SAFE HANDLING AND USE OF CARBON NANOTUBES

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safe work australia

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ABBREVIATIONS

List of Abbreviations

ADG Code	Australian Code for the Transport of Dangerous Goods
ALARA	As low as reasonably achievable
BSI	British Standards Institution
CE	Products bearing the CE mark comply with the provisions of European council directive 93/68/EEC
CNFs	Carbon nanofibres
CNTs	Carbon nanotubes
CSIRO	Commonwealth Scientific and Industrial Research Organisation
EDS	x-ray energy dispersive spectroscopy
EPA	Environment Protection Agency
HAZOP	Hazard and Operability
HEPA	High-efficiency particulate air
HSE	British Health and Safety Executive
JSA	Job Safety Analysis
LEV	Local exhaust ventilation
LOQ	Limit of quantitation
MWCNTs	Multi-walled carbon nanotubes
µg	Microgram
µm	Micron (micrometre)
nm	Nanometre
NIOSH	US National Institute for Occupational Safety and Health
OECD	Organisation for Economic Cooperation and Development
PAPR	Powered air purifying respirator
PCBU	Person conducting a business or undertaking
PPE	Personal protective equipment
REL	Recommended exposure limit
RPD	Respiratory protection devices
SWCNTs	Single-walled carbon nanotubes
SWPs	Safe work procedures
SDS	Safety data sheet
TEM	Transmission electron microscopy
TWA	Time-weighted average
UK	United Kingdom
WHS	Work health and safety
WHS&E	Work health and safety and environment
WPMN	Working Party on Manufactured Nanomaterials

INTRODUCTION

The potential risks from exposure to carbon nanotubes (CNTs) have been highlighted in numerous studies, including a recent review of the toxicology and health hazards associated with nanomaterials commissioned by Safe Work Australia (Toxikos 2009, see Appendix A for a list of references). Therefore, in order to help people work safely with carbon nanotubes, Safe Work Australia commissioned the CSIRO to develop guidance on the safe handling and use of carbon nanotubes.

This document provides two approaches to manage the risks:

- Risk management with detailed hazard analysis and exposure assessment (Part A)
- Risk management by Control Banding (Part B)

Either or both methods may be used, depending on the circumstances.

The '*Carbon Nanotube Health Safety and Environment Risk Management Tool'* at Appendix B can be used to assist risk management and can be modified to suit the workplace.

The guidance in this document is applicable to other forms of carbon nanofibres, such as carbon nanorods and carbon nanowires. It is also applicable to products containing carbon nanotubes and other forms of carbon nanofibres where these nanomaterials may be released during handling.

The document considers situations where carbon nanotubes are embedded in solid matrices (e.g. composites) and may potentially be released due to mechanical action, for example, by cutting or grinding.

This information is designed to be used by a person conducting a business or undertaking manufacturing CNTs or working with CNTs or products containing CNTs, workers in those organisations, occupational hygienists, work health and safety inspectors, health and safety representatives and other stakeholders.

What are carbon nanotubes?

Carbon nanotubes (CNTs) are a type of nanomaterial. They are hollow nanofibres, having two similar external dimensions on the nanoscale (1-100nm), with the third dimension significantly larger. They consist of curved graphene layers — graphene consists of a single layer of carbon atoms in a honeycomb structure. A nanometre is one-billionth of a meter; to put this in context, a sheet of paper is about 100,000 nanometres thick.

CNTs are primarily elemental carbon, but may contain varying amounts of metal impurities, depending on the method of manufacture. They can conduct electricity like metals or semiconductors, are good conductors of heat, they can be stiff and are up to 100 times stronger than steel, while being much lighter. Although the diameters of CNTs are at the nanoscale, their length is theoretically without limit and may grow to above 1mm. This means that they can have a very large aspect ratio, i.e. the ratio between their length and diameter, which can be higher than 100,000:1.

SINGLE-WALLED AND MULTI-WALLED CARBON NANOTUBES
In general, there are two groups of CNTs:

- Single walled carbon nanotubes (SWCNTs) are a single cylinder of carbon atoms forming a tube. They are normally around 1nm in diameter, but may be up to 5nm.
- Multi walled carbon nanotubes (MWCNTs) consist of two or more concentric layers of carbon nanotubes with a hollow core typically 2-30nm in diameter. For example, double-walled carbon nanotubes have two concentric layers. MWCNTs may be stiffer than SWCNTs and may potentially be of greater health and safety risk due to the possibility of piercing the body's pleural tissue.

Potential health concerns

The toxicity of CNTs is the subject of much discussion and experimentation. This document does not aim to consider or analyse this literature in detail. However, CNTs can be bio-persistent and have the potential to exist as fibre-like structures.

NIOSH (2010) reports that currently there are no studies reported in the literature of adverse health effects in workers producing or using CNTs. However use is not yet widespread, and there can be a long latency before the development of disease. The concern about worker exposure to CNTs arises from results of animal studies, showing adverse lung effects including pulmonary inflammation and fibrosis.

NIOSH (2010) also reports that animal studies have also shown asbestos-type pathology associated with exposure to longer, straighter CNT structures. Mesothelial tumors have been reported in a susceptible strain of mice after intraperitoneal injection of longer MWCNTs (10-20 µm in length) but not by short MWCNTs (<1 µm in length).

In a recent review, Toxikos (2009) reports: "Evidence leads to a conclusion that as a precautionary default: all biopersistent CNTs, or aggregates of CNTs, of pathogenic fibre dimensions could be considered as presenting a potential fibrogenic and mesothelioma hazard unless demonstrated otherwise by appropriate tests…" (Toxikos 2009).

There is also evidence that CNTs and structures of CNTs that are not of fibre-like shape may also be hazardous.

CARBON NANOTUBES HAZARDS
For the purpose of this document, all CNTs and structures of CNTs are considered to be hazardous, unless evidence shows otherwise.

Who has work health and safety duties relating to nanotechnologies?

Australia's work health and safety (WHS) legislation aims to protect the health and safety of researchers and workers developing, manufacturing or using engineered nanomaterials such as CNTs.

A person conducting a business or undertaking has the primary duty under the WHS Act to ensure, so far as is reasonably practicable, that workers and other persons are not exposed to health and safety risks arising from the business or undertaking. This duty includes ensuring, so far as is reasonably practicable, the safe use, handling and storage of substances.

Designers, manufacturers, importers and suppliers of substances must ensure, so far as is reasonably practicable, that the substance is without risks to the health and safety of persons who, at a workplace, use the substance for a purpose for which it was designed or manufactured.

Officers, for example, company directors, have a duty to exercise due diligence to ensure that the business or undertaking complies with the WHS Act and Regulations. This includes taking reasonable steps to ensure that the business or undertaking has and uses appropriate resources and processes to eliminate or minimise risks.

Workers have a duty to take reasonable care for their own health and safety and must not adversely affect the health and safety of other persons. Workers must comply with any reasonable instruction and cooperate with any reasonable policy or procedure relating to health and safety at the workplace.

The duties above apply to nanotechnologies and nanomaterials, for example, CNTs, as they do to other technologies, substances and materials more generally.

Additionally, there are specific WHS Regulations for workplace chemicals, which also cover engineered nanomaterials:

- the manufacturer or importer of a substance must determine whether the substance is a hazardous chemical, and if it is determined to be hazardous chemical, to prepare a safety data sheet and correct label
- the supplier of a hazardous chemical to a workplace must ensure that the current safety data sheet for the chemical is provided
- a person conducting a business or undertaking must ensure that hazards in relation to using, handling or storing a chemical at the workplace are identified, and the associated risk is eliminated or minimised so far as is reasonably practicable.

Risk management methods — Overview

Risk management, including work with CNTs, is focused on preventing incidents, injury, illness, property damage, and environmental harm.

The general risk management process, which is applicable to working safely with CNTs, is illustrated in Figure 1. It shows that risks may be controlled with or without conducting a detailed risk assessment. If, after identifying a hazard, you already know the risk and how to control it effectively, you may implement the controls without further assessment.

Guidance on the general risk management process is available in the *Code of Practice: How to Manage Work Health and Safety Risks.*

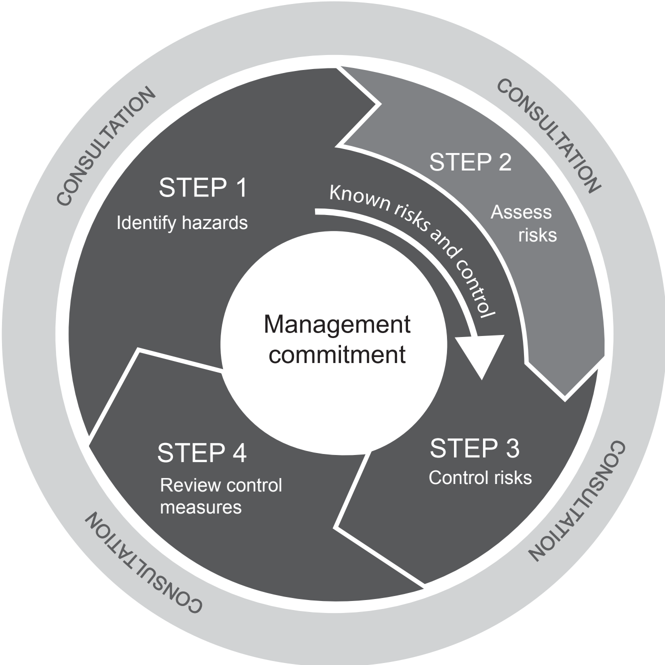

FIGURE 1: THE RISK MANAGEMENT PROCESS

This document provides guidance on two options to manage the risks.

Method 1 — Carbon nanotubes risk management with detailed hazard analysis and exposure assessment [1]

This approach should be used when it is necessary to gather and evaluate information on characteristics of the carbon nanotubes or structures of carbon nanotubes and/or on potential levels of exposure throughout the process and associated work, to assess risk. The approach involves:

- collecting relevant information to identify the hazards
- assessing the risks
- implementing appropriate control measures, and
- monitoring and reviewing the effectiveness of control measures.

Information can be collected from external sources, including the manufacturer and supplier. This will include information on:

- physical and chemical characteristics of carbon nanotubes
- potential health effects
- control options.

1 Information from the British Standards Institution (BSI) Guide to *Safe Handling and Disposal of Manufactured Nanomaterials* (BSI 2007), NIOSH's Current Intelligence Bulletin: *Occupational Exposure to Carbon Nanotubes and Nanofibers*, draft for public comment (NIOSH 2010) and the British HSE's *Risk Management of Carbon Nanotubes* (HSE 2011) has been used to inform this approach.

Specialised knowledge of the production processes, analysis methods and controls will be required to undertake a full risk management process.

Method 2 — Carbon nanotubes risk management by Control Banding

Control banding for CNTs involves a simplified form of the risk management approach, where specific controls are recommended based on process risk. The CNTs are considered to be hazardous, therefore the controls are based on the potential level of exposure. Control banding can be used when production and manufacturing processes are well understood, potential exposure routes are known and safe work procedures are developed.

As with Method 1 above, this approach involves implementing appropriate controls for specific processes and monitoring and reviewing control effectiveness.

Consultation

Consultation is critical to the success of both risk management methods.

CONSULTING WORKERS

A person conducting a business or undertaking must consult, so far as is reasonably practicable, with workers who carry out work for the business or undertaking and who are (or are likely to be) directly affected by a work health and safety matter.

Consultation involves sharing of information, giving workers a reasonable opportunity to express views and taking those views into account before making decisions on health and safety matters. As exposure to CNTs could impact on workers' health and safety, workers must be consulted on matters such as arrangements for working with CNTs.

Workers must be consulted when:

- identifying hazards and assessing risks to health and safety
- making decisions about ways to control those risks.

If the workers are represented by a health and safety representative, the consultation must involve that representative.

CONSULTATION, CO-OPERATION AND CO-ORDINATION OF ACTIVITIES WITH OTHER DUTY HOLDERS

A person conducting a business or undertaking must consult, co-operate and co-ordinate activities with all other persons who have a work health or safety duty in relation to the same matter, so far as is reasonably practicable.

By drawing on the experience, knowledge and ideas of your workers and other parties you are more likely to identify all hazards and develop effective risk controls.

Further guidance on consultation requirements is available in the *Code of Practice: Work Health and Safety Consultation, Co-operation and Co-ordination.*

PART A

METHOD 1 — RISK MANAGEMENT WITH DETAILED HAZARD ANALYSIS AND EXPOSURE ASSESSMENT

Preparation for the risk management process

ESTABLISH THE CONTEXT OF THE WORK

- Who is responsible for ensuring that the risks associated with the work are identified and controlled?
- Is there current safety information available on the toxicity of the specific types of CNTs being used in the workplace?
- What quantities of CNTs will be used? Research quantities (minor) or industrial (manufacturing or production) scale quantities?
- How will the risk control methods be implemented, monitored and validated?
- Is satisfactory health and safety information currently available such as safety data sheets (SDS) made specifically for the CNTs being used, reliable safe work procedures or other safety instructions?

It is important to document both the information which is available and the knowledge gaps. For commercial CNTs, some of the information should be available on the SDS. In using these sheets, however, it is necessary to evaluate the extent to which suppliers have taken into account the nanoscale form and nature of the substance. For example, an SDS for graphite will not accurately reflect the hazardous nature of CNTs with the same chemical composition. It is also necessary to identify people who could be exposed. This could include production employees, employees working in adjacent facilities, ancillary or support-services employees such as cleaners or maintenance workers, contractors on site, visitors, supervisors and managers, students, office workers, and people outside, e.g., neighbours.

Appendix B provides a risk management tool that can be used to assist in the development and implementation of a 'Risk Control Plan'. The tool can be modified to suit the particular risk profile of the workplace.

STEP 1 - HAZARD IDENTIFICATION

Current evidence suggests that all CNTs should be treated as hazardous, unless evidence suggests otherwise. However, it is important to understand if they are fibre-like and thus present fibre hazards and to understand other potential hazards associated with their production or handling. This is the focus of Step 1.

Answering the following questions can assist in identifying these hazards.

1.1 Carbon nanotubes characterisation

- What types of CNTs are being used; single-walled or multi-walled?

  Thicker, stiffer CNTs may be more likely to be fibre-like
- What quantities of CNTs are being used?

  The greater the quantity used, potentially the greater the exposure risk
- Are the CNTs loosely or tightly bound together?

  CNTs, and particularly SWCNTs, can be very tightly bound together. They readily agglomerate and aggregate. A very large clump of CNTs may be less hazardous than loosely bound CNTs because:
  - Loose CNTs may be able to penetrate deeper into lung tissues
  - Loose CNTs may be fibre-like and cause pathogenic responses
- Are the CNTs modified or functionalised, or coated with a chemical? Is this chemical hazardous?

  Functionalisation may make the CNTs more biodegradeable and hence less hazardous. The chemical coating on the CNT may also be hazardous
- Are there any contaminants or metallic catalysts present, such as iron or nickel? If so, are any of them known to be harmful or reactive?
  - Some CNTs may contain heavy metals that are known carcinogens
  - Residual metallic catalysts may cause formation of reactive oxygen species, which may lead to inflammation.
- What is the length, width and aspect ratio (length:width) of the CNTs?

  The 'fibre-like' character of CNTs is of concern especially when the aspect ratio is greater than 3:1 and the length is greater than 5 microns as the fibres are less easily cleared from the body. Using CNTs with a smaller aspect ratio or shorter CNTs may be safer, however research has shown that these forms of CNTs may still be hazardous to the lungs if inhaled.

1.2 Other potential hazards

- Are any reagents, gases or chemical compounds used with the CNTs classified as 'hazardous chemicals', such as flammable (e.g. acetylene), explosive, acidic or toxic chemicals?
  - All hazardous chemicals used need to be included in the workplace hazardous chemicals register and controlled appropriately.
- Are any electrical systems used in, or near, areas where CNTs are used? CNTs are highly conductive and electrical systems may need to be protected against short circuiting by dusts containing CNTs settling on electrical components.
  - All electrical systems should be intrinsically safe, that is, devices and electrical infrastructure (wires, switches, lights, etc) that are shielded, low voltage, low current or spark proof may be required.

This document specifically deals with hazards associated with handling of CNTs. In relation to managing the risks associated with the use of plant and equipment in the workplace, for example production furnaces, mixing, fibre processing or fabric processing plant, refer to the *Code of Practice: Managing the Risks of Plant in the Workplace.*

Safety hazards are considered in the CSIRO's safety data sheet for MWCNTs (CSIRO 2009). CNTs are not considered to be dangerous goods. In relation to fire and explosion hazards the following points are noted:

- CNTs are difficult to combust and ignite.
- However in general, accumulations of fine dust (420 microns or less) may burn rapidly and fiercely if ignited; once initiated larger particles up to 1400 microns diameter will contribute to the propagation of an explosion.

STEP 2 — RISK ASSESSMENT

The purpose of this step is to determine the level of exposure, and using this information together with hazard information determined in Step 1, to undertake risk evaluation.

2.1 Exposure assessment

POTENTIAL ROUTES OF ENTRY INTO THE BODY

- Inhalation
- Dermal absorption and skin penetration
- Ingestion
- Intra-ocular

For most airborne particulate materials in workplace settings, particularly those that are poorly soluble such as CNTs, the primary health concern is for damage to the respiratory system via inhalation exposure.

COLLECTING INFORMATION TO DETERMINE THE POTENTIAL EXPOSURE TO CNTS

This may involve a walk-through of the process to identify potential exposure points. Each of the individual tasks using or handling CNTs needs to be assessed. Examples of tasks include:

- Production, including synthesis and growing of CNTs
- Packaging, storage and transporting
- Manufacturing using CNTs, including processing and manipulation
- Experimental research with CNTs
- Cleaning and maintenance
- Disposal

This information should answer the following questions:

- What are the tasks where people can be exposed to CNTs? Is the material or process dusty or likely to produce aerosols of CNTs?
- Does the process include cutting, shearing, grinding, abrasion, or other mechanical release of CNTs or materials containing CNTs?
- Will weighing, measuring and mixing processes create dusts or aerosols of CNTs?
- Will the CNTs be added to a solution? Is the solution hazardous?
- Who can be exposed during each of the tasks identified above, e.g., the individual undertaking the task, adjacent workers, visitors, contractors, managers and others?
- What are the potential routes of human exposure, e.g., inhalation, ingestion and dermal absorption?
- What is the chance of the exposure occurring? Consider routine work, accidental releases and maintenance (not just during normal activities).
- How often is exposure likely to occur, for example continuous over a working shift, intermittent, rarely?

- Is there evidence of dusts or aerosols of CNTs being present in the air or on the surfaces of the workplace, or other locations where people could be exposed, for example floors, bench tops, ducts, filters, other fittings and fixtures?
- Is there any relevant existing measurement data for airborne concentrations, for example number of fibres, and their mass, length, width and aspect ratio?

HAZOP is a risk assessment technique that could be used to predict adverse outcomes through production and manufacturing processes. See Australian Standard *AS IEC 61882 — 2003 Hazard and Operability Studies (HAZOP Studies) — Application guide for more information*.

Environmental Aspects
Is there the potential for CNTs to be liberated into the environment, to the:

- Air
- Water
- Sewer
- Land

2.2 Exposures for different tasks

The potential for exposure to CNTs will vary according to the task or undertaking, and should be determined for each task (see Table A).

There is currently only limited information about whether CNTs embedded in solid matrices (e.g. composites) have the potential to be released during mechanical action, for example, by cutting or grinding. Bello (2009) did not identify any free CNTs released during the cutting of composites containing CNTs. Further research on this topic is underway globally, but in taking a precautionary approach it should be assumed that CNTs can be released unless evidence suggests otherwise.

TABLE A: TASK EXPOSURES

Task Exposure Assessment The type of tasks undertaken in the workplace will determine the exposure risk	
Assessed Exposure	**Example of Tasks/Scenarios**
High	■ Tasks that are likely to produce airborne CNTs ■ CNTs are handled in dry state or powder form, e.g. weighing and measuring ■ Manufacture of CNTs — e.g. synthesis, growing ■ Scraping and packing of dry CNTs ■ Opening bags of dry CNTs and adding them to a hopper
Moderately High	■ Blending CNTs into polymers ■ CNTs are mechanically manipulated, e.g. weave, knit, twist, pull, cut, grind, scrape, etc ■ Cutting/grinding polymers containing CNTs if CNTs can be released from the matrix ■ CNTs in solution which are likely to be atomised
Moderately Low	■ Extruding and manipulating polymers containing CNTs ■ Processing, shaping, moulding of polymers containing CNTs ■ Cutting/grinding polymers containing CNTs if CNTs are unlikely to be released from the matrix ■ Solutions containing CNTs are mixed or agitated
Low	■ CNTs cannot be detected in air using appropriate measuring and monitoring techniques ■ CNTs are embedded in a polymer type matrix and no machining ■ Painting, coating or packaging of extruded product

2.3 Risk evaluation

Risks should be prioritised for action. The most important information is:

- How potentially hazardous are the CNTs? This is informed by considering their characteristics, e.g. length, aspect ratio, form, and impurities present in the CNTs.
- Can people be exposed to CNTs in any processes or tasks? What is the likely level of exposure?

Risk = Level of Exposure x Severity of Hazard

Using the information from the hazard identification and exposure assessment, priorities and resources can be assigned to the management of these risks commensurate with the level of risk.

The level of risk will be highest if the CNTs can exist as fibre-like structures and there are potentially high levels of inhalation exposure.

2.4 Exposure limit for carbon nanotubes

Currently there is no Australian National Exposure Standard specifically for CNTs. NIOSH (2010) has proposed a recommended exposure limit (REL) of 7$\mu g/m^3$ for carbon nanotubes and nanofibres. This is the upper limit of quantitation (LOQ) of NIOSH Method 5040, currently NIOSH's recommended analytical method for measuring airborne CNTs. NIOSH notes that at this exposure level (7$\mu g/m^3$), animal data-based risk estimates indicate that workers may have >10% excess risk of developing early-stage pulmonary fibrosis if exposed over a full working lifetime, and thus efforts should be made to reduce airborne concentrations of CNTs as low as possible below the REL.

This respirable mass-based REL provides a means to identify job tasks with potential exposures to CNTs and to ensure that appropriate measures are taken to limit worker exposure (NIOSH 2010).

STEP 3 — RISK CONTROL

The most important step in managing risks involves eliminating them so far as is reasonably practicable, or if that is not possible, minimising the risks so far as is reasonably practicable.

3.1 Risk control strategies

The control mechanisms selected in consultation with workers must provide adequate protection for the risk profile determined in Step 2. The aim is to eliminate the hazard, or to minimise the severity of the hazard and levels of potential exposure.

ALARA PRINCIPLE — REDUCING EXPOSURES TO AS LOW AS REASONABLY ACHIEVABLE

Our understanding of the toxicity of CNTs is limited but growing, however evidence suggests that a number of forms may be highly hazardous if inhaled. Though of lesser concern, there is also potential for dermal and ingestion toxicity associated with CNTs.

Unless there is evidence to the contrary, a precautionary approach to control is warranted and exposures should be reduced to ALARA.

This approach underpins the choice of controls for activities within the organisation. The ALARA Principle should be used in the application of the 'Hierarchy of Controls' to reduce risks in the workplace.

THE HIERARCHY OF CONTROL

There are a number of ways to control the risks associated with CNTs. Some control measures are more effective than others. Control measures can be ranked from the highest level of protection and reliability to the lowest. This ranking is known as the *hierarchy of control* (see Table B).

You must always aim to eliminate a hazard and associated risk first. If this is not reasonably practicable, the risk should be minimised by using one or more of the following approaches:

- Substitution
- Isolation
- Engineering controls
- Administrative controls
- Personal protective equipment (PPE).

Administrative control measures and PPE rely on human behaviour and supervision and when used on their own, tend to be the least effective ways of minimising risks.

TABLE B : HIERARCHY OF CONTROLS

The general approach is to use the highest control practicable. In practice, a combination of controls will give the best protection.	
Eliminate	Avoid using potentially hazardous CNTs or the processes which cause exposure.
Substitute/ Modify material or process	Change the material/process to reduce the hazards, by for example: ■ modifying the CNT fibre properties, e.g. fibre length ■ handling CNTs in liquid media ■ Binding CNTs in solid media ■ reducing the amount of CNTs handled, or ■ changing work procedures or production techniques.
Isolate or Enclose	All operations which involve the likely release of CNTs into the air are performed in contained installations, or where personnel are otherwise isolated from the process e.g. fully sealed glove boxes, or in a facility that can be operated remotely from a protected area.
Engineering Control	All processes where there is the potential of creating dusts or aerosols of CNTs are carried out in areas with efficient local exhaust or extraction ventilation. A well designed exhaust ventilation system such as a fume cabinet with a high-efficiency particulate air (HEPA) filter should effectively remove CNTs. Ductless HEPA filtered safety cabinets and recirculating HEPA filtered micro-biological safety cabinets can be used with small quantities (less than 1 gram) of CNTs, as long as they are subject to rigorous maintenance and checks are carried out to ensure they are effective at all times (HSE, 2011). Wet cutting is recommended for cutting solid articles containing CNTs. Selection of appropriate engineering controls will depend on the level of risk.
Administrative Control	Safe working procedures (SWPs) are developed for using, handling, storing, transporting and disposing of CNTs. Workers should be trained to ensure they understand the risks involved with the work, the SWPs, safety labels and other parts of the Risk Control Plan. Workers also need access to up-to-date safety information including; SDS, toxicology and monitoring information. Collect information about the type of materials being used and the duration of their use. Such information will help to build up a profile of potential exposures, which could be important if any health effects are observed at a later date.
Personal Protective Equipment (PPE)	PPE is a last resort control measure or a supplemental option to help support higher levels of exposure control. PPE may include respiratory protection devices, dermal protection and eye protection. The WHS Regulations include requirements for the selection, use and maintenance of PPE.

Appropriate controls must also be provided for other hazardous chemicals used in the workplace. For further guidance refer to the *Code of Practice: Managing Risks of Hazardous Chemicals in the Workplace.*

3.2 Minimising the risk

Assuming the potential hazards cannot be eliminated, i.e. the use of CNTs is necessary, options to minimise the risk by reducing the hazard severity must be considered:

- Using CNTs that are less than 5 microns long (RMIT University 2010)
- Reducing the level of metallic impurities, e,g. iron and cobalt
- Adding chemically-attached functional groups to the sidewalls to make CNTs less biopersistent

Whether these options for minimising the risk are feasible will depend on the particular application of the CNTs.

3.3 Controls for handling CNTs to prevent exposure by different routes

Information on controls for preventing exposure to CNTs should also be available on relevant SDSs.

INHALATION EXPOSURE

Higher Order Controls

- Storing and handling the CNTs in solutions
- Embedding CNTs in matrices
- Designing the process to minimise the amount of CNTs handled to reduce potential exposures.
- Isolate, enclose or use engineering controls, e.g. by carrying out tasks, including packaging for distribution, in a ducted fume cupboard with a HEPA filter, or by using other suitable effective local exhaust ventilation (LEV) fitted with a HEPA filter. When using other types of LEV try to enclose the process as much as possible (HSE 2011).

REDUCING EXPOSURE TO AIRBORNE CNTS — EXAMPLE

An assessment of airborne exposure to MWCNTs in a research laboratory manufacturing and handling MWCNTs found a total particulate concentration of 430 $\mu g/m^3$ for a blending process in the absence of exposure controls (Han 2008). The implementation of ventilated enclosure of the blending process reduced airborne concentrations of MWCNTs from 172.9-193.6 tubes/cm^3 to 0.018-0.05 tubes/cm^3. At airborne levels of 0.018-0.05 tubes/cm^3, the airborne MWCNTs concentration is significantly below the NIOSH REL of 7 $\mu g/m^3$.

Current knowledge indicates that a well designed exhaust ventilation system with a high-efficiency particulate air (HEPA) filter should effectively remove nanoparticles. See Nanosafe *'Efficiency of fibrous filters and personal protective equipments against nanoparticles,'* January 2008 DR-325/326-200801-1 http://www.nanosafe.org (Nanosafe 2008).

Ductless HEPA filtered safety cabinets and recirculating HEPA filtered micro-biological safety cabinets can be used with small quantities (less than 1 gram) of CNTs, as long as they are subject to rigorous maintenance and checks are carried out to ensure they are effective at all times (HSE 2011).

Bello (2009) did not identify any free CNTs released during the cutting of composites containing CNTs. The research also showed that the wet cutting process used released significantly less fine and ultrafine particles and other fibres than was the case with dry cutting. Wet cutting did not produce exposures that were significantly different to the background.

Engineering controls need to have a scheduled maintenance and testing program (e.g. involving air velocity testing), to ensure they meet relevant Australian Standards and are operating at optimum efficiency, and appropriate work practices should be used in conjunction with these controls to ensure their effectiveness.

Lower Order Controls — Personal Respiratory Protection Devices (RPD)

Certified P2 or P3 high efficiency particulate filters and masks complying with the relevant Australian Standard should be used where needed to supplement higher levels of exposure control. Disposable P2 masks are suitable in lower risk situations and only when the mask is fitted correctly using both elastic straps. Half face reusable masks can be fitted with P2 or P3 filters but they will only function at P2 efficiency. Only full face reusable masks fitted with P3 filters will function at P3 efficiency.

PERSONAL RESPIRATORY PROTECTION DEVICE SELECTION

All wearers of RPD should undergo face-piece fit testing to ensure correct fitting and comfort. Non-disposable respirators should be cleaned and serviced in a fume cabinet. PPE, especially respiratory protection devices, needs a significant investment in training, supervision and maintenance if it is to provide the intended level of protection. Incorrect selection, fitting or maintenance can render it ineffective, potentially exposing the user to airborne CNTs.

If PPE is to be used at the workplace, the person conducting the business or undertaking must ensure that the equipment is:

- selected to minimise risk to health and safety
- suitable for the nature of the work and any hazard associated with the work
- a suitable size and fit and reasonably comfortable for the person wearing it
- maintained, repaired or replaced so it continues to minimise the risk
- used or worn by the worker, so far as is reasonably practicable.

A worker must, so far as reasonably able, wear the PPE in accordance with any information, training or reasonable instruction.

DERMAL EXPOSURE AND SKIN PENETRATION

Higher Order Controls

Higher order controls described above, e.g. isolation and enclosing the process, that reduce inhalation exposures will also reduce dermal exposures by reducing the amount of material settling on the skin from the air.

Dermal exposure can also be reduced by re-engineering the work process to minimise splashes, and to avoid immersion into CNT containers or solutions.

Lower Order Controls — Personal Protective Equipment

The risk assessment may indicate a need for protective clothing:

- Evidence suggests that air-tight fabrics made of nonwoven textile may be more efficient in protecting workers against nanoparticles than fabrics made of woven cotton or polyester (Nanosafe, 2008). The challenge when selecting appropriate protective apparel is to strike a balance between comfort and protection. Garments that provide the highest level of protection are also the least comfortable to wear for long periods of time (NIOSH 2010).
- Close-fitting safety glasses or prescription safety glasses with side shields should provide adequate eye protection for handling CNTs for most situations. A full face respirator will provide good eye protection. Contact lenses may pose a special hazard and their use should be avoided.
- Generally, gloves will also be required, except where processes are fully enclosed or isolated from workers.
- Over booties may be required to ensure that CNTs are not tracked through the facility.

NIOSH (2010) recommend using light-coloured gloves, lab coats, and work bench surfaces to facilitate observation of contamination by dark CNTs and CNFs. Covering work surfaces with disposable white paper may also assist with the detection of fugitive CNTs in the workplace.

PPE — CLOTHING SELECTION

- Non-woven disposable materials have been tested and found to be more efficient at preventing nanoparticle penetration when compared to cotton, woven fabric or paper materials, however, they are also the least comfortable to wear for long periods of time.
- Other considerations when selecting and using PPE:
  - Long trousers — without cuffs should be worn
  - Closed toe impermeable shoes should be worn
  - Contaminated clothing must be laundered in specialised laundry facilities — do not wash contaminated clothing at home.

PPE — GLOVE SELECTION

There are four basic criteria for the selection of protective gloves — they should:

- Be appropriate for the risk(s) where they are to be used, e.g. be suitable for solvents used
- Be suitable for the ergonomic requirements of the wearer
- Fit the intended wearer correctly
- Prevent exposure without increasing the overall risk, e.g. manual handling risk.

Other glove considerations:

- Neoprene has low penetration properties but it may cause a reduction in dexterity
- Disposable polymer gloves, e.g. nitrile, also have low penetration properties
- Gloves should be changed regularly
- Double gloving will increase protection

INGESTION EXPOSURE

In order to prevent accidental ingestion (direct or indirect), CNTs should be handled in accordance with good personal hygiene and safety practice. Wash hands with soap and water before breaks and at the end of the workday. Personal protective clothing including laboratory coats should never be worn in public places such as offices, tea rooms, lounge areas, or other areas outside the workplace where they could be a source of contamination. A designated area should be provided, adjacent to the work area, where personal protective clothing can be put on and taken off. CNT contaminated clothing should not be taken home for cleaning or disposal; it should be laundered in an industrial laundry equipped with decontamination facilities, or it should be disposed of in accordance with the CNT disposal information below.

SUMMARY OF CONTROL OPTIONS

HIGHER ORDER CONTROLS

- Fully isolated process areas with remote control operation booths
- Intrinsically safe electrical systems (to protect against short circuiting)
- Negative pressure workrooms and laboratories
- Local exhaust and ventilation with HEPA filtration
- Fully ducted fume cupboards
- HEPA filtered recirculating fume cabinets (for quantities <1g of CNT)
- Glove boxes

LOWER ORDER CONTROLS

- Non-woven disposable protective clothing
- Gloves
- Protective eye wear:
  - Full face respirator
  - Glasses
- Respirators:
  - Disposable certified P2 mask
  - Reusable
    - Half face P2
    - Full face P3
    - Negative pressure, PAPR with P3

3.4 Controls for tasks with different risk levels

High Risk Tasks: Tasks that are likely to produce dusts and aerosols (e.g., growing, production, scraping, packing, unpacking, measuring or mixing dry CNTs).

Controls

Isolated processing, negative pressure work areas where operators work from a remote control booth and secure access into the workplace, e.g. electronic swipe card access into high risk areas.

Moderately High Risk Tasks: Tasks where there is the potential for being exposed to dusts and aerosols (e.g., blending CNTs into polymers, cutting or grinding polymers containing CNTs if CNTs can be released from the matrix).

Controls

Negative pressure work areas with good local exhaust ventilation with HEPA filtration, process enclosure, secure access into the workplace, e.g. electronic swipe card access, and an appropriate PPE regime.

Moderately Low Risk Tasks: Tasks where there is a low potential for being exposed to CNT dusts and aerosols (e.g., extrusion of materials containing CNTs).

Controls
Good local exhaust ventilation with HEPA filtration, comprehensive administrative controls and an appropriate PPE regime

Low Risk Tasks: Tasks with little or no potential for being exposed to CNT dusts and aerosols (e.g., Working with extruded polymers containing CNTs e.g., painting or coating finished products).

Controls
Comprehensive administrative controls and an appropriate PPE regime.

CHECKING CONTROLS CHOSEN
The controls chosen can be compared with the controls recommended by the 'Control Banding' approach to risk management (METHOD 2).

3.5 Controls for specific activities

CLEANING AND MAINTENANCE
When developing procedures for cleaning up nanomaterial spills or contaminated surfaces, consideration must be given to the potential for exposure during clean-up. Inhalation exposure and dermal exposure will likely present the greatest risks. Cleaners and maintenance personnel need to follow safe working procedures relevant to their tasks and should ensure that they are using appropriate PPE to protect against possible exposure. An example of a specific task which may give rise to potential exposure is filter replacement.

Wet methods are preferred for the clean-up of CNT spills. Methods for wet cleaning up are:

- Mist smaller areas with water containing mild detergent. Wipe with light coloured disposable wipes until clear then double bag wipes for disposal. (See Disposal of Carbon Nanotubes below).
- Larger areas, such as floors, should be cleaned using a wet vacuum with HEPA filtration or wet mopping technique with a disposable mop head.

Note: Do not use compressed air for cleaning

Cleaning and maintenance workers should be inducted into the facility and understand the hazards and controls used to minimise the risks of working with CNTs. Routine cleaning and maintenance tasks should be identified and controlled via the Risk Control Plan. A Job Safety Analysis (JSA) should be completed before any non-routine cleaning or maintenance procedure is undertaken.

PACKAGING AND TRANSPORT
It is recommended that precautions are taken during transport in order to prevent accidental spillage. CNTs are not classified as dangerous goods; however they should be kept separated from foodstuffs. It is recommended that CNTs are contained within two separate containers, one rigid impermeable container with a screw top or similar resealable closure, e.g., a clear polymer container with a screw top lid; and one flexible such as a resealable impermeable plastic bag — one container within the other. For more information on packaging dangerous goods see the *Australian Dangerous Goods Code (7th Edition):* Packing Instruction P002 (NTC 2007).

EMERGENCY MANAGEMENT

Spills and Accidental Release

Because of the potential for spillages and accidental release of CNTs, it is essential that an emergency response plan is established. This plan should be commensurate with the size of the spill or accidental release of CNTs. A large accidental release may require attendance by the appropriate emergency services. The plan should be readily accessible and available to all who may need it in case of emergency.

Dedicated spill kits should be readily available for use.

All clean-ups should be carried out in such a way as to ensure that exposure to personnel is as low as reasonably practicable. Workers who might be required to deal with such events must 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 is to be worn, as well as guidance on the safe disposal of any waste collected during the clean-up.

In the event of a spillage or accidental release, on-site personnel are to determine the extent of the area potentially affected and demarcate the area to restrict access by non-essential personnel. Measures are also to be put in place to reduce the likelihood of spreading nanomaterials from the affected area, for example the use of 'tacky' walk-off mats at the affected area's exit points. A suitable evacuation point upwind from prevailing winds should be identified in case all personnel need to be evacuated from the workplace.

First Aid

First Aid procedures should be developed consistent with the information contained in the SDS and should cover inhalation, ingestion, eye contact and skin contact.

SPILLS AND ACCIDENTAL RELEASE

- Consider the need to evacuate personnel from the area and move upwind.
- Clean up all spills as soon as it is practicable to do so safely.
- Avoid contact with skin and eyes using gloves and safety glasses and a disposable non-woven coverall with hood.
- Avoid inhalation of dust using a respirator — use a full face respirator with P3 filter.
- Use wet clean up procedures and avoid generating dust.
- Prevent spill or runoff from entering drains, sewers or water courses.
- Recover product wherever possible. Avoid generating dust.
- Put residues in labelled plastic bags, double bagged, or other sealed containers for disposal.
- If contamination of drains or waterways occurs, advise EPA or local water authority.

DISPOSAL OF CARBON NANOTUBES

Australian Environment Protection Agencies currently make no specific reference to the disposal of CNTs, however the UK Environment Agency takes the position that unbound CNT waste is hazardous waste. Taking a precautionary approach, CNT-bearing waste should be considered as hazardous, unless evidence suggests otherwise.

A plan for storage and disposal of CNTs and CNT contaminated waste should be developed. Any material that has come into contact with CNTs (that has not been decontaminated) should be considered as belonging to a CNT-bearing waste stream. This includes PPE (e.g., aprons, jackets, coveralls) wipes, blotters and other disposable laboratory materials used during research and production activities. Material from CNT-bearing waste streams should not be put into the regular waste or down sink drains. Surface contamination should be evaluated and decontamination should follow the processes outlined for cleaning and maintenance above. Equipment used to manufacture or handle nano-objects should be decontaminated before it is disposed of or reused. Wastes, including cleaning solutions, rinsing water and wipes used for decontamination should be treated as CNT-bearing waste.

High temperature incineration at a hazardous waste incinerator is a preferred disposal method (HSE 2011). Other technologies may be suitable if it can be demonstrated that they render the wastes safe. CNT waste should be double-wrapped in sealed polythene bags and stored in a secure, well labelled waste receptacle while awaiting collection by an authorised waste treatment service. The waste treatment service should provide adequate documentation of the disposal conditions and incineration temperature. Vitrification or the encapsulation of CNTs into glass or ceramic structures is a relatively new process still under development. It may be an alternative disposal technique for the future.

3.6 Risk Control Plan

The Risk Control Plan uses the information about potential hazards identified in Step 1, and the assessment made about the potential risks associated with these hazards as determined during Step 2. It should clearly outline implementation expectations, accountabilities and responsibilities. Everyone involved in the undertaking whether directly or indirectly should have an understanding of the risks and an appreciation of the controls used to manage these risks.

The Carbon Nanotube Health, Safety and Environment Risk Management Tool (Appendix B) can be used to document the Risk Control Plan and control measures.

3.7 Control validation

The controls chosen can be compared with the controls recommended by the ‘Control Banding’ approach to risk management (METHOD 2 in Part B of this document).

It is also important to validate controls through regular quality assurance of the CNTs and air monitoring to check the hazard hasn’t changed (see Step 4 – Monitor and Review).

STEP 4 — MONITOR AND REVIEW

The objective of the monitoring and review phase is to assess the effectiveness of the controls, and where possible, to improve the controls and further reduce the risk. The effectiveness of the controls used to manage risk should be reviewed within an agreed timeframe commensurate with the risk and the undertaking, including a check that they are working as expected. Monitoring and review can also include regular safety audits to ensure that controls are being used appropriately and that no additional hazards are introduced inadvertently into the workplace.

4.1 Emissions and exposure measurement and monitoring

Specialised equipment and measuring techniques are required to sample the air for the presence of CNTs. It is recommended that a qualified Occupational Hygienist, specially trained in monitoring atmospheric particulates, is engaged to take these measurements.

Workplace air should be monitored to determine process emissions or worker exposure levels. When feasible, personal sampling is preferred to ensure an accurate representation of the worker's exposure, whereas area sampling (e.g., size-fractionated aerosol samples) and real-time (direct reading) emissions measurements may be more useful for evaluating the need for improving engineering controls and work practices. The concentration of particles in workplace air needs to be taken before, during and after working with CNTs to see if there may be process emissions. It is also important to compare these results with particle concentrations taken immediately outside the work area (external environment) and in a 'control' area of the workplace, e.g., a remote office or in the workplace canteen, to check that any change observed is due to the process and does not result from an external change.

AIR MONITORING

General advice on air monitoring and measurement is available from the Safe Work Australia website and the OECD Working Party on Manufactured Nanomaterials (WPMN) emissions assessment procedure: *'Emission Assessment for Identification of Sources and Release of Airborne Manufactured Nanomaterials in the Workplace: Compilation of Existing Guidance'* (OECD WPMN 2009).

Work is currently being undertaken, both in Australia and overseas, to validate and improve measurement techniques for CNTs.

NIOSH (2010) has proposed a Recommended Exposure Limit (REL) of 7μg/m^3 for CNTs, determined as elemental carbon by NIOSH Method 5040. In work environments where exposure to other types of elemental carbon (e.g., diesel exhaust, combustion products) and fibrous particulates might occur, the use of additional analytical techniques can help to better characterize exposures. For example, analysis of airborne samples by transmission electron microscopy (TEM) equipped with x-ray energy dispersive spectroscopy (EDS), can help to verify the presence of CNTs and CNFs from other possible elemental carbon containing particles (e.g., diesel soot, carbon black) (NIOSH 2010).

4.2 Health monitoring and record of operations

There are no current tests that are specific to CNTs that can be used for health monitoring. However a prudent approach, in the current state of knowledge, is to collect information about the materials being used and the duration of use and potential or actual exposures. Such information will help to build up a risk profile of potential exposures which could be important if any health effects are observed at a later date.

PART B

METHOD 2 — RISK MANAGEMENT BY CONTROL BANDING

Control banding for CNTs involves a simplified form of the risk management approach, where specific controls are recommended based on process risk. CNTs are considered to be hazardous, therefore the recommended controls are based on the potential level of exposure. Control banding can be used when production and manufacturing processes are well understood, potential exposure routes are known and safe work procedures (SWPs) are developed and followed.

The controls selected by use of METHOD 1 can be compared with those recommended in METHOD 2.

This method of controlling risks involves the following 4-step approach. This is a precautionary approach, developed using practical experience at CSIRO.

Step 1. Determine the 'Exposure Potential' i.e. the amount of CNTs that are likely to be airborne, using the information in the two tables below.

- The 'Quantity Risk Factor' considers the amount of CNTs that is handled (Table 1).
- The 'Task Exposure Assessment' considers the type of activity involving the use of CNTs (Table 2), and the likelihood of that task leading to exposure.
- A combination of these factors gives the 'Exposure Potential' (Table 3).

Step 2. Use the matrix (Table 3) below to find the Control Band (1-4) depending on quantities used and task exposure (the 'Exposure Potential')

Step 3. Apply the controls indicated for the appropriate Control Band (Table 4)

Step 4. Monitor, review and validate the effectiveness of the controls used to manage risk (Refer to Step 4 in Part A of this document)

Consultation with workers in progressing through each of these steps is essential.

To check the effectiveness of controls in preventing exposure, the use of air monitoring is recommended.

Table 1 — Quantity Risk Factor

Quantity Risk Factor: The amount of CNTs that could potentially be used in the process at any time. Reducing the quantities of CNTs used will assist in reducing the risk factor.	
Quantity	**Description**
A	above 1 kilogram
B	above 100 grams to 1 kilogram
C	above 10 grams to 100 grams
D	micrograms to 10 grams

Table 2 — Task exposure assessment

Task Exposure Assessment

The type of tasks undertaken in the workplace will determine the exposure risk e.g. whether CNT's will become airbone. Tasks with a high exposure potential should be minimised where possible.

Assessed Exposure	Example of Tasks/Scenarios
High	■ Tasks that are likely to produce airborne CNTs ■ CNTs are handled in dry state or powder form, e.g. weighing and measuring ■ Manufacture of CNTs — e.g. synthesis, growing ■ Scraping and packing of dry CNTs ■ Opening bags of dry CNTs and adding them to a hopper
Moderately High	■ Blending CNTs into polymers ■ CNTs are mechanically manipulated, e.g. weave, knit, twist, pull, cut, grind, scrape ■ Cutting/grinding polymers containing CNTs if CNTs can be released from the matrix ■ CNTs in solution which are likely to be atomised ■ Strong agitation of solution or sonication
Moderately Low	■ Extruding and manipulating polymers containing CNTs ■ Processing, shaping, moulding of polymers containing CNTs ■ Cutting/grinding polymers containing CNTs if CNTs are unlikely to be released from the matrix ■ Solutions containing CNTs are mixed or agitated
Low	■ CNTs cannot be detected in the air using appropriate measuring and monitoring techniques ■ CNTs are embedded in a polymer type matrix and no machining ■ Painting, coating or packaging of extruded product

STEP 2 — DETERMINE THE CONTROL BAND

Table 3 — Matrix to Determine the Control Band (1-4)

Exposure Potential Determining the exposure potential, and hence the recommended control band, based on the quantity of CNTs handled, and the likelihood that CNTs will become airborne.				
	High Assessed Exposure	Moderately High Assessed Exposure	Moderately Low Assessed Exposure	Low Assessed Exposure
Quantity A	4	4	3	2
Quantity B	4	3	3	2
Quantity C	4	3	2	1
Quantity D	3	2	1	1

STEP 3 — APPLY CONTROLS

Table 4 — Controls Recommended for Control Bands (1-4)

These controls are recommended for the handling of CNTs and should be supported by appropriate administrative controls. The choice of controls for any activity must be appropriate for all chemicals involved, not just the CNTs.

Control Band 4		
Inhalation Controls	**Dermal Controls**	**Environmental Controls**
Normal operations ■ Fully isolated work area with remote control operations ■ SWP has to be developed for entering the isolated workroom ■ Intrinsically safe electrical systems ■ Wet cutting of solid articles containing CNTs Emergencies (e.g. spills) ■ P3 Particulate – Full Face respirator (PAPR) Clean-up & maintenance ■ Specific training required ■ JSA required to determine level of control and use of either P2 or P3 respirator Exhaust air ■ Single pass through HEPA filtered exhaust ventilation to external environment fitted with scrubbers	Normal operations ■ Fully isolated work area with remote control operations ■ SWP has to be developed for entering the isolated workroom Clean-up & maintenance ■ Full Tyvek coverall and hood ■ Double nitrile gloves ■ Disposable over-booties for shoes ■ Protective eye wear ■ Long trousers — no cuffs Emergencies (e.g. spills) As part of full PPE kit for emergencies: ■ Full Tyvek coverall and hood ■ Double nitrile gloves ■ Disposable over-booties for shoes ■ Eye protection provided by full face respirator ■ Long trousers — no cuffs	■ Bunds and drain covers readily accessible ■ Emergency clean-up SWP documented and clean-up materials readily available, e.g., sealed containers, spades, mops, mist or fog generating equipment

Control Band 3		
Inhalation Controls	**Dermal Controls**	**Environmental Controls**
Normal operations ■ Intrinsically safe electrical system for high exposure potential situations ■ Sealed glove box or biological cabinet for measurement or physical manipulation ■ Negative pressure work area ■ Local flexible exhaust ventilation (LEV) for 'Quantity A' (>1kg) with moderately low exposure risk ■ P2 Particulate – Half face respirator reusable or disposable when working with LEV ■ Wet cutting of solid articles containing CNTs Emergencies (e.g. spills) ■ P3 Particulate – Full Face respirator (PAPR) Clean-up & maintenance ■ Specific training required ■ JSA required to determine level of control and use of either P2 or P3 respirator Exhaust air ■ Single pass through HEPA filtered exhaust ventilation to external environment fitted with scrubbers	Normal operations ■ Tyvek lab coat ■ Close fitting safety glasses ■ Nitrile gloves — change regularly ■ Long trousers — no cuffs Clean-up & maintenance ■ Tyvek lab coat ■ Protective eyewear ■ Disposable over-booties for shoes ■ Nitrile gloves — change regularly ■ Long trousers — no cuffs Emergencies (e.g. spills) ■ Full Tyvek coverall and hood ■ Double nitrile gloves ■ Disposable over-booties for shoes ■ Protective eye wear ■ Long trousers — no cuffs	■ Bunds and drain covers readily accessible ■ Emergency clean-up SWP documented and clean-up materials readily available, e.g., sealed containers, spades, mops, mist or fog generating equipment

Control Band 2		
Inhalation Controls	**Dermal Controls**	**Environmental Controls**
Normal operations ■ Negative pressure work area ■ Fume cupboard ■ Local flexible exhaust ventilation for 'Quantity A' (>1kg) with low exposure risk ■ P2 Particulate – Half face respirator reusable or disposable ■ Wet cutting of solid articles containing CNTs Emergencies (e.g. spills) ■ P3 Full face or P2 half face reusable respirator (depending on quantity spilled) ■ Clean-up & maintenance ■ P2 half face reusable respirator Exhaust air ■ Single pass exhaust ventilation to external environment	Normal operations ■ Nitrile gloves — change regularly ■ Tyvek lab coat ■ Close fitting safety glasses ■ Long trousers — no cuffs Clean-up & maintenance ■ Tyvek lab coat ■ Protective eyewear ■ Nitrile gloves — change regularly ■ Long trousers — no cuffs Emergencies (e.g. spills) ■ Nitrile gloves — change regularly ■ Tyvek lab coat ■ Protective eye wear ■ Disposable over-booties for shoes ■ Long trousers — no cuffs	■ Bunds and drain covers readily accessible ■ Emergency clean-up SWP docume nted and appropriately sized spill kit and containment equipment readily available

Control Band 1		
Inhalation Controls	**Dermal Controls**	**Environmental Controls**
Normal operations ■ Negative pressure work area ■ Local exhaust ventilation for processes with higher inhalation exposure risk ■ P2 Particulate – Half face respirator reusable or disposable ■ Wet cutting of solid articles containing CNTs Emergencies (e.g. spills) ■ P2 Particulate – Half face respirator reusable or disposable Clean-up & maintenance ■ P2 Particulate – Half face respirator reusable or disposable Exhaust air ■ Single pass exhaust ventilation to external environment	Normal operations ■ Nitrile gloves ■ Lab Coat ■ Close fitting safety glasses ■ Long trousers — no cuffs Clean-up & maintenance ■ Nitrile gloves ■ Lab Coat ■ Close fitting safety glasses ■ Long trousers — no cuffs Emergencies (e.g. spills) ■ Nitrile gloves ■ Lab Coat ■ Close fitting safety glasses ■ Long trousers — no cuffs	■ Emergency clean-up SWP documented and spill kit readily available

APPENDIX A — REFERENCES

Bello D, Wardle BL, Yamamoto N, 2, Guzman de Villoria R, and Hallock M (2009). Exposure to nanoscale particles and fibers during machining of hybrid advanced composites containing carbon nanotubes. Journal of Nanoparticle Research,11 (1):, 231-249.

BSI (2007). *Nanotechnologies – Part 2: A guide to safe handling and disposal of manufactured nanoparticles, BSI PD 6699-2:2007,* British Standards Institution (BSI).

CSIRO (2009). *Multi-walled carbon nanotubes*. MSDS. 1 June 2009. http://www.csiro.au/files/files/pr6a.pdf

Han JH, Lee EJ, Lee JH, So KP, Lee YH, Bae GN, Lee SB, Ji JH, Cho MH, Yu IJ.(2008) Monitoring multiwalled carbon nanotube exposure in carbon nanotube research facility. Inhal Toxicol., 20(8):741-9.

HSE (2011). *Risk management of carbon nanotubes*. Information Sheet. www.hse.gov.uk/pubns/web38.pdf

Ku BK, Emery MS, Maynard AD, Stolzenburg MR and McMurry PH (2006). In situ structure characterization of airborne carbon nanofibres by a tandem mobility-mass analysis. Nanotechnology, 17:3613-3621.

Nanosafe (2008). *Efficiency of fibrous filters and personal protective equipments against nanoparticles,* DR-325/326-200801-1, Nanosafe2. http://www.nanosafe.org/home/liblocal/docs/Dissemination%20report/DR1_s.pdf

NIOSH (2010). Current Intelligence Bulletin: *Occupational Exposure to Carbon Nanotubes and Nanofibers.* Draft for Public Comment, November 2010.

NTC (2007). *Australian Dangerous Goods Code (7th Edition):* Packing Instruction P002, National Transport Commission.

OECD WPMN (2009). *Emission Assessment for Identification of Sources and Release of Airborne Manufactured Nanomaterials in the Workplace: Compilation of Existing Guidance,* OECD Working Party on Manufactured Nanomaterials.

RMIT University (2010). *Engineered Nanomaterials: Investigating substitution and modification options to reduce potential hazards* http://www.safeworkaustralia.gov.au/AboutSafeWorkAustralia/WhatWeDo/Publications/Pages/RP201008EngineeredNanomaterialsInvestigatingSubstitutionAndModification.aspx

Standards Australia (2003). *Hazard and Operability Studies (HAZOP Studies) — Application guide,* Australian Standard, AS IEC 61882 — 2003.

Toxikos (2009). *Engineered nanomaterials: A review of the toxicology and health hazards* http://www.safeworkaustralia.gov.au/AboutSafeWorkAustralia/WhatWeDo/Publications/Pages/RR200911ENReviewOfToxicology.aspx

APPENDIX B — CARBON NANOTUBE HEALTH, SAFETY AND ENVIRONMENT RISK MANAGEMENT TOOL

Use this tool to identify and control health, safety and environmental risks associated with carbon nanotubes (CNTs) in the workplace.

Carbon Nanotube Health, Safety and Environment Risk Management Tool		
Project: Date:	Work Area:	
Preparation for the Assessment		
Description of tasks/processes involving the use, manipulation and production of carbon nanotubes		
Outline sources of relevant health and safety information, legislation		
Step 1. Identify the Hazards Identification — Define the characteristics of the fibre/particle		
	Response	Comments/Description
Composition known	Yes ☐ No ☐	
Type of CNT	SWCNT MWCNT	Other e.g. combination
Quantity used	µg/mg/g/kg	
Are CNTs bound together tightly or loosely	Tight ☐ Loose ☐	
Surface modified or coated?	Yes ☐ No ☐	
Contaminants e.g. from metallic catalysts	Yes ☐ No ☐	
Frequency of use	daily/weekly/monthly	
Particle/fibre length	µm	
Particle/fibre width	nm	Aspect ratio (length/width)

Step 2. Risk Assessment		Step 2.1. Exposure Assessment		Step 2.2. Risk Evaluation	
Assess the risk of exposure from each of the tasks/activities	**Task/activity undertaken? Yes √**	**Inhalation and Ingestion (1)***	**Absorption (2)***	**Current Control**	**Additional Controls required? Yes √ (Go to Step 3)**
CNT synthesis	☐				
Sample preparation e.g. weighing, measuring, opening packages, decanting, moving	☐				
Mechanical processes e.g. scraping, mixing, cutting, grinding, abrasion, agitation	☐				
Aerosol, dust, fume or vapour generation (including solutions, suspensions, slurries)	☐				
Spraying/coating/painting	☐				
Release of CNTs from processing/packaging/coatings/wrappings	☐				
Poor hygiene e.g. eating in the work area	☐				

(1)* Does the work involve any processes that may result in the generation of aerosols, dusts, fumes or vapours?

(2)* Is there the potential for CNTs to come into contact with exposed skin? (Dermal/mucous membrane)
Assess the risk of exposure from each of the tasks/activities to:

- Skin or damaged skin due to e.g. cuts, abrasions or wounds
- Mucous membranes (mouth, eyes, nose)

Step 2. Risk Assessment – Other HSE Risks and Considerations		Step 2.2. Risk Evaluation	
Potential Issue	**Yes √**	**Analysis and Data**	**Additional Controls Required Yes √ (Step 3)**
Are other hazardous chemicals used e.g. flammable, toxics (e.g. heavy metals), acidic, others?	☐	Chemical Dangerous Goods Class Health Hazards Risk & Safety Phrases (R & S Phrases)	
Are any incompatible chemical reagents or substances used? (Check the SDS)	☐		
Potential environmental release and impact ■ Release to air ■ Release to water ■ Release to sewer ■ Release to land	☐	Potential impact	
Are there plant and/or equipment risks? A plant risk assessment will need to be completed as per local WHS Regulations	☐	Type of plant/equipment risks	
CNTs are highly conductive. Are intrinsically safe electrical systems needed to protect against e.g. short circuit?	☐		
Final Product — potential WHS&E impacts			
Are CNTs likely to be liberated from the final product by the end user during normal use e.g. by washing, manipulation or normal wear and tear	☐		
Are CNTs likely to be liberated during other unintended processing e.g. by cutting, grinding, sheering, ripping or dumping	☐		

Step 2. Risk Assessment — Other Production Activities	Yes √	Step 2.2. Risk Evaluation	
Cleaning and Maintenance		**Analysis and Data**	**Additional Controls Required Yes √ (Step 3)**
SWP completed for general cleaning and maintenance ■ Ventilation and extraction systems ■ Plant and equipment servicing and repairs ■ Cleaning and disposal techniques documented ■ Appropriate laundry facilities available	 ☐ ☐ ☐ ☐		
Is appropriate PPE available?	☐		
Are cleanup materials and equipment available? ■ Strong disposable wet wipes ■ Dedicated HEPA vacuum cleaner ■ Other e.g. spades, mops, etc. Describe.	 ☐ ☐ ☐		
Packaging and Transport – CNTs are not classified as Dangerous Goods (according to ADG Code, Edition 7)			
Two containers should be used — one rigid and resealable, one flexible	☐		
As a precautionary approach, consider transport in accordance with ADG Code *Edition 7 (P002)*	☐		
Are SDS, labels and safety instructions available?	☐		
Emergency Management			
■ SWP completed for emergencies e.g. for spills and accidental loss of containment, or in case of fire or flood ■ First aid procedures defined? ■ Appropriate PPE readily available?	☐ ☐ ☐		
Disposal Procedures. How are wastes to be disposed? Tick each box as appropriate. **NB Includes contaminated wipes, PPE, clothing, filtering and weighing media**			
Initial Containment	Encapsulation in polymer matrix ☐	Double bagged and placed in secure bins for collection ☐	
Ultimate Disposal	Secure land fill ☐	High temperature incineration ☐	Vitrification into glass or ceramics ☐

Personal Protection Equipment and Clothing — Use only as a backup protection for processing operations. PPE may be the primary source of protection in case of emergencies, or for plant cleaning and maintenance.				
Respirators. Correct face fit is essential — test each respirator before use. Tick as required.				
■ Better Protection	Full face – Powered Air Purifying Respirators (PAPR)	☐	Full face – P3 high efficiency particle filter(s)	☐
■ Good Protection	Half face – P3 high efficiency particle filter(s)	☐	Half face – P2 high efficiency particle filter(s)	☐
■ Low Protection	Disposable P2 mask	☐		
Gloves – tick as required. There are many different type and styles available – suitability needs to be assessed. Double gloving is recommended where increased protection is required.				
■ Better Protection	Neoprene (May be dexterity concerns)	☐		
■ Good Protection	Nitrile	☐		
■ Low Protection	Latex, vinyl	☐		
Clothing – tick as required.				
■ Better Protection	Full chemical suit, e.g., Type 5 CE Category 3 e.g. coverall with hood (not to be used in flammable environments)	☐		
■ Good Protection	Non-woven coverall	☐	Non-woven coverall with hood	☐
■ Low Protection	Non-woven lab coat	☐	Woven fabric lab coat (not recommended)	☐
Eye Protection – tick as required.				
■ Good Protection	Full face respirator	☐		
■ Low Protection	Australian Standard safety glasses	☐		

Enter the health and safety or environmental risk identified (Step 2 above) into the following table and document the additional controls required to eliminate or reduce risk for implementation into the workplace.

Step 3 – Risk Control Plan						
Process/Activity	**Hazard Type**	**Risk Description**	**Comment/Proposed Control**	**Timeframe**	**Status**	**Action**

Step 4. Monitoring and Review.			
	Yes √	Comments/Proposed Controls	Action
Health Monitoring			
Is health monitoring required for any chemicals in the facility?			
Is information about use of CNTs being recorded and kept, e.g. names of people working in the area, type of materials being used and duration of use			
Air Monitoring			
Is air monitoring required?			
How will monitoring be undertaken?			
How will the effectiveness of controls be validated during the review	Airflow/ventilation testing ☐ Wipe testing ☐	Safety audit and inspection ☐ PPE Use and Maintenance ☐	Dust sampling ☐ Safety literature review ☐
How frequently do controls implemented to manage risks need to be reviewed?	Weekly ☐	Monthly ☐ Annually ☐	Biennially ☐

Approval and Sign-off	Name	Signature	Date
Line Manager/Supervisor			
Project/Production Team Rep			
Health, Safety & Environment Specialist/Consultant			

THIS GUIDE PROVIDES INFORMATION ON THE SAFE HANDLING AND USE OF CARBON NANOTUBES IN THE WORKPLACE.