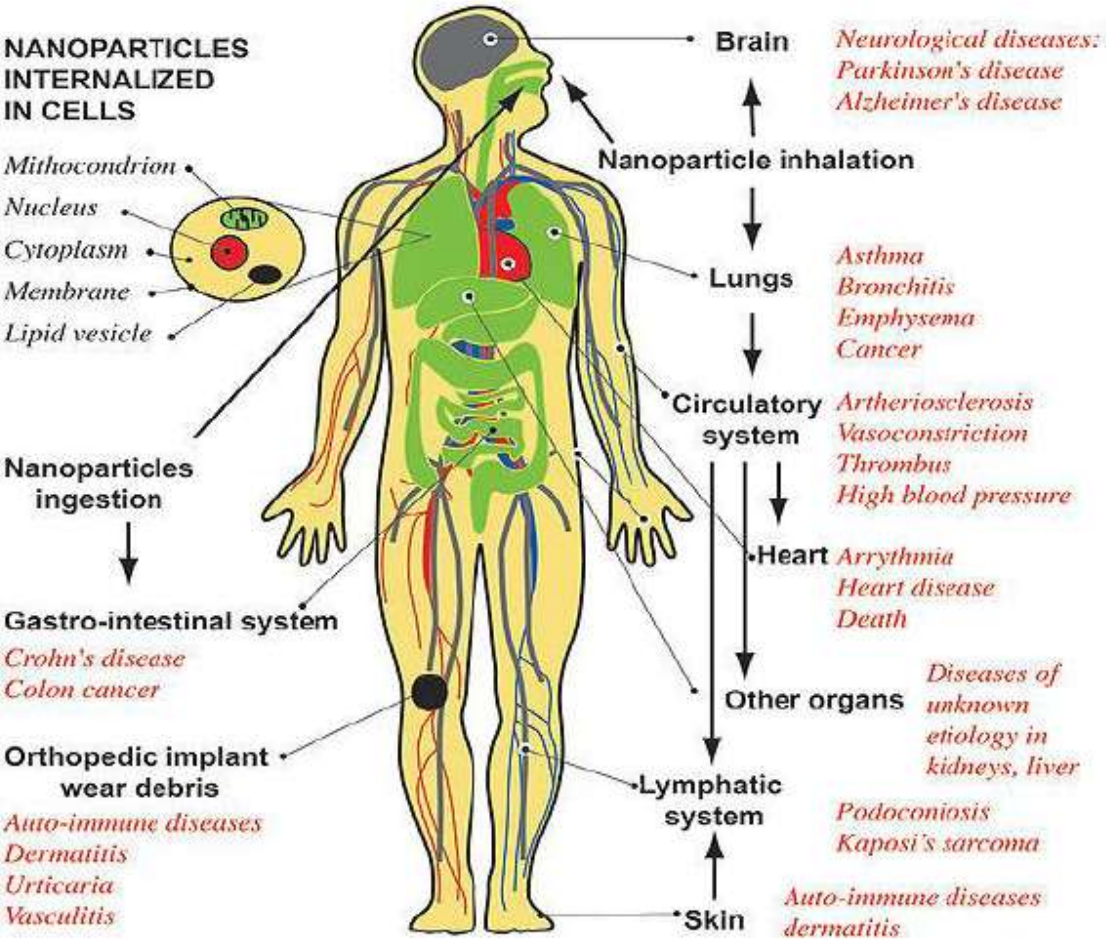

Figure 4: Diseases associated to nanoparticle exposure.

Proper parameters to assess the workers exposure to ENMs and methodology to measure them are still under discussion (see also results reported on occupation exposure in WP6 in D6.58 and D6.66). Indeed, ENMs exposure is characterized by a high number of particles with a negligible mass. For this reason, the traditional mass concentration measurement is not adequate because it is difficult to discriminate them from background levels. However, several workplace surveys and some authors proposed OELs expressed in terms of mass concentration. As an example, the following table, extracted from [22] confirms what stated.

Particle mass was the original metric used for the exposure assessment of coarse materials. More relevant indicators have emerged for describing nanoparticle aerosols, including particle number, surface and mass concentrations, and criteria relating to their size or shape. Some of the instruments developed around these indicators enable a continuous measurement. The Fig.5 lists the equipment based on continuous measurement of size, number and surface area parameters for the collected aerosol, where CNC= Condensation Nuclei Counter, CPC = Condensation Particle Counter, TEOM = Tapered Element Oscillating Microbalance, NSAM = Nanoparticle Surface Aerosol Monitor, SMPS = Scanning Mobility Particle Sizer, ELPI = Electrical Low Pressure Impactor (see also experimental results received in D6.71).

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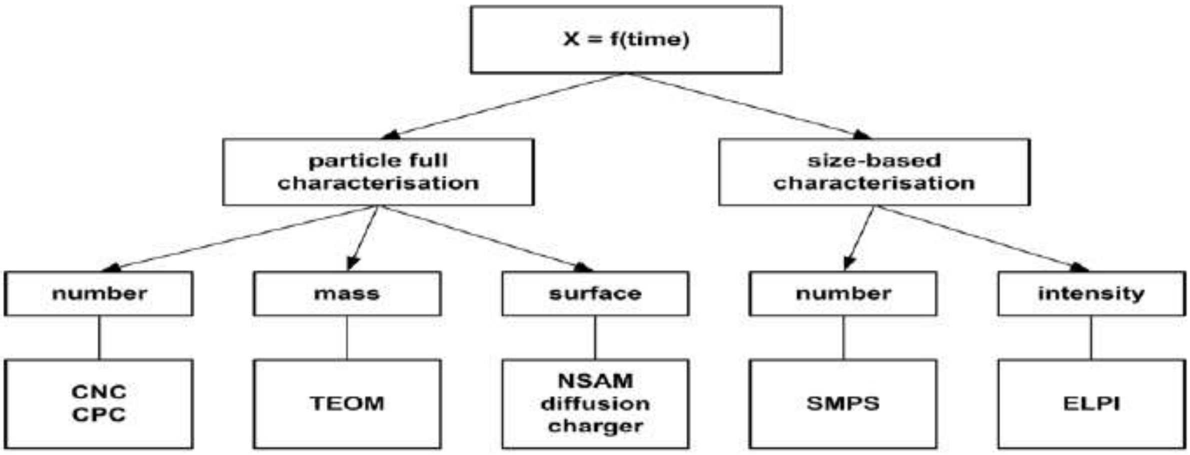

Figure 5: Classification of nano instruments according to the analysed property.

8. Recommendations for emergency plans involving nanoparticles

A major accident involving or not nanomaterials can occur in every time that larger quantities of a potentially toxic or reactive substance are present. An accident could occur in a factory during the production process or in storage area or during road transport.

In order to assess the risk of a major accident, production facilities and processes must be investigated. The key factor is whether or not the facilities have special protection against release of nanomaterials into the environment, for example using airlocks or air filtration systems. The production of nanomaterials often takes place in closed systems, where the risk of release is lower. On the other hand, as a result of the extremely low ignition energy, many explosion hazards exist during the processing and handling of nanomaterials, such as the result of friction, collision, mixing, grinding, drilling, sanding or binding them into a matrix – for example adding nano-silver to paints and varnishes – may take place in an open facility.

The general production conditions must also be scrutinised. Factors which could trigger or worsen a major accident might include placing flammable or volatile materials in a particular environment or process where conditions such as high temperature or pressure prevail.

The severity of nanomaterial explosions will not be controlled by the particle size but rather by the combustion of the pyrolysis gas/air mixture, thereby an emergency plan could be implemented following the emergency plans typical of fire and explosion hazards of combustible dust. See for example, Firefighting Precautions at Facilities with Combustible Dust, a guide prepared by Occupational Safety and Health Administration U.S. Department of Labour.

The companies processing nanomaterials must have a contingency plan adapted for the case of fire. The local fire service should be informed about the stored quantities, the type of chemicals, and about the measures required to combat the effects of the accident.

In such companies pre-incident surveys at facilities should be performed. Emergency responders should treat nanomaterials as a special hazard. Emergency responders need to know about dust hazards in advance. This helps them plan appropriate actions and avoid creating additional hazards to themselves or occupants. All locations where combustible dust is used (including process or conveying equipment), produced (for example, cutting or grinding equipment), or stored (including all vessels, containers, or collectors) should be identified in the survey. The pre-incident survey should cover metal dusts carefully. Note the presence of water-reactive metals and metal dusts.

The pre-incident survey forms the basis of how emergency responders plan for and handle incidents. Responders and facility representatives should discuss compatible extinguishing agents and appropriate attack methods during the survey.

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Equipment and buildings with known combustible dust hazards (metallic dusts) should be equipped with devices or systems to prevent an explosion, minimize its propagation, or limit the damage it causes. In general, constructional measures are indispensable for a safe handling of ENMs. However, it is thinkable that the safety procedures used in the chemical industry are sufficient.

During production, manufacturing, and storage of suspended ENMs, a detention basin is needed. The rooms should also not have any direct connection to the sewer system, or the connection needs to be equipped with a possibility for closure during an accident. For ENMs in powder form, the ventilation and the configuration of the building are crucial because they determine if ENMs are released through damaged windows/ceilings or through ventilation into the environment. In both cases, fire prevention measures such as fire doors, separate storage rooms for organic solvents, and separate fire compartments are essential. Other technical measures can prevent or limit a major accident: for example, sprinkler equipment in the store room, pressure-controlled installations and ventilation switch off in case of a major accident. However, these measures belong to the standard accident prevention measures for readily flammable substances stored in the same room.

Moreover, to prevent or mitigate dust explosions, the following precautions are necessary:

• Fire attack: Choose defensive mode when warranted.

• Extinguishing agent: Select agent compatible with burning or nearby material.

• Hose streams: Use low-pressure medium fog streams to avoid dust clouds.

• Fire extinguishers: Apply agent gently to avoid dust clouds.

• Access and ventilation: Consider proper timing before introducing oxygen.

• Power shutdown: Coordinate equipment shutdown with facility personnel.

• Tools and equipment: Do not introduce ignition sources.

As described in section 5, the scenarios for major accidents strongly depend on the used ENMs and other chemicals on the same site as well as factors specific for the situation or the site:

Form of ENMs: suspended or as powder

Presence of flammable or explosive substances (e.g., metallic ENM or organic solvents)

Type of containment

Risk of accident during transport

Safety measures.

To avoid risk during transportation and to reduce the possibility of ENMs dispersion, it is important that all shipments of nanomaterials, regardless of whether they meet the definition for hazardous materials or not, should be consistently packaged using the equivalent of a Packing Group I container.

Finally, also organisational measures are important: restriction of access and an exhaustive training of the personnel represent effective measures. Even though personal protective equipment (PPE) should never be considered as the first line of defence against contaminants, nevertheless they must always be used in order to minimise users' exposure to nanoparticles.

9. Conclusions

In this report, many aspects related to the risk of ENMs have been examined starting from the definition of nanomaterial and its possible revision. An overview and analysis of the existing legislation has been accomplished highlighting the difficulties of the REACH implementation. The different types of nanomaterials currently on the market regarding and critical properties have been examined as well as their uses, the produced amount, the registration under REACH and the declared type of hazard. Scenarios of major accidents involving nanomaterials have been taken into consideration including production processes, transport and manufacturing and storage.

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Possible risks associated with an accidental explosion of nano-powders have been assessed and suggestions given to reduce fire and explosion risks. Also the environmental fate of manufactured nanomaterials has been examined taking into account human exposure and safety hazards at nanotechnology workplaces. Moreover, the monitoring of number or mass concentrations of nano-powders has been recommended through the use of specific instrumentations at factories where nano-powders are manufactured, stored or handled. Finally, some suggestions about emergency plans involving nano-powders have been proposed.

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