



# Guidance for the Management and Assessment of Nanomaterials in Research

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## Details of revisions

Level	Details	Date	Initial

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# 1 Introduction

## 1.1 Purpose

The purpose of this document is to provide information and details to aid the development of risk management strategies for the use, storage, management, transportation and disposal of nanomaterials at all Curtin University sites.

## 1.2 Aim

The aim of this document is to outline Curtin University's process and expectations for managing and assessing nanomaterials and their associated risks to ensure:

- That arrangements are in place to minimise the risk of adverse health effects and protect the safety of staff, students, contractors and members of the public, due to exposure to nanomaterials.
- That people with various roles are informed of their responsibilities in regard to the safe use, storage, management, transportation and disposal of nanomaterials.
- The mitigation of adverse environmental impacts.
- Compliance with State and Commonwealth regulatory requirements.

## 1.3 Exclusions

The following is not included as part of this guidance document:

- Chemical management.
- Class 1 Dangerous goods.
- Class 2 Dangerous goods (including cryogenic liquids).
- Underground bulk storage tanks.
- LPG and LNG.
- Waste management.
- Class 7 Dangerous goods - radioactive materials.
- Biologicals.
- The built environment - asbestos, natural mineral fibres (NMF), CFCs.
- Concessional spirits.
- Emergency management.

For each of these, either refer to alternative guidance documents or ensure an appropriate individual management plan and risk assessment are completed, appropriately reviewed and approved. Specialist input may be required in some of these areas.

## 2 Roles, Responsibilities and Authorities

This document applies to all Curtin University staff, students and contractors who are required to use nanomaterials within the scope of their duties at Curtin University.

All staff, students and contractors who purchase, use, manage, transport and dispose of nanomaterials on behalf of Curtin University are required to undertake their responsibilities in line with the Health and Safety Responsibilities Procedures, located:

<http://policies.curtin.edu.au/findapolicy/docs/Health%20and%20Safety%20Responsibilities%20Procedures%20-%20April%202013.pdf>

Table 1 provides an outline of various roles and responsibilities in regard to chemical management. Nanomaterials are chemicals that are either naturally or have been deliberately engineered on the 'nanoscale'.

Table 1. Roles, Responsibilities and Authorities

Role	Responsibility for Health and Safety (from H&S Responsibilities Procedures)	Responsibility for Chemical Management	Authority
Health, Safety and Emergency Management Department	To provide specialist advice and support to areas in relation to Hazardous Substances, Dangerous Goods, Regulated Chemical Waste Disposal and Controlled Substances.  Co-ordinating and administering the Curtin University ChemAlert Database  To provide specialist advice and support for the planning of emergency procedures To co-ordinate any communication between Curtin and emergency authorities for the purpose of planning	Maintaining the Chemical Management System and related Guidelines.  To ensure emergency planning is undertaken	Yes – Can authorise the issue of guideline and management documents
Managers/Supervisors	To undertake effective health and safety measures to ensure compliance with the Occupational Safety & Health Act 1984 and other legislative requirements.	To undertake effective chemical management measures to ensure compliance with the Occupational Safety & Health Act 1984 and other legislative requirements.	No

Individual workers/students	To comply with the Occupational Safety & Health Act 1984 and all reasonable directive given in relation to health and safety at work, to ensure compliance with University and Legislative health and safety requirements.	To comply with the Occupational Safety & Health Act 1984 and all reasonable directive given in relation to chemical management at work, to ensure compliance with University and Legislative health and safety requirements.	No
Office of Research and Development – Poisons advisor	Not listed	To provide advice and guidance on the appropriate management and storage of poisons  Aid communication and coordinate with relevant authorities on Curtin's management of poisons.  Maintaining the Poisons Act Compliance Management Plan and related Guidelines	Advisory
University Chemical Safety Committee	Not listed	To provide advice to the University on matters relating to chemical safety.	Advisory



### 3 Definitions

#### 3.1 Nanoparticles

These are ultra-fine particles having a diameter between 1 and 100 nanometres (nm) and may be suspended in a gas or liquid, or embedded in a matrix in the case of composites. Nanoparticles (NPs) can occur naturally or engineered using nanotechnology.

#### 3.2 Engineered nanomaterials

Engineered nanomaterials are designed with specific properties in mind. Engineered nanomaterials encompass nano-objects and nanostructured materials. The former are defined as materials with one (nanoplate), two (nanorod) or three (nanoparticle) external dimensions in the nanoscale (i.e. between approximately 1 and 100 nm). Examples of nanostructured materials are nanocomposites composed of nano-objects embedded in a solid matrix or nano-objects bonded together in simple random assemblies as in aggregates and agglomerates or ordered as in crystals of fullerenes or carbon nanotubes.

#### 3.3 NOAA (nano-objects, agglomerates and aggregates)

Nano-objects, and their agglomerates and aggregates greater than 100 nm (NOAA) are applicable to engineered materials that consist of nano-objects such as nanoparticles, nanofibres, nanotubes and nanowires, as well as aggregates and agglomerates of these materials. The term NOAA applies to such components either in their original form or incorporated in materials or preparations from which they could be released to a certain extent during their lifecycle, including, as a result, downstream activities such as disposal.

#### 3.4 Nanomaterial types and characteristics

Table 2 provides details on some of the more common types of engineered nanomaterials to which this guide might be applied.

Table 2. Roles, Responsibilities and Authorities

Type of engineered nanomaterial	Description	Characteristics
Carbon black	Carbon black is virtually pure elemental carbon in the form of particles that are produced by incomplete combustion or thermal decomposition of gaseous or liquid hydrocarbons under controlled conditions. Its physical appearance is that of a black, finely divided powder or pellet. Its use in tyres, rubber and plastic products, printing inks and coatings is related to properties of specific surface area, particle size and structure, conductivity and colour. The primary particle size of carbon black is most commonly less than 100 nm, but commercial forms are aggregated, typically with dimensions greater than 100 nm. Carbon black is one of the top 50	Paracrystalline carbon high surface- area-to- volumeratio

industrial chemicals manufactured worldwide, based on annual tonnage.

Carbon nanotubes	Carbon nanotubes are allotropes of carbon with cylindrical structure, high-cylindrical fullerene aspect ratio different tube diameters and lengths as well as tubestructures (single or multi-walled, principally consisting of one to many layers of tubular graphene-like capped or uncapped) sheets. The principal types are usually grouped into SW (single-walled), DW (double walled), and MW (multi-walled) CNT. Diameters may vary from around 1 nm for SWCNT to more than 100 nm for MWCNT. Their lengths can exceed several hundred $\mu\text{m}$ .	
Dendrimers	Dendrimers are polymer particles in which the atoms are arranged in a branching structure, usually symmetrically about a core. Dendrimers are typically monodisperse with a large number of functionalisable peripheral groups. Many are currently being evaluated as drug delivery vehicles. Commercial CNT can often contain a significant amount of other carbon allotropes and inorganic nanoparticle catalysts.	Repetitively branched molecules
Fullerenes	Fullerenes comprise one of four types of naturally-occurring forms of carbon, first discovered in the 1980s. Their molecules are composed entirely of carbon and take the form of a hollow sphere. Fullerenes are similar in structure to graphite which comprises sheets of hexagonal carbon rings, but can also contain pentagonal or heptagonal rings which enable 3D structures to be formed. One of the most commonly described fullerenes is C <sub>60</sub> , known as a Buckminster fullerene or a buckyball. Fullerenes are chemically stable materials and insoluble in aqueous solutions. Potential applications include drug delivery, coatings and hydrogen storage.	carbon-only molecules (hollow sphere, ellipsoid, tube, or plane)
Metals and metal oxides, ceramics	This category includes a wide range of compact forms of nanoparticles, including ultrafine titanium dioxide and fumed silica. Such nanoparticles can be formed from many materials, including metals, oxides and ceramics. Although the primary particles have a compact form, these materials are often available only in agglomerated or aggregated form. They can be composites having, for example, a metal core with an oxide shell, or alloys in which mixtures of metals are present. This group of nanoparticles is generally less well defined in terms of size and shape, and likely to be produced in larger bulk quantities than other forms of nanoparticles. Applications include coatings and pigments, catalysis, personal care products, cosmetics and composites.	Ultrafine powders (e.g. Ag, Au, ZnO, TiO <sub>2</sub> , CeO <sub>2</sub> )
Nanoclays	Nanoclays are ceramic nanoparticles of layered mineral silicates. Nanoclays can be naturally occurring or engineered to have specific properties. Naturally occurring forms include several classes such as: montmorillonite, bentonite, kaolinite, hectorite, and halloysite.  Nanoclays also include organo-clays, i.e. clays that have been subjected to cation exchange, typically with large organic molecules, which partially or completely de-laminates the primary sheets.	Layered mineral silicates
Nanowires	Nanowires are small conducting or semi-conducting nanofibers with a single crystal structure, and a typical diameter of a few 10s of nm and a large aspect ratio. Various metals have been used to manufacture nanowires, including cobalt, gold and copper. Silicon nanowires have also been produced. Potential applications include inter-connectors in nano-electronic devices, photovoltaics and sensors.	Large aspect ratio
Quantum dots	Quantum dots are small (2 nm to 10 nm) assemblies of semiconductor materials with novel electronic, optical, magnetic and catalytic properties. Typically containing 1,000 to 100,000 atoms, quantum dots are considered to be something between an extended solid structure and a single molecular entity.  Semiconductor quantum dots exhibit distinct photo-electronic properties which relate directly to their size. For example, by altering the particle size, the light emitted by the particle on excitation can be tuned to a specific desired wavelength. Applications include catalysis, medical imaging, optical devices and sensors.	Semi-conducting crystal core (e.g. CdSe, CdS core, ZnS coat)

## 4 Instruction and Training

Arrangements must be put in place to ensure that all reasonable control measures identified in the risk assessment are properly and fully applied. Clear allocation of managerial responsibilities and accountabilities is particularly important in this respect. This will need to be clearly identified by the school or working group prior to starting work with a clearly defined hierarchical management/responsibility structure. The arrangements should include detailed records of training/refresher training of those individuals who have to apply the control measures, and that the procedures are working as effectively as they should.

Everyone who is involved or could be affected (other people in the working area or sharing the laboratory/workshop) should be provided with the information, instruction and training required to ensure their safety. It is necessary to inform and involve the staff, researchers and students in the risk assessment process. Without the informed and competent participation of staff, researchers and students, any risk management measures identified as necessary in the risk assessment are unlikely to be fully effective.

It is therefore important that as part of all inductions persons (including persons already occupying an area where new work is being located) know as a minimum:

- The names of the substances to which they are liable to be exposed and the risks to health created by exposure.
- Any relevant occupational exposure limits (OEL) or similar self-imposed (in-house) exposure limit that applies to the substances.
- The information on any safety data sheet that relates to the substance.
- The significant findings of the risk assessment.
- The precautions they should take to protect themselves and their fellow employees.
- The results of any monitoring of exposure, especially if these are >50% of any OEL.
- The collective results of any health surveillance (see 0).

## 5 Legislation and Standards

### 5.1 Acts and Regulations

There is currently no WA legislation dealing specifically with nanomaterials. However, legislation covering chemicals and occupational safety are applicable to nanomaterials.

In Australia, under the harmonised Work Health and Safety Regulations 2011 (WHS 2011), workplace hazardous chemicals are classified according to the GHS. For the purposes of transport, dangerous goods are classified according to the Australian Code for the Transport of Dangerous Goods by Road and Rail (the ADG Code). The latest edition of the ADG Code is the 7th edition.

For workplace health and safety regulations in Australia, a hazardous chemical refers to “a substance, mixture or article that satisfies the criteria for a hazard class in the GHS” (with a small number of changes as noted in the Work Health and Safety Regulations, WHS 2011). The same physical hazards covered in the GHS are also covered by the ADG Code.

The legislation that can be referenced when using nanomaterials can be found at the following websites.

Commonwealth law: <http://www.comlaw.gov.au/>

- Work Health and Safety Act 2011
- Work Health and Safety Regulations 2011 (Chapter 7)

State Law: <http://www.slp.wa.gov.au/Index.html>; <http://www.dmp.wa.gov.au/7617.aspx>

- WA Occupational Health and Safety Act (1984)
- WA Occupational Safety and Health Regulation (1996)

### 5.2 Standards, Codes of Practice and Guidance Material

This list of relevant standards includes:

- ISO/TS12901-1 (2012-11-15) Nanotechnologies – Occupational Risk management applied to engineered nanomaterials – Part 1 Principles and approaches
- ISO/TS12901-2 (2014-01-15) Nanotechnologies – Occupational Risk management applied to engineered nanomaterials – Part 2 Use of the control banding approach.

### 5.3 Safe Work Australia guidance

The Australian WHS Regulations require that no person at the workplace is exposed to a substance or mixture in an airborne concentration that exceeds the Australian workplace exposure standards.

Australian WHS laws apply to nanotechnologies and nanoparticles; however, there are specific issues associated with nanomaterials which impact on the provision of WHS laws including:

- the uncertainty surrounding the hazards properties of engineered nanoparticles
- the capability in measuring the emissions and exposures of nanoparticles in the workplace including personal exposure assessments.

## 6 Hazard and Exposure

### 6.1 NOAAs as hazardous materials

Hazard levels for nanomaterials are currently unestablished or incomplete. With the limited knowledge about the toxicity of some NOAAs and the concern that current safety data sheets do not adequately reflect the hazardous nature of such NOAAs, it is recommended that all nanomaterials in a particulate form or in a form where particles potentially could be released are considered potentially hazardous unless sufficient information to the contrary is obtained.

The current advice is to approach risk management of these materials conservatively. If there is no exposure, no dose will accumulate and, despite the potential toxicity of the particles, there will be no risk to health.

### 6.2 Health effects

The potential health risk of a substance is generally associated with the magnitude and duration of the exposure, the persistence of the material in the body, the inherent toxicity of the material, and the susceptibility or health status of the person. Since nanotechnology is an emerging field, there are uncertainties as to whether the unique properties of engineered nanomaterials also pose unique occupational health risks.

An important issue is whether the nanoscale version of a particular material poses risks that are significantly different in type or intensity than the macroscale forms of the same material. Experimental studies in animals have shown that the biological response (whether beneficial or detrimental) to certain incidental or engineered nanoparticles can be greater than that of the same mass of larger particles of similar chemical composition.

In addition to particle number and combined surface area, other particle characteristics might influence the biological response, including solubility, shape, charge and surface chemistry, catalytic properties, adsorbed pollutants (e.g. heavy metals or endotoxins), as well as degree of agglomeration.

### 6.3 Exposure routes

#### 6.3.1 Inhalation

As with most particles in the workplace, inhalation is considered to be the primary route by which nanomaterials in the form of free, unbound, airborne particles will enter the bodies of workers. Once inhaled, nanomaterials will deposit in the respiratory tract regions, depending upon their particle size. Specifically, nanoparticles will deposit in all regions of the respiratory tract.

The potential risks to health from inhalation of NOAAs, specifically bio-persistent NOAAs, may be summarised as follows:

- Nano-objects can reach parts of biological systems which are not normally accessible by larger particles.
- NOAAs have a much higher surface area than the same mass of larger particles.
- Engineered nanomaterials will have new, improved or enhanced properties compared to larger particles of the same material. Altered chemical and/or physical properties might be expected to be accompanied by altered biological properties, some of which could imply increased toxicity.
- Comparisons are being drawn between the bio-persistent high aspect ratio NOAAs (e.g. some forms of carbon nanotubes or nanowires) and asbestos (SWA, 2012c).
- For some NOAAs, a reduction in size has been shown to relate to increased solubility. This effect might lead to increased bioavailability of materials which are considered to be insoluble or poorly soluble at larger particle sizes.

The likelihood (or risk) of disease occurring depends on the physicochemical properties of the nanomaterial and the dose in the organ where disease can occur. Dose in humans is not assessed directly, but is estimated from the exposure, which for airborne particles is a combination of the concentration of particles in air, the inhalation rate, the particle size-specific deposition efficiency in the respiratory tract and the length of time the exposure lasts.

### **6.3.2 Dermal or ingestion**

Concerns have been raised about the potential risks to health arising from dermal exposure to some types of NOAAs, in particular nano-objects, based on the possibility of these materials penetrating the skin and entering the bloodstream. The ability of substances such as engineered nanomaterials to penetrate the skin depends on its physicochemical properties and size/surface characteristics; also whether the skin barrier is compromised or damaged, in which this absorption may more readily occur.

NOAAs may also exhibit greater gastro-intestinal and dermal uptake compared to larger-sized particles. Potential health effects due to ingestion have been postulated based on the possibility of NOAAs transferring across the gastro-intestinal wall.

## **6.4 Exposure scenario**

### **6.4.1 Physical form**

The actual stage in the NOAA's life cycle is an important parameter to consider as it can influence the potential for worker exposure and thus the selection of risk control parameters.

NOAA can be in different forms, as produced (e.g. as a powder), or as used (e.g. embedded in a solid matrix or attached to a substrate), suspended in a gas or in a liquid; or as waste. Each of these different stages will have its own exposure pattern.

Thus, the NOAA's physical form (i.e. exposure availability) should be characterised throughout the product lifecycle. This information is critical for the appropriate and safe handling of the material.

#### **6.4.2 Amount of NOAA**

The amounts of nanomaterial processed or manufactured in the workplace is one of the most important determinants of exposure. The presence of large amounts of NOAA in the workplace increases the potential for the generation of a higher concentration in the air and, therefore, can lead to higher exposures.

#### **6.4.3 Potential for dust generation**

Workplace processes, such as spraying, packaging, maintenance activities and dumping can lead to the generation of airborne particles. As a consequence, it is important to analyse the details of the operator's activities and process operations in order to estimate the potency of the process to release NOAA into the workplace air. This implies performing an inventory of the operators' tasks, including start and stop operations, process steps, etc.

#### **6.4.4 Quantitative exposure measurements**

Actual exposure measurements, when feasible, represent the best information for the selection of the appropriate exposure band. Therefore, they should be encouraged and when both personal sampling and area measurements are available the preference should be given to individual exposure measurements. The results should be taken into account when determining the corresponding exposure band. A specialist occupational hygienist may be needed to conduct this assessment.

#### **6.4.5 Fire and explosion**

Explosive dust clouds can be generated from most organic materials, many metals and even some non-metallic inorganic materials. The primary factor influencing the ignition sensitivity and explosive violence of a dust cloud is the particle size or specific surface area (i.e. the total surface area per unit volume or unit mass of the dust). As the particle size decreases the specific surface area increases. The general trend is for the violence of the dust explosion and the ease of ignition to increase as the particle size decreases; though for many dusts this trend begins to level out at particle sizes in the micrometre range. Generally, the explosive ability of NOAAs is broadly similar to conventional micron-scale powders.



## 7 Risk Management Approach

This document has been developed to provide information and details to aid the development of risk management strategies (including the design and construction of appropriate infrastructure) to ensure the safe working and use of NOAAs.

### 7.1 General management approach

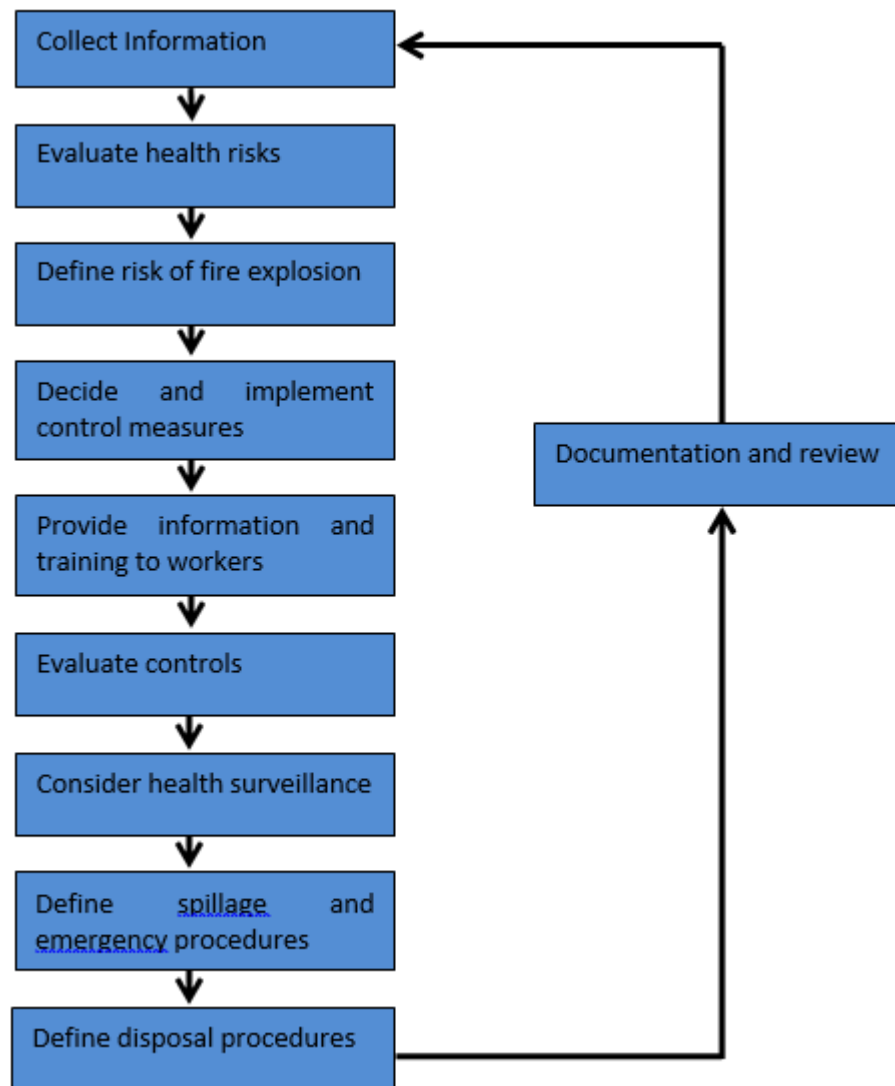
The health risk potential of engineered nanomaterials will depend on the nature of the nanomaterials, magnitude and period of exposures to airborne nanomaterials, and also on the transformation, release and dispersion. The implementation of exposure controls of nanomaterials in the workplace can be utilised to reduce the risk potential.

Risk assessment in the workplace follows a specific process comprising eight main steps:

- 1) Identify the hazards and assess the risks.
- 2) Decide what precautions are needed.
- 3) Prevent or adequately control exposure.
- 4) Ensure that control measures are used and maintained.
- 5) Monitor the exposure.
- 6) Carry out appropriate health surveillance.
- 7) Prepare plans and procedures to deal with accidents, incidents and emergencies.
- 8) Ensure employees are properly informed, trained and supervised.

One of the difficulties in applying this approach to nanomaterials is that the information available might be incomplete or, worse, incorrect. It is inappropriate in the absence of knowledge to assume that a nanoparticle form of a material has the same hazard potential as it has in a larger particulate form.

The general approach adopted for managing risks from NOAAs is illustrated in Figure 1.



**Figure 1 Approach to managing risks from NOAAs**

## 7.2 Gathering Information

The collection of information about the material, the work and the working practices involving NOAAs is vital to ensure an appropriate management strategy and an appropriate level of conservatism can be applied. It is important to consider both operational and other practices, such as maintenance and cleaning, including non-routine practices.

The following are examples of the types of information, and are not exhaustive:

- What are the commercial (or common) and technical names for the material?
- Is there a safety data sheet (SDS)?
- What is the chemical composition?
- What is the form of the nanomaterial (e.g. powder, agglomerated, pelletised)?
- Is nanomaterial present? In what proportions?
- Are the particles long and thin?

- What is the particle size distribution?
- How dusty is the material? How easily are particles released into the air?
- Is the material water soluble?
- How hazardous or toxic is the material?
- Are there materials which could be used instead of the nanomaterial that are potentially less hazardous, but still achieve the required end properties?

It is important to document both the information which is available and the information gaps. The information needs to be evaluated critically in terms of quantity and quality.

When considering answering the above questions the following pointers may aid in gathering information in sufficient detail:

**NOAA information and identification**

- NOAA name
- CAS Number
- structural formula/molecular structure
- composition of NOAA being tested
- basic morphology
- description of surface chemistry
- method of production

**Physicochemical properties and NOAA characterisation**

- agglomeration/aggregation
- solubility (e.g. in water or biologically relevant fluids)
- crystalline phase
- dustiness
- crystallite size
- representative TEM picture(s)
- particle size distribution
- specific surface area
- surface chemistry (where appropriate)
- catalytic or photocatalytic activity
- pour density
- porosity
- octanol-water partition coefficient, where relevant
- redox potential
- radical formation potential
- other relevant information (where available)

**NOAA toxicological data**

- pharmacokinetics (absorption, distribution, metabolism, elimination)
- acute toxicity
- repeated dose toxicity
- chronic toxicity
- reproductive toxicity
- developmental toxicity
- genetic toxicity
- experience with human exposure
- epidemiological data
- other relevant test data

When trying to gather information relating to the potential exposure scenarios the following questions should be considered (again this is not an exhaustive list):

- What are the processes which could lead to the release of NOAAs into the air or onto a surface?
- What are the tasks where people are potentially exposed to NOAAs (e.g. production, cleaning, accidental releases, maintenance, transport, storage and disposal)?
- Who can potentially be exposed during each task? The individual undertaking the task, adjacent workers, visitors, contractors, managers and others who might be exposed.
- What are the potential routes of human exposure (e.g. inhalation, ingestion, dermal penetration and accidental injection)?
- What is the chance of the exposure occurring? Consider operational work, accidental releases and maintenance (including non-scheduled maintenance).
- How often is exposure likely to occur (e.g. continuous over a working shift, intermittently or rarely)?
- What concentrations are people exposed to and for how long? This might require collection and assessment of existing data or collection of new data.

In addition, any relevant existing measurement data should be collected.

Emerging scientific evidence should be appropriately considered, and efforts made to keep up to date with the latest information. Relevant information will be available on safety data sheets, but it has been indicated that at the current time many of these do not adequately represent the nano forms of the material.

## 8 Control of Risk

### 8.1 Control of exposure

If exposure cannot be prevented, it should be adequately controlled. The hierarchy of control measures as applied to inhalation and dermal risks comprises the following:

#### Elimination

This is unlikely to be an option if the nanomaterial has been selected for its specific properties. However, consideration should be given as to whether the improved properties of the nanomaterial justify any enhanced risks associated with its use, including to the environment.

#### Substitution/modification

Change the nanomaterial or process to one which has less risk to human health, safety and the environment. Although it might not be possible to substitute that material or modify it without impacting on desired end properties, it might be possible to reduce the likelihood of exposure by, for example, binding powder nanomaterials in liquid or solid media. Dispersions, pastes or pelletised forms should be used instead of powder substances wherever this is technically feasible.

#### Enclosures/isolation

All operations in which there is deliberate release of NOAAs into the air or which involve the likely release of NOAAs into the air should be performed in contained installations, or where personnel are otherwise isolated from the process (e.g. in a cabin). This includes gas phase nanomaterial production and spray drying. All other processes involving the use of dry nanomaterials should be performed in enclosed installations where possible.

#### Engineering controls

All processes where there is a likelihood of dust formation should be carried out with extraction ventilation. Many types of extraction ventilation systems are available, including fume cabinets, fume hoods and dust extractors. Selection of appropriate controls will depend on the level of risk.

Regular maintenance and performance testing of extraction facilities should be carried out. Extracted air should not be re-circulated without exhaust air purification. General ventilation may also be appropriate.

Dermal exposure can be reduced by re-engineering the work process to avoid splashes or immersion.

#### Administrative controls

Procedural controls should accompany engineering controls. Procedural controls include reducing the number of personnel exposed or the time spent by personnel on the process,

limiting the process to specified areas and denying unauthorised persons access to these areas. The personnel involved should be informed of the specific hazards of free nanoparticles, the need for special measures, and the potential health effects of exposure to dusts. Routine monitoring should be carried out as needed. The use of medical surveillance should be considered.

Work wear should be cleaned by the user and stored separately from private clothing. Cleaning of workplaces should be carried out regularly, in line with risk control plans.

### **Personal protective equipment (PPE)**

Personal protection is a last option or a supplemental option to help support all of the other methods of exposure control.

- **Protection from inhalation exposure** - Certified respirators have been shown to provide stated level of protection for NOAAs and so are likely to form an important element of a control strategy where control of emissions at source is not practical. Appropriate types of respiratory protective equipment (RPE) include disposable filtering face-pieces, half and full facemasks and a range of powered (air supplied) hoods, helmets, blouses and suits. All wearers of tight fitting respirators (half-mask and full facemasks) should undergo face-piece fit testing to ensure correct fitting and proper wearing.

PPE, especially respiratory protection, needs a significant investment in training, supervision and maintenance if it is to provide the intended level of protection. Incorrect selection or fitting or insufficient use can render it ineffective.

- **Protection from dermal exposure** - The risk assessment might indicate a need for protective gloves, protection goggles with side protection and protective clothing. Nanosafe (2008) recommends the use of two layers of gloves. A number of other publications also note that it may be beneficial to use two layers of gloves. In regard to protective clothing, the report suggests: "For protective clothing, air-tight fabrics made of non-woven textile seem to be much more efficient to protect workers against nanoparticles than cotton. However these types of protective clothing may be less comfortable to wear". There are four basic criteria for the selection of protective gloves. They should:
  - 1) Be appropriate for the risk(s) and conditions where they are to be used.
  - 2) Be suitable for the ergonomic requirements and state of health of the intended wearer.
  - 3) Fit the intended wearer correctly.
  - 4) Prevent exposure without increasing the overall risk; assuming that the gloves are worn and maintained correctly.

## **8.2 Selection of controls**

In general, the purpose of applying controls is to ensure that exposure of the workforce is as low as reasonably practicable. In general, it is advisable to adopt a control as high in the control hierarchy as is technically and economically feasible.

It is difficult to make specific recommendations concerning the control approaches to be used in specific exposure situations. However several generic approaches can be applied which might be helpful.

### **8.2.1 Hazard-based control**

The basis of this approach is to allocate control methods based on knowledge of or assumptions about the hazardous nature of the materials being used.

### **8.2.2 Control banding**

Control banding (CB) is an approach by which control methods are selected based on knowledge or assumptions about the hazardous nature of the materials being used and the exposure potential of the situation. CB has frequently been used in risk management guidance for other particles and chemicals and is usually based on a matrix having the axes exposure and hazard into which various control approaches are placed. CB therefore requires the user to have knowledge of, or make judgments concerning, the relative hazard of the materials being used and/or the relative exposure potential of the material and situation.

### **8.2.3 “State of the art” approaches**

A limited number of studies have been published in peer-reviewed literature that describe the application and effectiveness of various control approaches for various exposure scenarios. While control approaches in general seem to be effective, there is evidence that indicates the potential for particle release into workplace atmospheres. Use of all control methods should therefore be supported by measurements of exposure or measurements of emissions, wherever possible.

## **8.3 Evaluation of the effectiveness of control**

The effectiveness of control approaches should be assessed. The purpose of applying controls as part of a precautionary approach, when hazard information is unavailable or when there is limited hazard information, is to ensure that exposure of the workforce is as low as practical. Collection of exposure information associated with the implementation of controls enables demonstration, and documentation, that effective control has been achieved.

Judgements considering whether effective control has been achieved could be made by comparison of measured levels.

## 9 Quantitative Management

### 9.1 Workplace exposure standards and exposure limits

Currently, there are only a limited number of exposure standards for nanoscale material. However, overseas agencies have recommended or proposed a number of exposure limits which are summarised in Table 3.

Table 3. Exposure standards for some types of nanoparticles

Substance	Type of standard	Size of material	Exposure standard (8 hr TWA mg/m <sup>3</sup> )
Carbon black	Australian WES	Nanomaterial	3
Carbon nanofibres including CNTs, Proposed	NIOSH REL	Nanomaterial	0.007
Fullerenes	AIST	Nanomaterial	0.39
Crystalline Silica	Australian WES	Respirable	0.1
Amorphous Silica	Australian WES	Inhalable	10
Fumed Silica	Australian WES	Nanomaterial	2
Titanium dioxide	Australian WES	Inhalable	10
Titanium dioxide	NIOSH REL	Fine size fraction	2.4
Titanium dioxide	NIOSH REL	Nanomaterial	0.3

WES	workplace exposure standard
CNT	carbon nanotubes
NIOSH	the National Institute for Occupational Safety and Health (USA)
REL	recommended exposure limit
Fullerenes	similar in structure to graphite
AIST	National Institute of Advanced Industrial Science (Japan)

#### Notes:

- NIOSH RELs for titanium dioxide is 10 hour TWA values not 8 hour TWA.
- NIOSH's proposed REL for carbon nanotubes (CNT) is based on a measurement detection limit of 7µg/m<sup>3</sup> of elemental carbon as an 8 hr TWA respirable mass airborne concentration.

### 9.2 BSI Benchmark Exposure Levels (BELs)

In 2010, Worksafe Australia published a document reviewing a British Standards Institute (BSI) guidance publication on Benchmark Exposure Levels (BELs). The BELs Guide provides recommendations for four nanoparticle hazard types (also see 9.2.1 and Table 4).

- Fibrous nanomaterials.



- CMAR nanomaterials.
- Insoluble nanomaterials.
- Soluble nanomaterials.

BELs differ from exposure standards, which are generally based on known health effects and the results of epidemiological studies. The use of BELs supports a precautionary approach to the control of exposures. The workplace exposure limits (WELs) are often available for the bulk material of various nanomaterial chemicals. Not all nanomaterials have bulk chemicals which have WELs.

Table 4. BSI categorisation of nanoparticle hazard types and example materials

<b>Nanoparticle hazard types</b>	<b>Suggested BEL</b>	<b>Groups of engineered nanomaterials</b>
Fibrous nanomaterials	0.01 fibres/ml	Carbon nanotubes, nanowires
CMAR nanomaterials	0.1 x *WEL bulk material Typically expressed as a mass concentration	Ni nanoparticles
Insoluble nanomaterials	0.066 x *WEL bulk material Typically expressed as a mass concentration	Nanocrystals, quantum dots, ceramic oxides, metals
Soluble nanomaterials	0.5 x * WEL	Lipid-type nanoemulsions, dendrimer-type drug delivery systems

\*WEL bulk material: i.e. exposure standard for the bulk form of the chemical

### 9.2.1 Hazard type groupings (BSI Guide)

Although the four nanoparticle hazard types provide a summary of the common types of engineered nanomaterials which occur in industry, it should be noted that some nanomaterials may cross over between different hazard types. Therefore, if you are using this approach, it is appropriate to review the BELs recommended in the BSI Guide by hazard type sequentially, examine measurement of exposure, and examine whether exposure levels below the BELs are achievable in practice.

#### Fibrous nanomaterials

Fibrous nanomaterials are insoluble nanomaterials defined by their high aspect ratio. They would conform with the definition of regulated fibres as used for counting purposes according to the World Health Organization, Safe Work Australia, and the British Health & Safety Executive, which is a particle of length >5 µm, and diameter <3 µm, and with an aspect ratio (length to diameter) of >3:1 (Donaldson et al, 2006). The most common nanomaterials in this group are carbon nanotubes and nanowires.

#### Nanomaterials classified as carcinogenic, mutagenic, asthmagenic or reproductive toxins (CMAR)

Nanomaterials classified as CMAR are nanoparticles already classified in their larger form as carcinogenic, a reproductive toxin, asthmagenic or mutagenic. Examples of CMAR nanomaterials are nickel nanoparticles or quantum dots which contain the carcinogen cadmium.

### **Insoluble nanomaterials**

This category is defined as insoluble or poorly soluble nanomaterials not in the fibrous or CMAR category. Common nanomaterials in this group are quantum dots (which may also be CMARs), fullerenes, TiO<sub>2</sub>, ZnO, Ag and CeO<sub>2</sub>.

### **Soluble nanomaterials**

Soluble nanomaterials, as defined in the BSI Guide, are nanomaterials which do not belong in the fibrous or CMAR category and which are soluble. Most engineered nanomaterials have low solubility. However, water soluble fullerenes have been found to be phototoxic. The cytotoxicity of water-soluble fullerenes disrupts normal cellular function through lipid peroxidation, responsible for cell membrane damage.

#### **9.2.2 BELs in the Australian context**

The CSIRO has adopted the same four nanoparticle hazard-based groups and BELs as the BSI Guide, and developed its own in-house risk assessment tool. The CSIRO perspective on the management of risk within their workforce is often supported by a tradition of good technical support.

Discussions with some nanotechnology industry representatives indicated that the existence of the BSI Guide was known, and industry would prefer quantitative risk assessment in most cases. The local industry may be in favour of BELs, provided they are supported by a solid body of toxicological knowledge. BELs can be attractive to industry because they could allow companies to have a sense of certainty about the expectations of the local regulatory bodies.

[APPENDIX A](#) provides additional details about setting self-imposed (in-house) BELs.

# 10 Qualitative Management

## 10.1 Introduction

Control banding (CB) is a qualitative risk management process. CB can be defined as:

A strategy or process in which a single control technology (such as general ventilation or containment) is applied to a defined range or band of exposure to a chemical (such as 1–10 mg/m<sup>3</sup>), that falls within a given hazard group (such as harmful by inhalation or irritating to respiratory system) (Safe Work Australia, 2010).

CB is a pragmatic approach which can be used for the control of workplace exposure to possibly hazardous agents with unknown or uncertain toxicological properties and for which quantitative exposure estimations are lacking.

In general, control banding is based on the idea that while workers can be exposed to a diversity of chemicals, implying diversity in risks, the number of common approaches to risk control is limited. These approaches are grouped into levels based on how much protection the approach offers (with “stringent” controls being the most protective). The greater the potential for harm, the greater the levels of protection needed for exposure control.

The control banding approach allows shifting from exposure assessment to exposure control and vice versa. Thus it can be performed either in a proactive way, based on anticipated exposures and using basic factors mitigating exposure potential, or in a retroactive way (or risk banding approach), based on a risk assessment that will take more exposure mitigating factors into account including control measures actually implemented or to be implemented.

The general structure of the control banding process is presented in Figure 2 and includes the following elements:

- Information gathering.
- Assignment of the NOAA to a hazard band: hazard banding.
- Description of potential exposure characteristics: exposure banding.
- Definition of recommended work environments and handling practices: control banding.
- Evaluation of the control strategy or risk banding.

### Hazard banding

Hazard banding consists in assigning a hazard band to NOAA on the basis of a comprehensive evaluation of all available data on this material, taking into account parameters such as toxicity, in vivo biopersistence and factors influencing the ability of particles to reach the respiratory tract, their ability to deposit in various regions of the respiratory tract, their ability to elicit biological responses. These factors can be related to physical and chemical properties such as surface area, surface chemistry, shape, particle size. (Refer to [APPENDIX B1.](#))

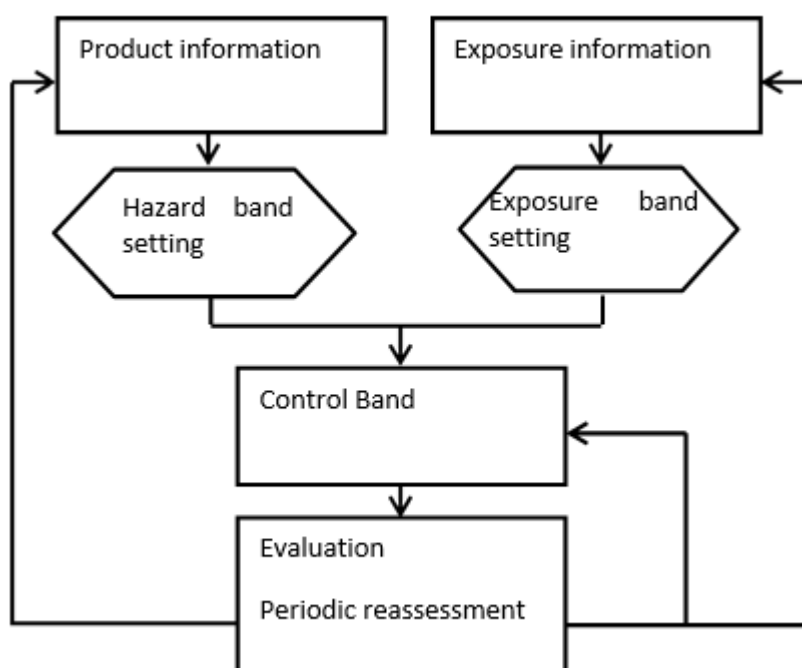
## Exposure banding

Exposure banding consists in assigning an exposure scenario (a set of conditions under which exposure may occur) at a workplace or a workstation to an exposure band on the basis of a comprehensive evaluation of all available data of the exposure scenario under consideration, e.g. physical form of NOAA, amount of NOAA, dust generation potential of processes and actual exposure measurement data. (Refer to APPENDIX B2.)

### 10.2 Proactive implementation

Work environments and handling practices may be defined on the basis of hazard banding as well as fundamental factors mitigating anticipated exposure potential, e.g. propensity of the material to become airborne, the type of process and amounts of material being handled.

Such an approach is used to determine the control measures appropriate for the operation being assessed but not to determine an actual level of risk, as the existing control measures, if any, are not used as an input variable in the exposure banding process.



**Figure 2 Control banding process**

Control bands are obtained by matching the hazard band and the exposure potential band according to the matrix given in Table 5.

Table 5. BSI categorisation of nanoparticle hazard types and example materials

Hazard Band	Exposure potential band			
	EB 1	EB 2	EB 3	EB 4
A	CB1	CB1	CB1	CB2
B	CB1	CB1	CB2	CB3
C	CB2	CB3	CB3	CB4
D	CB3	CB4	CB4	CB5
E	CB4	CB5	CB5	CB5

To achieve a balance of simplicity and effectiveness, five control categories (or bands) have been established, to assist in preventing exposure to NOAA. Conceptually, the five control approaches consist of:

**CB 1** - Natural or mechanical general ventilation

**CB 2** - Local ventilation: extractor hood, slot hood, arm hood, table hood, etc.

**CB 3** - Enclosed ventilation: ventilated booth, fume hood, closed reactor with regular opening

**CB 4** - Full containment: glove box/bags, continuously closed systems

**CB 5** - Full containment and review by a specialist: seek expert advice

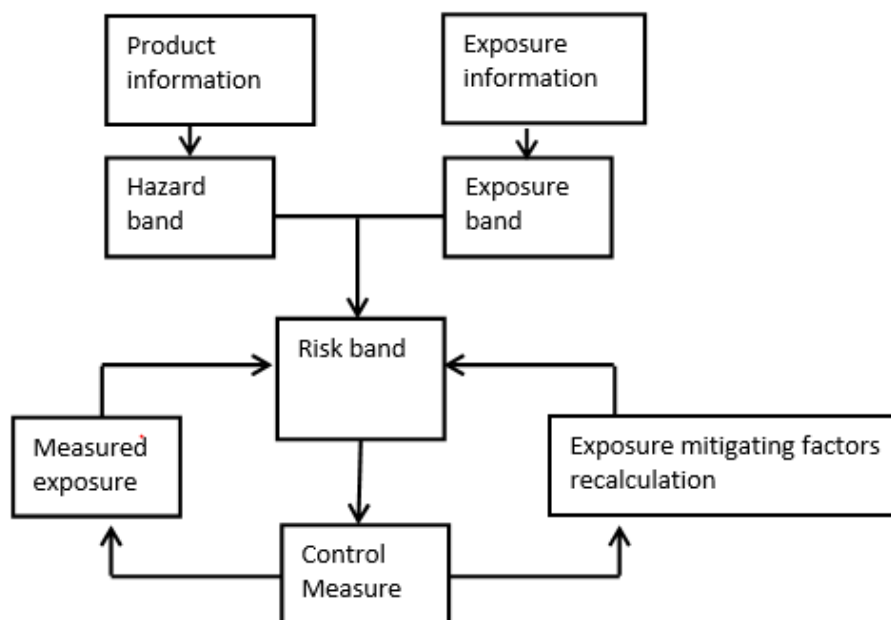
If the result of the control banding process is considered to be overly conservative, it is suggested to ask for expert occupational hygiene advice, considering the possibility to apply a lower control band. This decision should then be justified and the necessary documentation recorded.

### 10.3 Retroactive implementation

Control banding may be used either to evaluate the controls recommended as outputs of the proactive approach, or for risk assessment on its own. In that case, both hazard and actual exposure need to be characterised in order to define a risk level.

The approach then includes the following elements:

- assignment of the NOAA to a hazard band
- exposure banding
- overview of risks based on risk banding as a result of hazard and exposure banding
- iterative examination of control measures until the risk is reduced to an acceptable level
- design of an action plan based on the chosen specific control scenario.



**Figure 3 Evaluation and risk banding process**

The risk banding process is shown in Figure 3. In a risk banding strategy, emission, transmission and immission controls are taken into account to calculate the exposure band. This means that control measures which have already been implemented or might be implemented in a new process design, are being used as a variable input of the model. The hazard banding is the same as in the proactive approach (see APPENDIX B1).

After assignment of a hazard band to NOAA and a subsequent exposure banding is performed, a risk band is derived. A generic example is shown in Table 6. The resulting risk bands provide a relative ranking of risks from activities for individual workers. At this point in the risk banding process, no quantitative evaluation of exposure levels and hazard levels can be made because both exposure and hazards bands are based on qualitative considerations. The result of the risk banding should therefore be considered as a “priority band”.

Table 6. BSI categorisation of nanoparticle hazard types and example materials

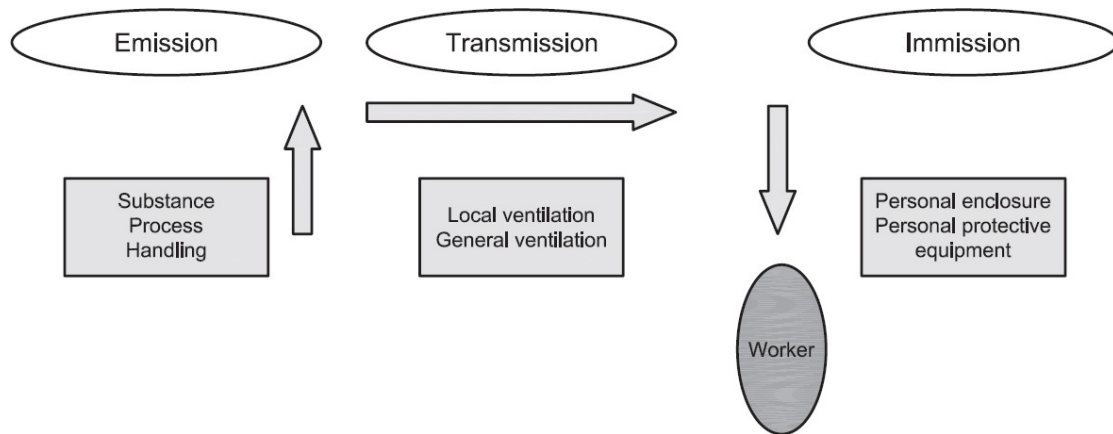
Hazard band	Exposure Band			
	1	2	3	4
A	Low	Low	Low	Medium
B	Low	Low	Medium	High
C	Low	Medium	Medium	High
D	Medium	Medium	High	High
E	Medium	High	High	High

# 11 Control Measures

Exposure should be minimised following the hierarchy of control.

## 11.1 Controls in the proactive approach

The severity of the NOAA hazard and the potential for emission are the factors which determine the recommended controls in the proactive approach to control banding. The outputs of the proactive approach are recommended controls to reduce emission, transmission and immission and hence to mitigate exposure, illustrated in Figure 4.



**Figure 4 Exposure mitigating factors**

### Reduction of emission

The reduction of NOAA emission from the source can be achieved in several ways such as handling NOAA in suspension into a liquid or dispersed into a paste or a solid matrix rather than in the form of dry powders; avoiding high energy processes or any activity likely to release free NOAA in the workplaces.

### Reduction of transmission

Reduction of transmission from the source towards the worker is possible in several ways. Two generic control measures are:

- Local control, e.g. containment and/or local exhaust ventilation.
- General ventilation, e.g. natural or mechanical ventilation.

### Reduction of immission

The reduction of emission has three generic control measures:

- Personal enclosure/separating the worker from the source, e.g. a ventilated cabin.

- Segregation of the source from the worker, i.e. isolation of sources from the work environment in a separate room without direct containment of the source itself.
- Use of personal protective equipment.

## 11.2 Further control measures

The need to implement further control measures would be determined by the priority band, high being highest priority. The following (generic) control measures can be distinguished.

- Measures that have impact at the source:
  - Removal of the hazardous product from the task.
  - Removal of the task from the process.
  - Modification of the product form.
  - Modification of the task, e.g. instead of 'frequent handling' the task can be modified to 'handling in closed systems'.
  - Replacement of the product by another product with a different composition, changing the hazard and possibly also the exposure.
  - Automation of the process, leading to a whole new exposure assessment.
  - Changing the order of tasks, e.g. adding powder to liquid instead of the other way around.
- Measures in an area directly around the source:
  - Glove box/bags.
  - Enclosure of the source in combination with local exhaust ventilation (e.g. fume cupboard).
  - Enclosure of the source.
  - Local exhaust ventilation.
  - Limiting the emission of a product (e.g. wetting powder).
- Measures affecting the worker's wide surroundings:
  - Creating and ensuring natural ventilation.
  - Installing mechanical general ventilation.
  - Use of a spray cabin.
- Adaptation of the workers situation:
  - Use of work cabins with clean air supply.
  - Use of work cabins without clean air supply.
- Personal protective equipment:
  - Use of respiratory protective equipment.

In comparison to the proactive approach, a retroactive approach presents a complete control strategy according to the STOP principle. This guides a user to start minimising exposure at the first order of control, i.e. measures that have impact at the source.



### **11.3 Evaluation of controls**

There are a number of ways whereby the effectiveness of the controls can be evaluated and validated:

- Measurement of exposure levels and comparison with published NOAA exposure standards or BELs.
- Determination of the hazard band for the NOAA - comparison of mass concentration measured exposure levels with the OEL ranges for the nanomaterial's hazard band.
- Characterisation of workplace aerosols based on number concentrations - information on evaluating exposure control approaches can be found in ISO/TS12901-1.
- Evaluation of controls in place using a risk banding approach.

This evaluation should be performed periodically, and control measures improved whenever needed.

### **11.4 Workplace area and personal exposure monitoring data**

When feasible, actual exposure measurements provide important information on the effectiveness of controls and workers protection level.

# 12 Measurement Methods for Evaluating Controls

Particle sampling and measurement is often needed to understand exposure and risk in workplace scenarios. Measurement can be used to support various activities, including:

- Identifying sources of nanomaterial emissions.
- Assessing the effectiveness of any control measure implemented.
- Ensuring compliance with any OEL or self-imposed (in-house) exposure standard.
- Identifying any failures or deterioration of the control measures that could result in a serious health effect.

Each of these tasks requires specific and often different types of instrumentation. In the workplace, airborne NOAAs will be a combination of primary particles and agglomerates (mainly) and aggregates. The need to detect and measure all these forms is a significant factor in determining an appropriate sampling strategy.

## 12.1 Selection of instruments

Many instruments are available that could be used to measure airborne NOAAs. New instruments are also being developed. A summary of currently available devices and methods (as of 2012) for direct measurement of number, mass and surface area concentration is provided in Table 7.

Table 7. Devices for direct measurement of number, mass and surface area concentration

Measured Object	Devices	Remarks
Measured particle number concentration	Condensation particle counter (CPC)	CPCs provide real-time number concentration measurements between their particle diameter detection limits. They operate by condensing vapour onto sampled particles and detecting/counting the droplet formed. Typically used with a 1,000 nm size selective inlet and able to detect down to around 10 nm.
	Differential mobility particle sizer DMPS	Real-time size-selective (mobility diameter) detection of number concentration, giving number-based size distribution.
	Electron microscopy: SEM, TEM	Offline analysis of electron microscope samples can provide information on size-specific aerosol number concentration.
Measured mass concentration	Size selective static sampler	Assessment of the mass of nano-objects can be achieved using a size-selective personal sampler with a cut-off point of approximately 100 nm and the sample analysed by gravimetric weighing or by chemical analysis. Although there are no commercial devices of this type currently available, some cascade impactors (Berner-type low pressure impactors or Microorifice impactors) have selection points

around 100 nm and can be used in this way.

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TEOM		Sensitive real-time monitors, such as the TEOM, can be used to measure nano-aerosol mass concentration on-line, with a suitable size-selective inlet.
Measured particle surface area concentration	Diffusion charger	Real-time measurement of aerosol active surface area. Note that active surface area does not scale directly with geometric surface area above 100 nm. Not all commercially available diffusion chargers have a response that scales with particle active surface area below 100 nm. Diffusion chargers are only specific to nano-objects if used with an appropriate inlet pre-separator.
	Electrostatic low pressure impactor	Real-time size-selective (aerodynamic diameter) detection of active surface area concentration. Note that active surface area does not scale directly with geometric surface-area above 100 nm.
	ELPI	
	Electron microscopy: SEM, TEM	Offline analysis of electron microscope samples can provide information on particle surface area with respect to size. TEM analysis provides direct information on the projected area of collected particles, which could be related to geometric area for some particle shapes.

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## 12.2 Sampling strategy

Currently, there is no single sampling method that can be recommended to be used to characterise exposure to all particulate forms of nanomaterials. Therefore, attempts to characterise workplace exposure to NOAAs usually involve a multifaceted approach incorporating more than one of the sampling techniques mentioned above.

This is typically a stepwise process that involves an initial assessment of particle number concentration using a simple device such as CPC. Identification of this release in itself may be sufficient to reconsider the control systems and adapt better engineering control measures to more effectively control the release.

If measuring exposures to specific NOAAs is of interest, personal sampling using filters or grids suitable for analysis by electron microscopy or chemical identification should be employed.

The use of a personal cascade impactor or a respirable cyclone sampler with a filter, though limited, will help to remove larger particles that are of limited interest and allow a more definitive determination of particle size. Analysis of these filters for air contaminants of interest can help identify the source of the respirable particles. Standard analytical chemical methodologies, including gravimetric analysis, should be employed. Typically, a qualified occupational hygienist is needed to conduct this assessment.

By using a combination of these techniques, an assessment of worker exposure to NOAAs can be conducted. This approach will allow a determination of the presence and identification of NOAAs and the characterisation of the important aerosol metrics.

## 12.3 Limitations

Measuring particle number concentration in isolation can be misleading. In all particle number concentration measurements, the integration limits over which a particular instrument operates are critical in understanding the reported results.

A further complication relates to the ambient airborne particles. Unless the workplace is operating under clean room conditions, airborne particles from external sources will enter the workplace and contribute to the levels of NOAAs in the area of the process under investigation. Other nanoparticles, which might be produced in the vicinity of the task/process that is monitored, e.g. from heaters or from electric motors, may also contribute towards overestimation.

One way to overcome this problem is to determine ambient or background particle counts prior to the commencement of manufacturing or processing of the NOAAs. Another method is to carry out simultaneous measurement in the “near field” (close to the process/task) and the “far field” (away from the task/process).

Filter sampling of airborne nanoparticles yields very small particle mass (less than 0.1 mg), and numerous errors are associated with gravimetric analysis of such low-mass samples. Errors caused by static electricity, vibration, and particle contamination should be eliminated, and filters should be conditioned and weighed under strict protocols designed to control effects of humidity and air temperature.

## 13 Health Surveillance

The primary criterion for health surveillance is a reasonable likelihood that an identifiable disease or ill-health effect associated with exposure to a particular substance will occur in the workplace concerned. It is also necessary that there are medically accepted techniques for detecting the disease or ill-health effect.

Based on experience with other particles such as crystalline silica and asbestos, exposure to recently developed forms of engineered NOAs might be expected that adverse health effects could have a long latency in development of disease associated with such exposure.

Studies in animals have shown adverse effects (e.g. pulmonary inflammation and fibrosis) at lower mass doses than for larger particles of the same chemical composition. This suggests the need to consider whether medical screening tests such as those used to detect occupational respiratory diseases might be appropriate for workers exposed to NOAs.

In any case, a prudent approach in the current uncertainty is to collect at least some limited information about the materials being used and the duration of use. Such information will help to build up a profile of potential exposures which could be important for future epidemiology studies, should any health effects emerge in the exposed population at a later date.

## 14 Prevention of Fire and Explosion

Prevention of fire and explosion is governed by national standards (AS/NZS60079-10-2).

Some types of nanoparticle products can be raised from a layer and become airborne more easily than coarser products, and can remain in suspension for a long time. The same principles applying to the management of fine powders, dusts or dusty materials should be considered for nanoparticles, with particular care taken in the case of easily oxidisable metallic dust. Explosion protection measures have been described for dust dispersions and for hazardous quantities of larger sized materials, and these can be applied to the handling of potentially explosive nanoparticles. For reactive or catalytically active nanoparticles, contact with incompatible substances should be prevented.

Fire prevention has to take into account existing regulations, especially electrical requirements. The design of electrical equipment protection should take account of the fine granulometry and very long settling time of nanoparticles, which necessitate dust protection. In addition, further precautions should be taken to avoid the risk of auto-ignition of NOAAs.

The selection of an extinguishing agent should take account of the compatibility or incompatibility of the nanomaterial with water. Some metallic dusts react with water to form, among other things, hydrogen, which ignites very easily. Chemical powders are available to extinguish burning metallic dust powders, though this has the effect of putting the metallic dust in suspension, thereby increasing the risk of deflagration. To reduce the risks of fire and deflagration, it might prove necessary to use controlled atmosphere production and storage processes, using carbon dioxide, nitrogen or another inert gas. This could introduce further hazards into the system, notably the risk of asphyxiation.

Anti-static shoes should be worn in areas where the materials are handled to reduce the build-up of static charge, which could potentially ignite the materials.

# 15 Spillages and Accidental Releases

## 15.1 Introduction

Due to the potential for spillages and accidental releases of NOAAs, it is essential that each user area has documented policies and procedures in place that are based on adequate pre-planning activities. This documentation should include incidental (small) and emergency (uncontrolled) spills/releases.

It is vital that suitable and sufficient risk assessments are completed to determine the exact course of action to be taken in the event of a nanomaterial spillage or accidental release. The methods used should be consistent with the level of hazard and the quantity of nanomaterial involved in the spill. All clean-ups should be carried out in such a way as to ensure that exposure to personnel is as low as practical.

Personnel who might be required to deal with such events should receive adequate information, instruction and training on assessing the extent of any spill/accidental release, the clean-up measures to be taken, and the PPE which should be worn, as well as guidance on the safe disposal of any waste collected during the clean-up.

## 15.2 The event of a spillage or accidental release

In the event of a spillage or accidental release, on-site personnel should determine the extent of the area potentially affected and demarcate the area to restrict access by non-essential personnel. Measures should also be put in place to reduce the likelihood of spreading NOAAs from the affected areas, for example the use of adhesive walk-off mats at the affected area's exit points.

In situations where on-site personnel might reasonably be expected to deal with a spillage or accidental release of NOAAs, consideration may be given to the use of:

- Wet wiping cleaning methods (dry sweeping should be avoided).
- Barriers to minimise air currents across areas affected by a spillage.
- Tested and certified "HEPA" vacuum cleaner methods for dealing with dry materials or residues from dried liquid spill areas.

When using HEPA filters, it is recommended that the effectiveness of these should be verified at a frequency consistent with manufacturers' recommendations and, where possible, dedicated HEPA vacuum cleaners should be used for clean-up operations. It is also good practice to record the type of material collected and avoid mixing potentially incompatible materials in the vacuum cleaner or filters.

The faculty along with emergency planning need to consider and document which, if any, situations should trigger an evacuation of personnel from an affected area. Consideration should also be given to the severity of spillages and accidental releases which on-site

personnel can be expected to deal with and when other agencies, such as the emergency services, WorkSafe and/or WA Department of Health, need to become involved.

All debris resulting from the clean-up of a spillage or accidental release (including any filters, wipes, absorbent mats and materials) should be considered as nanomaterial-bearing waste.



# 16 Disposal Procedures

## 16.1 Planning the storage and disposal of nanomaterials

A plan for storage and disposal of NOAAs or NOAAs contaminated waste should be developed, taking account of the hazard profile of the materials and the quantities involved.

When the nanomaterial has a known hazard profile, disposal should be planned in accordance to this profile in line with Western Australian waste requirements.

The waste management guidance given here is based on guidance developed and used by the US Department of Energy (DOE2007) and the UK Environment Agency (EA) Guidance for the disposal of hazardous materials (HWR01), and applies to hazardous or potentially hazardous nanomaterial bearing waste streams (solid and liquid waste), including:

- Pure NOAAs.
- Items contaminated with NOAAs, such as containers, wipes and disposable PPE.
- Liquid suspensions containing NOAAs.
- Solid matrices with NOAAs that are friable or have a nanostructure loosely attached to the surface such that they can reasonably be expected to break free or leach out when in contact with air, water, or other media when subjected to reasonably foreseeable mechanical forces.

Any material that has come into contact with dispersible engineered NOAAs (that has not been decontaminated) should be considered as belonging to a nanomaterial-bearing waste stream. This includes PPE, wipes, blotters and other disposable laboratory materials used during research activities.

Material from hazardous or potentially hazardous nanomaterial-bearing waste streams should not be put into the regular waste or down the drain.

Surface contamination should be evaluated and decontaminated. Equipment used to manufacture or handle hazardous or potentially hazardous nanomaterials should be decontaminated before it is disposed of or reused. Wastes (cleaning solutions, rinse waters, rags, disposable PPE) resulting from decontamination should be treated as nanomaterial-bearing waste.

## 16.2 Storage of nanomaterial waste prior to disposal

The following are appropriate approaches for collection and storage of hazardous or potentially hazardous nanomaterial waste prior to disposal.

### Storage in waste containers

Package nanomaterial-bearing wastes in compatible containers that are in good condition and afford adequate containment to prevent the escape of the NOAAs. NOAAs or wastes

should not be stored in storage silos or other large containers; particularly the more dispersible forms. Cleaning up spills could be very difficult if a large container fails. Label the waste container with a description of the waste and include available information characterizing known and suspected properties.

### **Storage in plastic bags**

Paper, wipes, PPE and other items with loose contamination should be collected in a plastic bag or other sealable container stored in the laboratory hood. When the bag is full, it should be closed and carefully placed into a second plastic bag or other sealing container, avoiding outside contamination. It should then be taken out of the hood and the outer bag be labelled with an appropriate waste label.

### **16.3 Disposal of nanomaterial waste**

Disposal of nanomaterial waste should comply with state and national regulations. Few national authorities have, so far, made any specific recommendations regarding disposal of nanomaterial waste. The disposal process should depend on an assessment of the hazard and physicochemical characteristics.

One example in the UK, guidance provided by the Environment Agency (EA), provides a framework for assessing whether a waste material is hazardous and a process by which it can be disposed. EA currently considers, as a precautionary approach, **classifying unbound carbon nanotubes as inorganic wastes containing dangerous substances with a threshold level of 0.1 % weight/weight. Their recommendation is that the waste can be rendered safe by incineration by exposure to temperatures above 850 °C for at least 2 seconds or by being treated chemically in such a way as to destroy the nanodimensional structure, which renders the material toxic.** They consider high temperature incineration at a hazardous waste incinerator as the preferred disposal method. However, this approach will not be suitable for all NOAAs and the potential release of the original and/or transformed nanoparticles should be considered and prevented. Other technologies may be suitable if it can be demonstrated that they render the wastes safe.

# 17 Revision and Updates

## 17.1 Revision procedure

This guidance document has been developed as a living document that reflects the changes in legislation, standards and guidelines available. This plan will therefore be subject to periodic review and new editions published. It is important that readers assure themselves that the current management plan is being referenced and that current standards including any amendments, legislation and/or guidance are being used.

As a minimum it is intended this document will be updated every three years.

Throughout this document various web links have been provided to Curtin's internal documents and other third party documents. These links are subject to change with updating information. Every effort will be made to ensure internal Curtin University links remain active. Curtin University has no control over external websites and/or documentation. If a link does not work it is recommended going to the home page of the website being referenced and search for the required document.

A revision history is provided at the front of this document.

## 17.2 Request/Recommendation log

A log of requests/recommendations shall be maintained by the document owner.

Change requests/recommendations should be submitted in the format below via email to:

[propertiesbusinesssupport@curtin.edu.au](mailto:propertiesbusinesssupport@curtin.edu.au)

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<b>Name</b>	<b>Company &amp; Position</b>	<b>Detail of Change Request</b>	<b>Urgency of Request (High, Medium, Low)</b>

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## 18 References and Further Reading

- ISO/TS 12901-2 Nanotechnologies — Occupational risk management applied to engineered nanomaterials —Part 2: Use of the control banding approach; First edition 2014-01-15
- Donaldson, K., Aitken, R., Tran, L., Stone, V., Duffin, R., Forrest, G., Alexander, A., 'Carbon nanotubes: A review of their properties in relation to pulmonary toxicity and workplace safety', *Toxicological Sciences*, 92, 2006, 5-22.
- Engineered Nanomaterials: Feasibility of establishing exposure standards and using control banding; Safe Work Australia, August 2010
- Engineered nanomaterials: Evidence on the Effectiveness of Workplace controls to prevent exposure; Safe Work Australia, November 2009
- Evaluation of Potential safety (Physicochemical) hazards associated with the use of engineered nanomaterials; Safe Work Australia, March 2013
- Human health hazard assessment and classification of Carbon nanotubes; Safe Work Australia, October 2012a
- Measurements of particle emissions from nanotechnology processes with assessment of measuring techniques and workplace controls; Safe Work Australia, September 2012b
- Nanosafe, Safe production and use of materials. Are conventional protective devices such as fibrous media, respirator cartridges, protective clothing and gloves also efficient for nanoaerosols? Dissemination report, DR-325/326-200801-1, 2008.  
[http://www.nanosafe.org/cea-tech/pns/nanosafe/en/Documents/DR1\\_s.pdf](http://www.nanosafe.org/cea-tech/pns/nanosafe/en/Documents/DR1_s.pdf)
- Nanotechnology – Government of Western Australia, Department of Commerce; WorkSafe Bulletin 3/2011
- Safe Handling and Use of Carbon Nanotubes; Safe Work Australia 2012c

# Appendix A – Examples of approaches to setting benchmark levels for nano-objects

## A.1 General

In the absence of specific OELs, for many types of NOAAs some focus has been given to setting of benchmark levels to provide pragmatic guidance for those trying to estimate and control exposures. This section elaborates the process in relation to one such approach which has been promulgated in the original version by Institut fuer Arbeitsschutz der Deutschen Gesetzlichen Unfallversicherung (IFA) in Germany.

## A.2 Approach for particles

In setting benchmark levels to assess the effectiveness of protective measures, it is crucial to point out that they should not be confused with health-based workplace limit values. There is limited toxicological data to support these benchmark levels.

Any pragmatic proposal for assessment of the effectiveness of protective measures against exposure to NOAAs should take account of the following requirements.

- As a result of missing information on a product, a precautionary approach should be adopted.
- Under no circumstances may a general dust limit value (currently given in mg/m<sup>3</sup>) be exceeded as an upper limit.
- The proposed recommended bench mark level should permit simple technical monitoring. More far-reaching, complex, imaging study methods cannot be employed in routine operations.
- To derive benchmark levels one has to consider the properties of NOAAs.
- The OECD's Working Party on Manufactured Nanomaterials has agreed on a prioritised list of nanomaterials that are to be addressed. For the majority of these materials, Table A1 shows the calculated particle number concentration (CPN) that corresponds to a mass concentration of
- 0.1 mg/m<sup>3</sup> for spherical particles with diameters, d, of 20 nm, 50 nm, and 100 nm. 0.1 mg/m<sup>3</sup> is one order of magnitude below the currently used dust limit values.

Table A1 Calculated particle number concentration CPN, corresponding to a mass concentration of 0.1 mg/m<sup>3</sup>, for differently size spherical particles of various nanomaterials

Table 1. Devices for direct measurement of number, mass and surface area concentration

Density p(g/cm <sup>3</sup> )	Calculated number of density of nano-particles	Calculated number of density of nano-particles	Calculated number density of nano-particles
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	of dimension 20nm $C_{PN},(cm^{-3})$	of dimension 50 nm $C_{PN},$ $(cm^{-3})$	of dimension 100 nm $C_{PN},$ $(cm^{-3})$
1,05	$22,74 \times 10^6$	$1,46 \times 10^6$	$181,90 \times 10^3$
1,35	$17,68 \times 10^6$	$1,13 \times 10^6$	$141,47 \times 10^3$
1,65	$14,47 \times 10^6$	$0,93 \times 10^6$	$115,75 \times 10^3$
4,24	$5,63 \times 10^6$	$0,36 \times 10^6$	$45,40 \times 10^3$
5,61	$4,26 \times 10^6$	$0,27 \times 10^6$	$34,04 \times 10^3$
7,30	$3,27 \times 10^6$	$0,21 \times 10^6$	$26,16 \times 10^3$
7,87	$3,03 \times 10^6$	$0,19 \times 10^6$	$24,26 \times 10^3$
10,49	$2,28 \times 10^6$	$0,15 \times 10^6$	$18,21 \times 10^3$
19,32	$1,24 \times 10^6$	$0,08 \times 10^6$	$9,89 \times 10^3$

Particle number concentration, CPN, is required for attainment of a mass concentration of 0.1 mg/m<sup>3</sup> with nanoparticles of the stated size, in nm.

The particle number concentration, CPN, of nano-particles at the benchmark level has been derived by Formula (1)

$$C_{PN} = \frac{c_m}{m_{NP}} \quad (1)$$

where

$c_m$  is the mass concentration;

$m_{NP}$  is the mass of a single nano-particle, calculated by Equation 2:

$$m_{NP} = \frac{\pi d^3 \rho}{6} \quad (2)$$

where

$\pi$  is the mathematical constant 3,141592654...;

$d$  is the diameter of the nanoparticles;

$\rho$  is the density of the nanoparticles.

**Note:** As an approximation, the density of the macroscopic bulk material is used and the nano-particles are assumed to be spherical nanoparticles with diameter,  $d$ .

For 100 nm particles with a density of 19,320 kg/m<sup>3</sup>, a particle concentration in air of 9,890/cm<sup>3</sup> of air would result in a mass concentration of 0.1 mg/m<sup>3</sup>. Application of the value of 20,000/cm<sup>3</sup>, as stated in the BSI PAS 136[2], to these particles with a size of 100 nm results in a mass concentration of approximately 0.2 mg/m<sup>3</sup>. This mass concentration is significantly below existing general dust limit values for the respirable dust fraction and thus can be viewed as an application of the precautionary principle.

Conversely, 20,000 of these particles with a size of 20 nm per cubic centimetre of air correspond to a mass concentration of only 0.0016 mg/m<sup>3</sup>. This would be substantially below any respirable dust limit value. At the same time, a concentration of 1,235,400 of these particles (with a size of 20 nm) per cubic centimetre, equivalent to 0.1 mg/m<sup>3</sup>, would be readily measurable and could be substantially reduced in application of the precautionary principle by technical protective measures.

Table A.2 also shows that the range in both the size of the nanoparticles and their density over more than one order of magnitude results in a range in particle number concentration of over three orders of magnitude. This range presents issues for current instruments like the CPC. In addition, the airborne concentration of the nanoparticles of interest might be difficult to distinguish from background particle concentration in typical industrial workplaces. The size and density of the nanoparticles should therefore be employed as classification criteria for derivation of the recommended benchmark levels.

### A.3 Approach for fibres

Applying the same arguments as above to nanofibres in general (i.e. nanorods and nanotubes), Formula (2) has to be modified according to Formula (4).

$$m_{NF} = \pi (d_e^2 - d_i^2) L \frac{\rho}{4} \quad (3)$$

where

$m_{NF}$  is the mass of a single nano-fibre;  $L$  is the length of the fibre;

$d_e$  is the exterior diameter of the fibre;

$d_i$  is the interior diameter of the fibre ( $D_i = 0$ : nanorod,  $D_i \neq 0$ : nanotube);

$\pi$  is the mathematical constant 3,141592654...;

$\rho$  is the density of the nanofibres.

Notes:

- The terms “nanofibre”, “nanotube” and “nanorod” are used here in the sense of ISO/TS27687.
- To define the density of a (single-wall) nanotube, as it was considered here, the mass of the wall was divided by the total volume of the tube. Another different definition of the density could refer to the size of an agglomerate of tubes and their respective mass which could result in different densities. In any case, one should clarify which definition of density is used. Therefore, in the following example carbon nanofibres using the density of graphite (2,26 g/cm<sup>3</sup>) and MWCNTs with a typical value of 0,32 g/cm<sup>3</sup> are compared (for simplicity, MWCNTs are considered as rods with that density).

Example: Table A2 shows the fibre number concentration which is necessary to reach a mass concentration of 0.1 mg/m<sup>3</sup> for fibres with a length of 5 µm, different exterior and interior diameters and densities.

Table 2. Calculated fibre number concentration,  $C_F$ , corresponding to a mass concentration of 0.1 mg/m<sup>3</sup>, for carbon nanofibers and MWCNTs with a length of 5 µm and different diameters

$\rho$ g/cm <sup>3</sup>	$d_e$ nm	$d_i$ nm	$C_F$ m <sup>-3</sup>	$C_F$ cm <sup>-3</sup>
2,26	0,5	0	$4,5 \times 10^{13}$	$4,5 \times 10^7$
	1		$1,1 \times 10^{13}$	$1,1 \times 10^7$
	2		$3 \times 10^{12}$	$3 \times 10^6$
	5		$5 \times 10^{11}$	$5 \times 10^5$
	0,5	0,4	$1,10 \times 10^{14}$	$1,10 \times 10^8$
	1	0,9	$8, \times 10^{13}$	$8,7 \times 10^7$
	2	1,9	$7,8 \times 10^{13}$	$7,8 \times 10^7$
	5	4,9	$7,3 \times 10^{13}$	$7,3 \times 10^7$
0,32	0,5		$3,18 \times 10^{14}$	$3,18 \times 10^8$
	1		$7,96 \times 10^{13}$	$7,96 \times 10^7$
	2		$2 \times 10^{13}$	$2 \times 10^7$
	5		$3 \times 10^{12}$	$3 \times 10^6$

Fibre number concentrations (CF) are required for attainment of a mass concentration of 0.1 mg/m<sup>3</sup> with fibres of length of 5 µm, different densities, exterior diameters and wall thicknesses (0.1 nm); all values are rounded.

Here the modified Formula (5) was used:

$$C_F = \frac{c_m}{m_{NF}} \quad (4)$$

where

C<sub>F</sub> is the fibre number concentration; c<sub>m</sub> is the mass concentration;

m<sub>NF</sub> is the mass of a single nanofibre.

In contrast to these results, BSI PAS 6699-2[14] recommends a number concentration of 104 fibres per cubic metre for fibrous NOAAs, with reference to the recommended British value for asbestos during remediation work, since bio-persistent nanotubes which satisfy the WHO fibre definition or have similar dimensions might have effects similar to those of asbestos.

However, workplace measurements have shown that concentrations of about 1 µg/m<sup>3</sup> can be reached when dealing with SWCNTs[73]. As can be shown from the example above, 1 µg/m<sup>3</sup> corresponds to about 109 fibres per cubic metre to 1011 fibres per cubic metre. This shows wide divergence between possible number-based benchmark values and practical experience.

At present, however, monitoring of the above value of 104 fibres per cubic metre in plants is hampered by a lack of collection methods of verified suitability, corresponding analysis methods, and criteria for counting the fibres and determining the fibre concentration.

In practical terms real-time instruments such as CPC would not be suitable to measure these low concentrations. 104 fibres per cubic metre is equivalent to 10<sup>-2</sup> fibres per cubic metre compared with typical lower detection limits of 10<sup>2</sup> fibres per cubic metre for these instruments. In addition, existing limit values for asbestos fibres concern free fibres in the workplace air whereas a lot of commercially available CNTs exist in complex structures e.g. from entangled bundles to pellets. No rule or convention is in place how these complex structures should be accounted for. An urgent need exists here for the development of analysis methods and conventions for interpretation.

#### A.4 Conclusions

The size and density of the nanoparticles should therefore be employed as classification criteria for derivation of the recommended exposure limits. Failure to consider this could result in orders of magnitude differences (in mass concentration terms) between aerosol exposures which are similar in number concentration terms.

For fibrous NOAAs the recommended BSI benchmark exposure level is a number concentration of 104 per cubic metre. However, this level may not be feasible to measure due in part to the lack of standardised counting methods for fibrous nanomaterials (how to count complex structures, etc.). In addition, the limit of quantification of CNTs on a mass basis is 1



$\mu\text{g}/\text{m}^3$ , which corresponds to approximately 109–1011 fibres per cubic metre. This indicates the need for developing sensitive sampling and analytical methods to detect and quantify CNT at health-based exposure limits.

More information on the original approach is given on the IFA website at [www.dguv.de/ifa/en/fac/nanopartikel/beurteilungsmassstaebel/index.jsp](http://www.dguv.de/ifa/en/fac/nanopartikel/beurteilungsmassstaebel/index.jsp).

## Appendix B - Hazard Band Setting

### B.1 Hazard bands

Hazard bands are defined, for a specific chemical, according to the severity level of the hazard resulting from the analysis of the available information as evaluated by knowledgeable and experienced professionals. This information can relate to various criteria for toxicity, described or suspected, in the literature or technical documentation (labelling, product classification).

The approach presented in the International Labour Organization Control Banding Toolkit is to group chemicals into one of five inhalation hazard groups (A to E) and the Skin (S) group according to the increasing severity described in GHS hazard classification applicable to the chemical. The dose ranges given in this table correspond to the criteria set for classification under GHS. Hazard band allocation can vary depending on any statutory provisions.

### B.2 Allocation of a NOAA to a hazard band

The hazard banding process follows a tiered approach which is summarised in Figure B.1.

a) Question 1: Has the NOAA already been classified and labelled according to national or regional legislation or GHS?

The completeness of the data set used for the classification and labelling should be evaluated and if classification and labelling is based on the lack of information, the “NO” option described below should be applied.

If “YES”, then the identified human health hazards of the material should be used to assign the NOAA to the corresponding Hazard Band.

If “NO” then proceed to Question 2.

b) Question 2: Is the NOAA solubility in water higher than 0.1 g/l?

It is important not to confuse solubility and dispersibility, as we are interested in the potential of a material to lose its particulate character and to change its form to a smaller molecular or ionic form. This is to be stressed as the distinction can be difficult in the case of colloidal suspensions of nanomaterials.

Table 1. B1 Hazard group allocation

	<b>Category A</b> No significant risk to health	<b>Category B</b> Slight hazard – Slightly toxic	<b>Category C</b> Moderate hazard	<b>Category D</b> Serious hazard	<b>Category E Severe</b> hazard
<b>OEL dust mg/m<sup>3</sup> (8-h time weighted average)</b>	1–10	0.1–1	0.01 – 0.1	< 0.01	
<b>Acute toxicity</b>	Low	Acute tox 4	Acute tox 3	Acute tox 1–2	
<b>LD50 oral route mg/kg</b>	> 2,000	300 – 2,000	50 – 300	< 50	
<b>LD50 dermal route mg/kg</b>	> 2,000	1,000 – 2,000	200 – 1,000	< 200	
<b>LC50 inhalation 4H (mg/l)</b>	> 5	1 – 5	1.5 – 1	< 0.5	-
<b>Aerosols/particles</b>					
<b>Severity of acute (life-threatening) effects</b>		STOT SE 2–3; Asp. Tox 1	STOT SE 1	-	-
<b>Adverse effects per oral route (mg/kg) (single exposure)<sup>a</sup></b>	-	Adverse effects seen ≤2,000	Adverse effects seen ≤300		-
<b>Adverse effects per dermal route (mg/kg) (single exposure)<sup>#</sup></b>	-	Adverse effects seen ≤2,000	Adverse effects seen ≤1,000	-	-
<b>Sensitisation</b>	Negative	Slight cutaneous allergic reactions*	Moderate/strong cutaneous allergic reactions Skin sens. 1*	-	Prevalent moderate to strong respiratory allergic reactions Resp. sens. 1
<b>Mutagenicity/ genotoxicity</b>	Negative	Negative	Negative	Negative	Mutagenic in most relevant in vivo and invitro assays. Muta 2 Muta 1A – 1B
<b>Irritant/corrosiveness</b>	None to Irritant Eye Irrit. 2; skin Irrit. 2 EUH066		Severe irritant skin/eyes Irritant to respiratory Tract STOT SE 3; Eye Dam. 1 Corrosive Skin Cor. 1A – 1B	-	-
<b>Carcinogenicity</b>	Negative	Negative	Some evidence in animals Carc. 2	-	Confirmed in animals or humans. Carc. 1A – 1B
<b>Developmental/reproductive toxicity</b>	Negative	Negative	Negative	Reprotoxic defects in animals and /or suspected or proved in humans Repr. 1A, 1B, 2	
<b>Likelihood of chronic effects (e.g. Systemic)</b>	Unlikely	Unlikely	Possible STOT RE 2	Probable STOT RE 2	
<b>Adverse effects per oral route (mg/kg-day) (90 chronic study) <sup>a</sup></b>			Adverse effects seen ≤ 100	Adverse effects seen ≤ 10	
<b>Adverse effects per dermal route (mg/kg-day) (90 day chronic study) <sup>a</sup></b>			Adverse effects seen ≤200	Adverse effects seen ≤ 20	
<b>IH/Occupational health experience</b>	No evidence of adverse health effects	Low evidence of adverse health effects	Probable evidence of adverse health effects	High evidence of adverse health effects	High evidence of severe adverse health effects

<sup>#</sup> Informative only as this part of ISO/TS 12901 focuses only on inhalation control.

The rationale for choosing solubility as one of the factors for allocating a NOAA to a hazard band is related to peculiarities of the toxicology of particulate matters. If a NOAA is highly soluble, then its potential hazard should be addressed with regard to its solutes toxicity, without any consideration on a nano-specific toxicity. Therefore, the hazard banding process should apply only to low solubility NOAA.

The threshold value of 0.1 g/l is proposed to distinguish between high and low water soluble materials.

- If the water solubility is more than 0.1 g/l, then the material's hazard should be considered as a classical chemical hazard and the risk should be addressed using either an appropriate control banding method currently applied in some industries in the chemical sector or any other appropriate risk assessment and control tool.
- A water solubility of less than 0.1 g/l leads to Question 3.

c) Question 3: Does the NOAA contain biopersistent fibres or fibre-like structures? Is it appropriate to apply the fibre toxicity paradigm to the NOAA?

Note: Biopersistence of fibres is defined as the ability of a fibre to remain in the lung in spite of the lung's physiological clearance mechanisms. These defence mechanisms are:

- Transportation of entire particles by the mucociliary escalator and by alveolar macrophages.
- Dissolution of fibres.
- Disintegration, where the fibre breaks into smaller particles that can be cleared.

In some situations, NOAA can exist in structures which are not fibre-like (e.g. globular structures), but which can potentially release fibres after inhalation. Such structures should be allocated to the highest hazard band. However, if toxicological data provide evidence that these structures toxicity is not driven by the fibre paradigm, it should then be allocated to a hazard band corresponding to its toxicity.

d) Question 4: Are there hazard indications for the NOAA?

Although in most cases, a full hazard characterisation for a NOAA is unavailable, a limited set of screening tests could allow for assignment to a lower hazard band provided that screening tests for toxicity end-points describing higher hazard bands returned negative results. In this approach existing hazard categorisation ranging from A (practically non-hazardous) to E (non-threshold effects such as carcinogenicity or sensitisation) can still be used. For example, if screening tests showed that a nanomaterial does not have carcinogenicity, mutagenicity, toxic to reproduction or sensitisation by inhalation (CMRS) properties, then it can be assigned to the hazard band D. Correlation between toxicity end-points and hazard bands is given in Table 1, while a preliminary review of the applicability of testing guidelines to nanomaterials has been published elsewhere.

e) Question 5: Is there a hazard band for the bulk material or an analogous material?

If toxicological information on the NOAA is very limited or non-existent, the hazardous properties of the bulk material or an analogous material (an analogous material can be a NOAA) provide a basis for hazard categorisation of NOAA and should be considered. If there are several choices for analogous materials, the most toxic one should be taken into account.

However, it has to be stressed that it is not yet known to which extent the toxicity of NOAA is influenced by the toxicity of the corresponding bulk or analogous material and this uncertainty should be taken into account when allocating the NOAA to a hazard band.

In case there is no indication of a bulk or analogous material, the NOAA should either be assigned to the maximum hazard band (E), or a comprehensive toxicological hazard assessment be performed by a toxicologist and a hazard band determined according to the toxicological data.

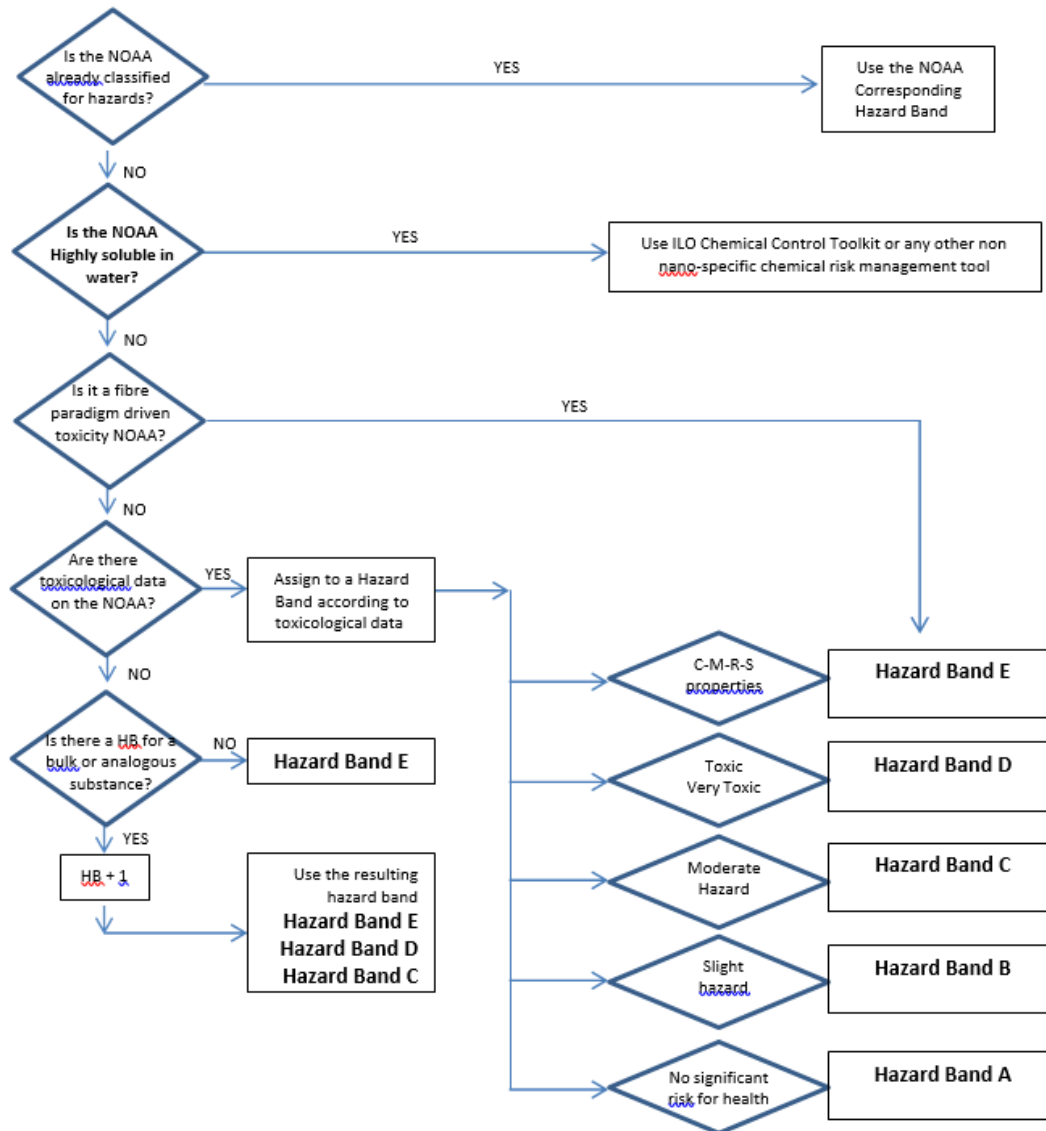


Figure B1 Decision tree for hazard banding

## B.2 Exposure band setting

### B.2.1 Preliminary remarks

In the proactive use of control banding, following the hazard banding process, the second step is intended to determine an expected level of workers exposure which is designated as an exposure band (EB, ranging from EB 1 the lowest exposure to EB 4 the highest exposure).

Matching the hazard band and the exposure band through a control banding matrix determines the appropriate level of control i.e. the control band.

The exposure bands characterise the potential for NOAA to become airborne under normal conditions of the process or the operation, regardless of any control measures that could already be implemented and therefore should not be considered as an actual assessment of workers exposure.

The exposure bands are defined according to the emission potential of a specific NOAA, whether free, or dispersed into a liquid or solid matrix. They take into account the physical form in which it is produced or used and, where applicable, the state of the matrix incorporating the NOAA. The physical form is a key parameter to consider, in order to assess the NOAA's emissivity from the product and hence the potential operator exposure level when it is handled.

Before any allocation to an exposure band, it is necessary to identify and characterise each work station in regard to its exposure potential related to the processes or handling operations performed by the workers.

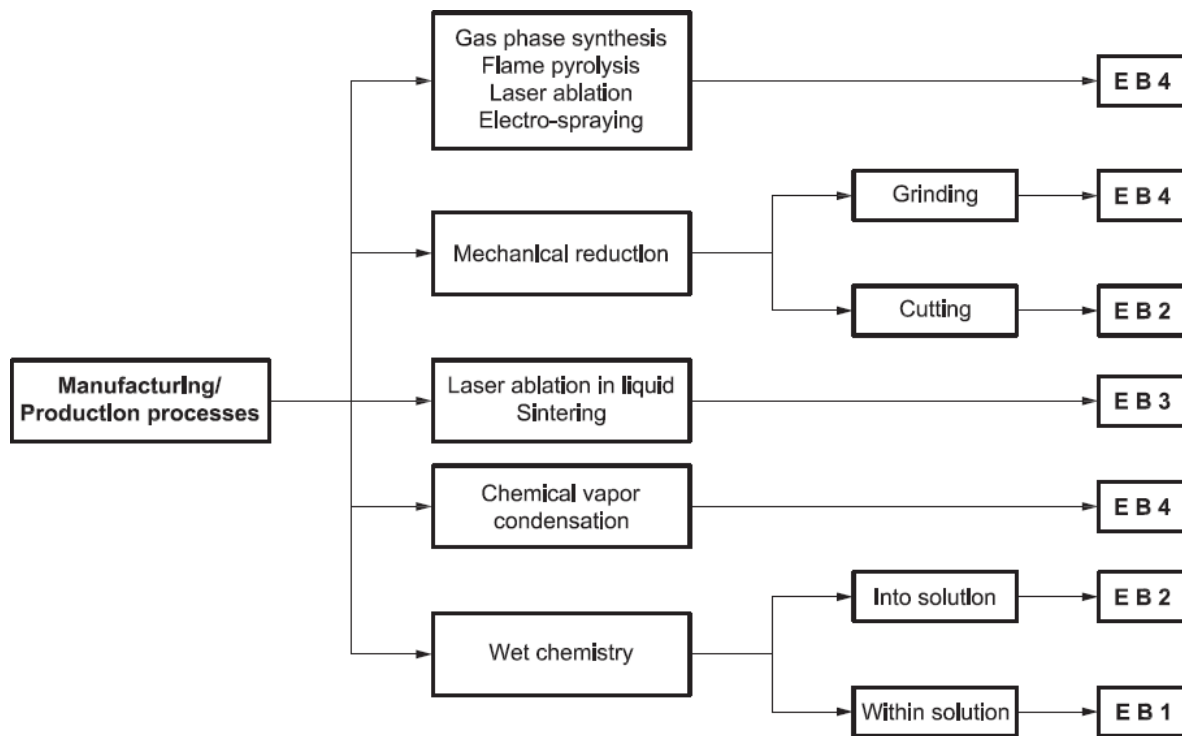
The type of process or handling operation is also of utmost importance for determining the likelihood of workers' exposure. Whatever the physical form of the material, in order to set an appropriate exposure band, it is necessary to make some assumptions on certain characteristics of the material like friability, viscosity, volatility and on the process or handling operation and its ability to release NOAA aerosols or dust in the workplaces. All these parameters contribute to the likelihood for a specific NOAA to be released in the workplace.

As the responses will ultimately determine the exposure band, issues such as deciding whether NOAA are strongly or weakly bound to a matrix, or whether a process has a high or low potential of aerosol generation should be addressed by the organization's health and safety officer or any other staff member well informed about materials' characteristics, nature of the processes of interest and health and safety related issues.

### **B.2.2 Synthesis, production and manufacturing of NOAA**

The likelihood of exposure to NOAA during synthesis, production and manufacturing processes is highly dependent upon the type of process and the type of equipment involved in the process. In some cases, due to physico-chemical or technical reasons, the process needs to be enclosed (e.g. in gas when an extremely low pressure or an inert atmosphere is required). Thus, the presence of an intrinsic barrier being part of the equipment might lead to allocate the workstation to a low exposure band. However, in order to avoid underestimating a possible risk of leaks of NOAA during the process, it is recommended not taking into account these intrinsic barriers during the exposure banding process. Evidently, these barriers should be taken into account as protective measures during the final control banding process.

The exposure band setting according to most types of processes is presented in Figure B2.



**Figure B2 Exposure banding process; Synthesis, production, manufacturing**

### B.2.3 Material dispersed in a solid matrix

In this case, the solid material being used contains NOAA or has a surface covered with NOAA.

The likelihood for those materials to release free single NOAA in the workplace during the process or activity depends upon two parameters:

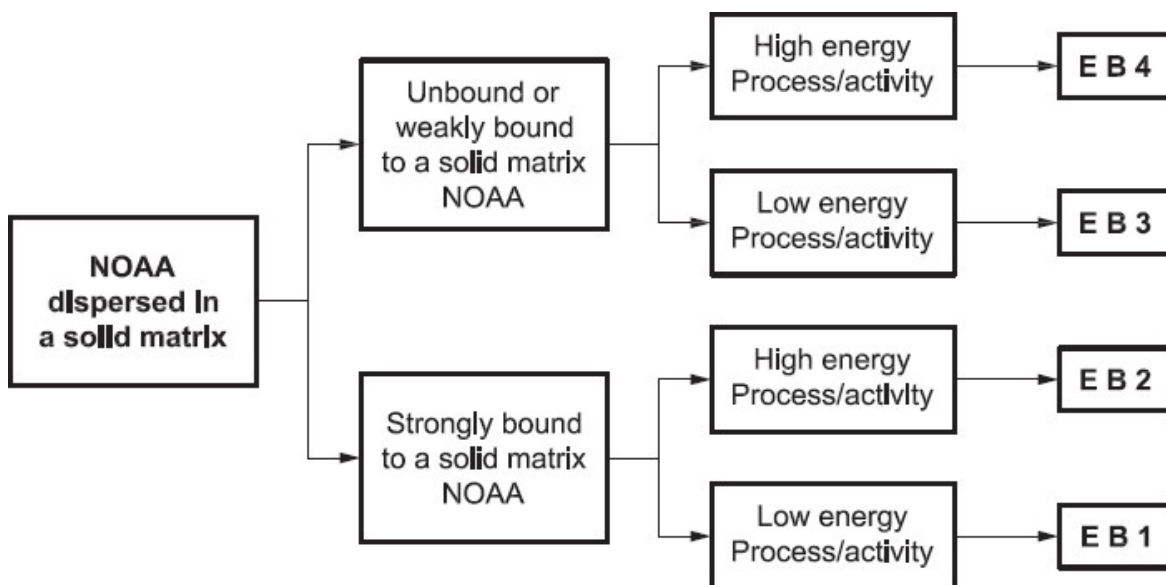
- The strength of the bonding between the NOAA and the solid matrix.
- The degree of energy involved during the process or the activity.

A material composed of NOAA that are unbounded or weakly bounded to the matrix is more likely to release free airborne primary NOAA when it is subjected to a low or high energy process activity.

A material composed of NOAA that are strongly bonded to the matrix is less likely to release free airborne NOAA but can release nanocomposite particles comprising primary NOAA engulfed in matrix components when it is subjected to high energy process or activity.

Processes such as grinding, milling and cutting with band saws or discs saws can be considered as high energy activities while manual cutting or moulding can be considered as low energy processes.

The exposure banding process is described in Figure B3.



**Figure B3 Exposure banding process: NOAA dispersed in solid materials**

#### **B.2.4 Material in suspension in a liquid**

The likelihood for NOAA in solutions to become airborne under normal working conditions depends mostly on the amount of material being handled, on the nature of the liquid and more specifically its viscosity and volatility, and on the type of process.

In processes where deliberate aerosolisation takes place, whatever the amount of NOAA handled, the exposure band should be set at the maximum level 4.

In manufacturing, use and handling operations, the potential for workers exposure depends upon the amount of NOAA being handled by a worker and per task (less or more than a 1 g of NOAA), and on the risk of aerosol or dust generation according to the characteristics of the liquid and the type of process.

The exposure banding scheme is described in Figure B4.

#### **B.2.5 Material in powder form**

When NOAA are handled as powders, workers' exposure depends upon the amount being handled, on the propensity of this specific NOAA to become airborne, this being related to dustiness, moisture content and the type of process.

The exposure banding process is described in Figure B5.



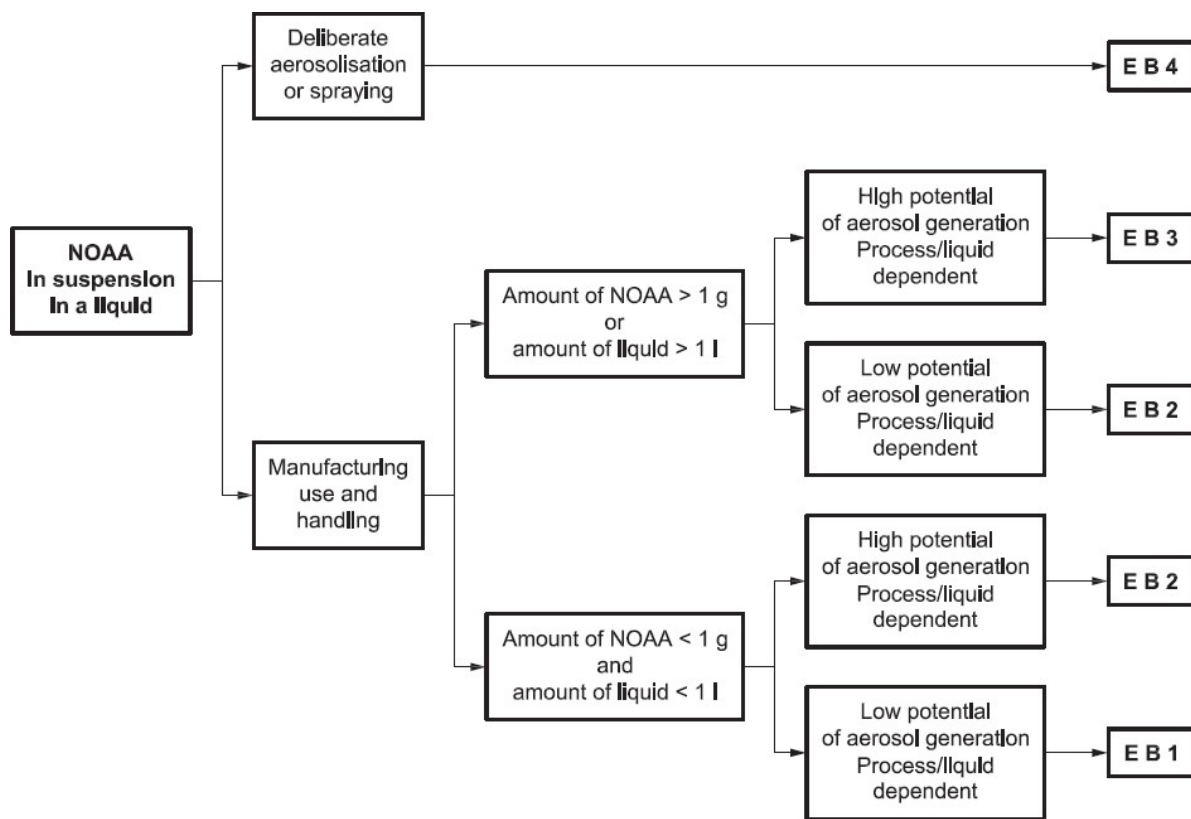


Figure B4 Exposure banding process: NOAA in suspension in a liquid

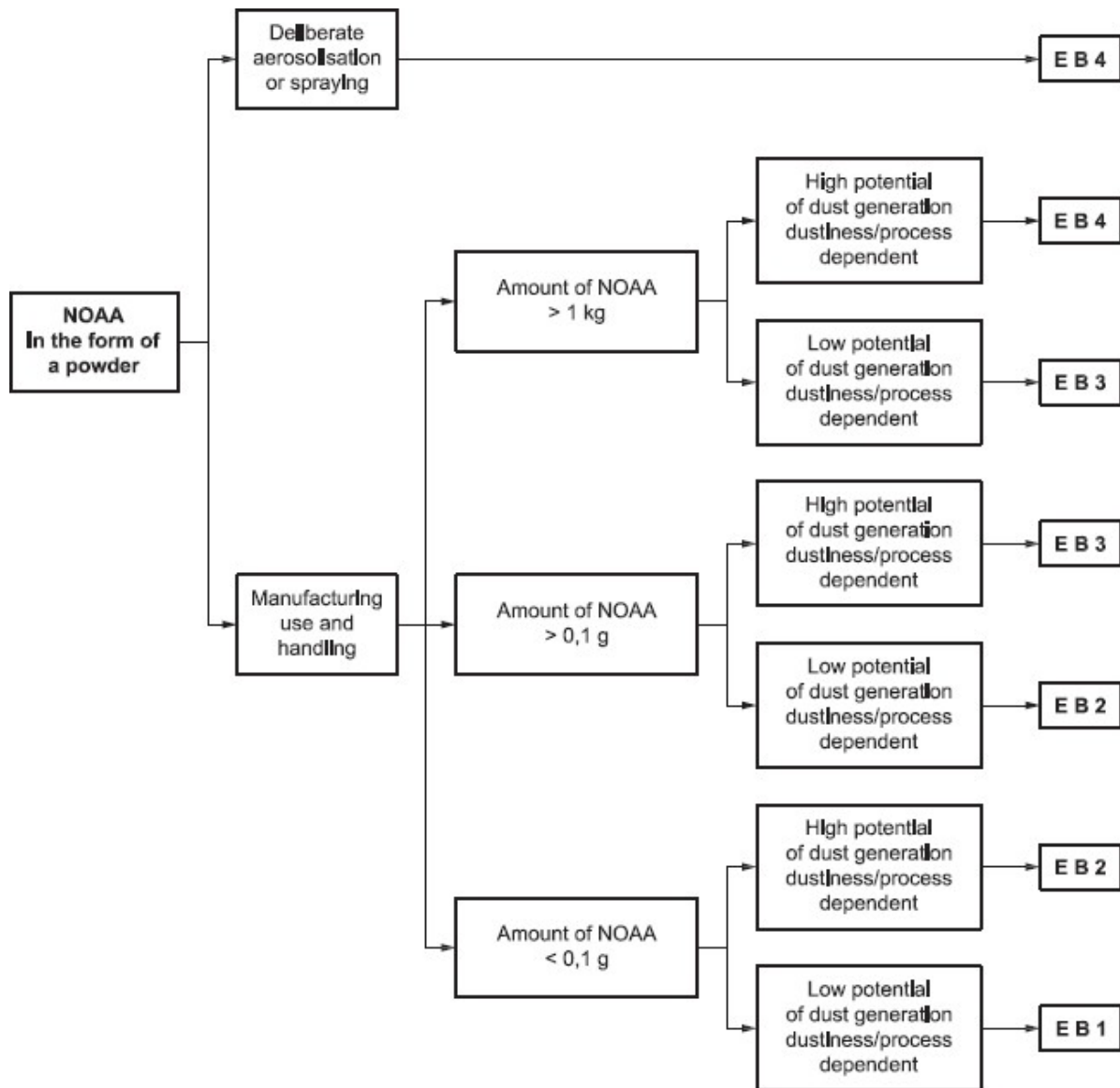


Figure B5 Exposure banding process: NOAA in powder form