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STRATEGIES, TECHNIQUES AND SAMPLING PROTOCOLS FOR DETERMINING THE CONCENTRATIONS OF MANUFACTURED NANOMATERIALS IN AIR AT THE WORKPLACE

Series on the Safety of Manufactured Nanomaterials
No. 82

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Series on the Safety of Manufactured Nanomaterials

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STRATEGIES, TECHNIQUES AND SAMPLING PROTOCOLS FOR DETERMINING THE CONCENTRATIONS OF MANUFACTURED NANOMATERIALS IN AIR AT THE WORKPLACE

IOMC

INTER-ORGANIZATION PROGRAMME FOR THE SOUND MANAGEMENT OF CHEMICALS

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Environment Directorate
ORGANISATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT
Paris, 2017

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Nos. 44-54, These items are the dossiers derived from the Testing Programme on Manufactured Nanomaterials which are located at:
http://www.oecd.org/chemicalsafety/nanosafety/testing-programme-manufactured-nanomaterials.htm

No.55, *Harmonized Tiered Approach to Measure and Assess the Potential Exposure to Airbone Emissions of Engineered Nano-objects and their Agglomerates and Aggregates at Workplaces. (2015)*

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The Organisation for Economic Co-operation and Development (OECD) is an intergovernmental organisation in which representatives of 35 industrialised countries in North and South America, Europe and the Asia and Pacific region, as well as the European Commission, meet to co-ordinate and harmonise policies, discuss issues of mutual concern, and work together to respond to international problems. Most of the OECD's work is carried out by more than 200 specialised committees and working groups composed of member country delegates. Observers from several countries with special status at the OECD, and from interested international organisations, attend many of the OECD's workshops and other meetings. Committees and working groups are served by the OECD Secretariat, located in Paris, France, which is organised into directorates and divisions.

The Environment, Health and Safety Division publishes free-of-charge documents in eleven different series: **Testing and Assessment**; **Good Laboratory Practice and Compliance Monitoring; Pesticides; Biocides; Risk Management; Harmonisation of Regulatory Oversight in Biotechnology; Safety of Novel . Foods and Feeds; Chemical Accidents; Pollutant Release and Transfer Registers; Emission Scenario Documents;** and **Safety of Manufactured Nanomaterials.** More information about the Environment, Health and Safety Programme and EHS publications is available on the OECD's World Wide Web site (www.oecd.org/chemicalsafety/).

The Inter-Organisation Programme for the Sound Management of Chemicals (IOMC) was established in 1995 following recommendations made by the 1992 UN Conference on Environment and Development to strengthen co-operation and increase international co-ordination in the field of chemical safety. The Participating Organisations are FAO, ILO, UNDP, UNEP, UNIDO, UNITAR, WHO, World Bank and OECD. The purpose of the IOMC is to promote co-ordination of the policies and activities pursued by the Participating Organisations, jointly or separately, to achieve the sound management of chemicals in relation to human health and the environment.

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FOREWORD

The OECD Joint Meeting of the Chemicals Committee and Working Party on Chemicals, Pesticides and Biotechnology (the Joint Meeting) held a Special Session on the Potential Implications of Manufactured Nanomaterials for Human Health and Environmental Safety in June 2005. This was the first opportunity for OECD member countries, together with observers and invited experts, to begin to identify human health and environmental safety related aspects of manufactured nanomaterials. The scope of this session was intended to address the chemicals sector.

As a follow-up, the OECD Workshop on the Safety of Manufactured Nanomaterials was organised (December 2005), in Washington, D.C. to determine the "state of the art" for the safety assessment of manufactured nanomaterials with a particular focus on identifying future needs for risk assessment within a regulatory context.

Following the conclusions and recommendations of the Workshop [ENV/JM/MONO(2006)19], the OECD Council established the OECD Working Party on Manufactured Nanomaterials (WPMN) as a subsidiary body of the OECD Chemicals Committee in September 2006. This programme concentrates on human health and environmental safety implications of manufactured nanomaterials (limited mainly to the chemicals sector), and aims to ensure that the approach to hazard, exposure and risk assessment is of a high, science-based, and internationally harmonised standard. It promotes international co-operation on the human health and environmental safety of manufactured nanomaterials, and involves the safety testing and risk assessment of manufactured nanomaterials.

The objective of this document is to contribute to existing knowledge regarding methods for measuring characteristics of airborne nanoparticles and controlling occupational exposure to airborne nanoparticles, and to gather data on nanoparticle emission and transport in various workplaces. As such, it includes the findings of research undertaken in non-industrial nanotechnology workplaces involving the measurement of nanomaterials emissions and exposures. The six case studies presented in this document demonstrate how measurement and assessment of nanomaterials can be undertaken and how results can be interpreted.

Finally, it is worth mentioning that this document contributed to the development of the document "Harmonized Tiered Approach to Measure and Assess the Potential Exposure to Airborne Emissions of Engineered Nano-Objects and their Agglomerates and Aggregates at Workplaces" published as No.55 in the OECD Series on the Safety of Manufactured Nanomaterials [ENV/JM/MONO(2015)19].

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PREFACE

Approach for Nanomaterials Emissions and Exposure Measurement

1. This report finds that a three-tiered assessment process may be used effectively and supports previous recommendations on the use of a three-tiered approach [51, 76, 77, 105].

- Tier One
  - The Tier One assessment involves a standard industrial hygiene survey of the process area and is predominantly focussed on gathering qualitative information, with some quantitative measurement, to identify likely points of particle emission.
- Tier Two
  - Tier Two assessment involves characterising particle number and mass concentration, to evaluate emission sources, breathing zone exposure of process operators, incidental and background particles, and effectiveness of particle emission controls. A complementary set of instruments such as a portable condensation particle counter (CPC), optical particle counter (OPC), and photometer can be used effectively.
- Tier Three
  - A Tier Three assessment involves repeating Tier Two measurements, together with simultaneous collection of particles for off-line analysis of mass or fibre concentration, particle morphology and chemical composition. Filter and electrostatic precipitator based samples can be collected for chemical analysis, SEM, TEM, EDX and XRD. Off-line analysis can be compared to real-time measurement results. Additional real-time instruments such as an SMPS, APS, OPS or ELPI may be used in the Tier Three assessment.

2. Results from either Tier Two or Tier Three, or both, can be compared with particle control values for decision-making about controls.

3. The use of particle number and mass concentration during Tier 1 and 2 assessments across both the sub and supermicrometre size range, relative to the background, is a practical screening indicator of when a process may require control of particle emission and this overcomes issues with background particle concentration variation. It also allows use of non-complex instruments such as CPC, OPC and photometers. This approach is deliberately pragmatic because no single instrument is capable of simultaneously measuring all nanomaterial traits of interest, some other instrumentation is large and bulky, some measurement methods are complex and expensive to utilise, and instrumentation and methods for characterisation of personal aerosol exposure to sub-micron particles are limited.

4. In contrast, the Tier 3 assessment provides the opportunity to utilise complex instruments and methods to characterise both particle exposure and emission in terms of agglomeration, aggregation, primary particles, fibre morphology, particle morphology and chemical composition.

5. Though variable, the background particle number concentration, i.e. the *local particle reference value* can be used as a particle control value. It cannot be used to make conclusions about exposure related health effects, but provides for replicable decision making regarding control of emissions.

6. The findings of this report support application of a three-tiered approach described by a number of authors, including the OECD in *Emission Assessment for the Identification of Sources and Release of Airborne Manufactured Nanomaterials in the Workplace: Compilation of Existing Guidance. ENV/JM/MONO(2009)16* [76]. Additional measurement detail is provided in this report to refine the approach. While the focus in the report is on workplace measurements, the methods described can be applied to determine the concentrations of manufactured nanomaterials in air generally. Finally, further work was done to examine the tiered approaches on the OECD project harmonized tiered approach to measure and assess the potential exposure to airborne emissions of engineered nano-objects and their agglomerates and aggregates in workplaces [112].

7. The six selected processes included in the particle measurements are all from research and devlopment, laboratory scale processes or experimental settings, which do not reflect all the processes throughout the life cycle of nanomaterials, e.g. the processes and activities in the use phase. However, while the research in this study was undertaken in non-industrial workplaces, previous work has shown that the three-tiered approach can be applied effectively in industrial situations [52]. Nevertheless, strategies described in this report may be refined as further work is undertaken, such as examining their applicability in industrial situations and further examination of the decision criteria proposed on whether to proceed to the next Tier in an assessment. For this reason, this document can be considered a “living text” which may be updated, in the light of new knowledge, at a later stage.

AKNOWLEDGMENTS

8. This report utilises the findings in the research report on: Measurements of particle emissions from nanotechnology processes, with assessment of measuring techniques and workplace controls by Queensland University of Technology and Workplace Health and Safety Queensland, commissioned by Safe Work Australia [101]. The research was first undertaken by Peter McGarry (Principal Researcher), Lidia Morawska (Project Leader), Howard Morris, Luke Knibbs, and Andrea Capasso. The report was then submitted for comments to the experts participating in the WPMN project *Exposure Measurement and Exposure Mitigation of Manufactured Nanomaterial*. The final draft was forwarded to the *OECD Working Party on Manufactured Nanomaterials (WPMN)* for its endorsement.

9. This report also considered work undertaken by other groups and organisations to provide advice on nanomaterials emissions and exposure assessment.

EXECUTIVE SUMMARY

10. This report presents the findings of research undertaken in non-industrial nanotechnology workplaces involving the measurement of nanomaterials emissions and exposures. The six case studies presented demonstrate how measurement and assessment can be undertaken and how results can be interpreted. Analysis of the results informs the validity of measurement techniques and an assessment of the effectiveness of measurement techniques and workplace controls. The case studies also provide data on nanomaterial emission and transport in various non-industrial workplaces.

11. The report then considers these research findings together with work undertaken by other groups and organisations to provide advice on the measurement of nanomaterials emissions and exposures.

Scope of the research project – 6 case studies

12. The scope of this study involved investigating the characteristics and behaviour of particles arising from the operation of six nanotechnology processes, subdivided into nine processes for measurement purposes.

13. The research included real-time measurement of sub, and supermicrometre particle number and mass concentration, count median diameter, and alveolar deposited surface area, using condensation particle counters, an optical particle counter, DustTrak photometer, scanning mobility particle sizer, and nanoparticle surface area monitor, respectively. Off-line particle analysis included scanning and transmission electron microscopy, energy-dispersive x-ray spectrometry, and thermal optical analysis of elemental carbon. Sources of fibrous and non-fibrous particles were included.

Summary of main findings of the research project

14. Measurement of background concentrations of particles, i.e. without nanotechnology processes operating, showed workers at each of the nanotechnology processes are constantly exposed to varying concentrations of both sub and super micrometre particles. This *local background particle exposure*[1] arises from sources of particles ubiquitous in the general environment. Therefore it is essential that this *local background particle* concentration be accounted for when characterising the emission of particles, and assessing exposure of nanotechnology workers arising from the operation of nanotechnology processes. The range of mean l*ocal background particle* concentration for the nine nanotechnology environments included in this study were particle number concentrations (PNC): $PNC_{20\text{-}1000nm}$ - 5.5×10^2 particles cm^{-3} to 1.1×10^4 particles cm^{-3}, $PNC_{300\text{-}3000nm}$ - < 1 to 37 particles cm^{-3}, and particle mass (PM) concentration: $PM_{2.5}$ – 1 µg m^{-3} to 25 µg m^{-3}.

15. Mean particle concentrations measured at emission points of the nine processes showed that for seven of the processes the $PNC_{20\text{-}1000nm}$ and $PM_{2.5}$ were the same order of magnitude as that of the *local particle background concentration*, with the other two processes being one order of magnitude higher. Of the five processes for which $PNC_{300\text{-}3000nm}$ was characterised, three were of the same order of magnitude as

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[1] local work area eight-hour time-weighted average particle number or mass concentration that excludes any contribution of particles from the nanotechnology process. This value is specific to each work environment.

that of the local particle background, one was an order of magnitude higher, and one was two orders of magnitude higher.

16. Particle number and mass concentration within the sub and supermicrometre size range consistently showed significant particle variation associated with the nanotechnology process when compared to background. Evaluation of peak particle concentrations relative to the *local background particle* concentration showed the median value of the peaks exceeded the *local background particle* concentration by a factor of five or more as follows: $PNC_{20-1000nm}$ - five of seven processes, $PNC_{300-3000nm}$ – two of seven processes, and $PM_{2.5}$ - five of seven processes.

17. Characterisation of peak concentration values, across both the sub and supermicrometre size range, relative to the background is a practical screening indicator of when a process may require control of particle emission and this overcomes issues with background particle concentration variation. It also allows use of non-complex instruments such as CPC, OPC and photometers.

18. Count median diameter (CMD) values obtained simultaneously with PNC and $PM_{2.5}$ values for six processes using a scanning mobility particle sizer with an upper particle measurement size of 160 nm, showed the CMD during operation of the process was similar to the background. An analysis of the data from all three measurements together indicates that particle emissions and exposures from these nanotechnology processes are unlikely to be exclusively ultrafine in nature.

CONSIDERING FINDINGS OF THIS STUDY AND OTHER WORK UNDERTAKEN IN THIS FIELD: ADVICE ON PARTICLE ASSESSMENT

19. A detailed assessment of workplace nanomaterial exposure and emissions involves characterising temporal and spatial particle number and mass concentration when evaluating emission sources, breathing zone exposure of process operators, incidental and background particles, and effectiveness of particle emission controls. The results of research in this study clearly indicate that a complementary set of instruments, such as a portable condensation particle counter (CPC) (e.g. the P-Trak), optical particle counter (OPC), and photometer (e.g. the DustTrak) can be used to gather both temporal and spatial data in terms of particle emission. This supports the findings of previous work [51, 76, 77]. As reported in the document, the research work was undertaken with instruments from one instrument manufacturer. However, other equipment manufacturers can also supply similar instrumentation with potentially similar performance.

20. There are two types of particles that workers can be exposed to as a result of processes involving manufactured nanomaterials; (a) manufactured nanomaterials emitted from the process and (b) incidental nanoparticles, e.g. combustion particles, resulting from operation of the process machines. It is necessary to differentiate between the two types of particles.

21. In addition, if required, filter and electrostatic precipitator based samples can be collected with relative ease for off-line analysis by electron microscopy and energy-dispersive x-ray spectrometry.

22. In regard to measurement of larger particles i.e agglomerates and aggregates of nanomaterials, there are some issues to be considered:

1. OPC measurements

    - There can be an issue if particles used to calibrate the instrument differ significantly to those of the aerosol of interest. For example, where fibrous particles are encountered and the OPC has been calibrated for spherical particles, there can be resultant undercounting by the OPC. However, this can be addressed by simultaneously measuring mass concentrations.

    - As an example, from the results of carbon nanotube aerosol measurement, electron microscopy indicated that the presence of particles with dimensions greater than 10µm, a significant $PM_{2.5}$ response was evident but insignificant $PNC_{>3000nm}$ was recorded by the OPC.

2. Photometer measurements

    - Photometers (e.g. DustTrak) are a very useful screening instrument to assess emissions. However, they do not provide true gravimetric mass concentration data, but provide an estimate based upon the measured response to light scattering of particles. The light scattering detected by the instrument is a function of particle size, shape, and refractive index which may differ significantly amongst different sources of aerosols. Hence, photometers should not be used as a substitute for the sampling and analytical method recommended for declared national exposure standards or exposure limits.

23. A company or laboratory may set its own in-house control limits for nanomaterials, but these must be equal to or lower, i.e. more stringent, than applicable national regulatory limits.

24. Organisations may also utilise the following hierarchy of *Particle Control Values* when assessing in detail the significance of particle emission and exposure, most preferred first:

- A country's national exposure standards or limits, e.g. Recommended Exposure Limits (US NIOSH) or Australian Workplace Exposure Standards
- National exposure standards or limits from another country
- Proposed workplace exposure limits – from research results
- Benchmark exposure levels – which have some consideration of health effects
- Local particle reference values derived from characterising background particle levels

25. This approach may be refined in the future as further guidance on the setting of occupational exposure limits for nanomaterials is developed.

26. Ease and speed of analysis is also a factor. For fast screening analysis, measurements with CPC, OPC and photometer can be compared with local particle reference values based on the local background particle concentration.

27. In this study, $PM_{2.5}$ measurement is employed for mass concentration. The respirable fraction (PM_4) is broadly used in the field of industrial hygiene and occupational exposure limits are often proposed as the value for respirable fraction, e.g., RELs and OELs for nano-TiO_2 and CNTs proposed by US NIOSH and Japan AIST. Both size fraction measurements can be used, but the size fraction measured should align with the relevant administrative/regulatory size fraction.

28. This study finds that a three-tiered particle assessment process may be used effectively, as outlined in points 14 to 16. This approach is similar to three-tiered approaches recommended by other authors [51,76,77,105], with some difference in fine detail, e.g. (a) recommending the use of photometers and (b) the specific excursion criteria used in Tier Two.

29. While the research in this study was undertaken in non-industrial workplaces, previous work has shown that the three-tiered approach can be applied effectively in industrial situations [52].

30. The assessment results for each tier are used to assess whether emissions and exposures are controlled effectively and hence for decision-making about controls used. It may not be necessary to utilize all three tiers. Tier One assessment alone, or Tier One plus Tier Two assessments may be sufficient.

31. **Tier One:** the Tier One assessment involves a standard industrial hygiene survey of the process area and is predominantly focussed upon the gathering of qualitative information. Quantitative data is gathered to identify likely points of particle emission relative to the background. The information gathered during Tier One is used to inform the Tier Two measurement process if needed, e.g. if potential or actual releases are identified in Tier One, but the information is insufficient for decision-making about controls.

32. **Tier Two:** the Tier Two assessment process is designed to be relatively simple to implement and as such does not involve off-line particle analysis. A CPC, OPC and photometer are used. Steps in the Tier Two process include:

a) Measure real-time *local background particle exposure* in terms of number and mass concentration during periods when the process of interest is not in operation.

I. Plot the time-series data.
II. Calculate the average of the *local background particle* concentration particle number and mass concentration – this is the *local particle reference value*[2].

33. In situations of low or high background particle number concentration absolute concentrations need to be taken into consideration to ensure the local particle reference value is appropriate.

1. <u>Low background concentration – Option for local particle reference value</u> If background concentration < 1000 particles/cm^3 as measured by CPC, then apply excursion criteria based on a background concentration of 1000 particles/cm^3 as measured by CPC.

2. <u>High background concentration – Option for local particle reference value</u> If background concentration > 20000 particles/cm^3 as measured by CPC, then apply excursion criteria based on a background concentration of 20000 particles/cm^3 as measured by CPC. This adopts a similar approach to BSI [71] and IFA [83] in setting of the benchmark particle concentration level.

34. The procedures used in the present report demonstrate how to characterise background particle levels in non-industrial situations. This issue can be more complex in industrial situations, where a simple nano-/ non-nano activity comparison without any additional sources of particles is less frequently achievable.

b) Measure real-time particle number and mass concentration data at emission points, within the breathing zone of workers, and at the perimeters of process enclosures and extraction ventilation, during operation of the process.
I. Plot the time-series data
II. Calculate the time-weighted average of the real-time particle number and mass concentration
III. Identify the presence of peak particle concentration values. Exclude peak particle values that are within ± the manufacturer stated accuracy of the instrument of the time-weighted average of the real-time particle number and mass concentration
IV. Calculate the peak particle number and mass concentration values for the process operation

35. Depending on the type of process, it may be necessary to run equipment with and without nanomaterials to differentiate between; (a) manufactured nanomaterials emitted from the process and (b) incidental nanoparticles produced by the equipment.

c) Calculate the ratio of the peak particle number and mass concentration values for the process operation to that of the *local particle reference value*.

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[2] the local background particle exposure, expressed as a particle number or mass value, is used as a benchmark for deciding when control of human exposure to particle emission arising from the nanotechnology process is required. This value is determined from extensive evaluation of the local background particle exposure. This is not an occupational exposure limit (OEL) or Workplace Exposure Standard (WES), but is intended as a pragmatic guidance level.

d) Compare this ratio to the corresponding general excursion guidance criteria (see below) as a trigger to review of particle controls and/or conduct a Tier Three assessment.

36. General *excursion guidance criteria* - a nanotechnology process could be considered to require modified controls or further assessment if emission or exposure levels exceed certain levels for defined time periods. In this study, the conditions are if:

a. eight-hour TWA exposure > particle control value, or

b. short term emissions or exposures exceed three times the particle control value for time periods that add up to more than a total of 30 minutes per eight-hour working day, or

c. *a single short term value for emission or exposure exceeds five times the particle control value.*

37. While similar to Tier Two approaches recommended previously [51,76,77,105], the following detail is noted:

- Estimation of mass concentration by use of photometer is recommended only in this approach
- Different excursion criteria are used in all approaches to determine whether increase over background particle number concentration is significant

38. An example of an alternative way of deriving excursion guidance criteria and local particle reference values from background particle concentrations is to use a statistical approach that takes into account the variability in background concentrations.

39. **Tier Three:** A Tier Three assessment involves the repeat of the Tier Two measurements but this time with simultaneous collection of particles for off-line analysis of mass or fibre concentration, particle morphology and chemical composition. The results of the off-line analysis can also be compared to real-time measurement results. A Tier Three assessment can include:

- Collection of aerosols onto a filter membrane connected to a sampling pump or TEM grid within an electrostatic precipitator, with analysis by SEM/XRD and TEM/XRD respectively.

- Utilisation of the sampling and analytical method recommended for a national exposure standard or limit, proposed workplace exposure limit, or benchmark exposure level.

- Use of more complex measuring instruments e.g a scanning mobility particle sizer (SMPS) with the minimum particle measurement size possible for ultrafine particle concentration and count median diameter measurement.

- Using an Aerodynamic Particle Sizer (APS) or Optical Particle Sizer (OPS) for information on the size distribution of particles above 300nm in size (e.g. agglomerates).

- Differentiation between aggregates, agglomerates and primary particles using a combination of TEM and specific surface area analysis (e.g. by BET).

A Tier 3 assessment is needed for:

a. evaluating exposures against exposure standards or limits where the sampling is required as part of the analytical method, or
b. comparing exposures against number concentration benchmarks defined for the range 1-100nm, which requires the use of instruments such as an SMPS, or
c. examining processes that can potentially emit high toxicity substances where low emissions are a concern. An example is if the process can potentially emit fibres or structures of fibres of pathogenic fibre dimensions, e.g. according to the WHO definition (particles with diameter < 3 µm, length > 5 µm, and aspect ratio (length to width) greater than or equal to 3 to 1 [30]).

TRIGGERS FOR PARTICLE CONTROL STRATEGIES

40. Where **Tier 2** results indicate that the calculated ratio of the median peak particle concentration measured during process operation to *local particle reference value* does not exceed the *excursion guidance value*, further assessment or changes to particle control strategies are not generally required. However, further assessment may be required in the case of nanomaterials that are potentially highly hazardous.

41. Where the results of **Tier Three** assessment confirm the excursion in particle concentration is associated with the nanotechnology process, particle control strategies should be considered. The choice of control, for example an engineering control or personal protective equipment, should be based on the measured exposure levels and; (a) relevant particle control values, or (b) any known or suspected toxicity of the nanomaterial. Measurement of particle concentrations during the use of local extraction ventilation, fume cabinets, mechanical dilution ventilation, and process enclosures clearly validated all were able to reduce exposure and emission by orders of magnitude in particle concentration.

42. The minimum recommended capture velocity for a hot process is 0.25 – 0.5 m s^{-1} so as to overcome local interferences and the intrinsic release velocity of the contaminant. This assumes that the condition of the dispersion of contaminant is that it is released with practically no velocity into quiet air. The capture velocity required can be higher for different conditions of dispersion. Thus to control exposure, it is recommended that the minimum capture velocity used is at least 0.25 m s^{-1}, and the LEV hood/s are positioned close to the particle source and relative to the position of local workers so as to move the particles away from the breathing zone of process workers.

ABBREVIATIONS

CMD	Count median diameter
CNT	Carbon nanotube
CPC	Condensation Particle Counter
DustTrak	DustTrak Aerosol Monitor
µm	Micrometre
nm	Nanometre
OPC	Optical Particle Counter
PM	Particulate Matter
PNC	Particle Number Concentration
P-Trak	Model 8525 P-Trak Ultrafine Particle Counter
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscope
TWA	Time-Weighted Average

GLOSSARY[3]

Agglomerate - collection of weakly bound particles or aggregates or mixtures of the two where the resulting external surface area is similar to the sum of the surface areas of the individual components [1].

Aggregate - particle comprising strongly bonded or fused particles where the resulting external surface area may be significantly smaller than the sum of calculated surface areas of the individual components [1].

Excursion guidance criteria – triggers for implementation or assessment of exposure controls used in conjunction with *particle control values*. Some examples of criteria used for chemicals generally are [109]:

- eight-hour TWA exposure > *particle control value,* or
- short term emissions or exposures exceed three times the *particle control value* for time periods that add up to more than a total of 30 minutes per eight-hour working day, or
- a single short term value for emission or exposure exceeds five times the *particle control value*.

Local background particle concentration (LBPC) – local work area eight-hour time-weighted average particle number or mass concentration that excludes any contribution of particles from the nanotechnology process. This value is specific to each work environment. This value should be determined following repeated measurement of the particle number and mass concentration when the nanotechnology process in not in operation. The results of such measurement should be converted to an 8-hour time-weighted average value and the median of all values used as the basis for the recommended *local particle reference value*.

Local background particle metrics – particle metrics such as PNC, CMD, alveolar deposited surface area and $PM_{2.5}$ concentration values during periods when the relevant nanotechnology process was not in operation.

Local particle reference value – the local background particle exposure, expressed as an average of the particle number or mass value, used as a benchmark for deciding when control of human exposure to particle emission arising from the nanotechnology process is required. This value is determined from extensive evaluation of the local background particle exposure. This is not an occupational exposure limit (OEL) or Workplace Exposure Standard (WES), but is intended as a pragmatic guidance level.

Nanomaterial – material with any external dimension in the nanoscale or having internal structure or surface structure in the nanoscale [110].

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[3] Italics font has been used throughout the text for terms included in this glossary.

Nanoparticle – a nano-object with all three external dimensions in the nanoscale size range of approximately 1nm to 100nm [1]. See also ultrafine particle.

Nanoscale – size range from approximately 1 nm to 100 nm [1].

Particle control values – particle reference values for deciding when control of human exposure to particle emission arising from the nanotechnology process is required. These reference values include a range of particle metrics such as mass, particle number concentration and include national exposure standards set by regulatory authorities, recommended exposure limits, exposure limits proposed by researchers, and Local Background Particle Reference Values based upon background nanomaterial levels.

Particle number concentration (PNC) – concentration of all particles within a defined size range.

Peak particle exposure – the highest particle number or mass recorded during the nanotechnology process.

$PM_{2.5}$ – Particle Mass concentration of particles with an aerodynamic diameter smaller than 2.5 µm.

PM_4 – Mass concentration of respirable size fraction particles.

Process particle exposure (eight-hour TWA) – particle number concentration or mass resulting from the nanotechnology operation multiplied by measurement time and divided by eight hours. See explanation of time-weighted average below.

Short term exposure limit (STEL) – usually measured over 15 minutes (TWA).

Submicrometre particles – particles smaller than 1 micrometre in diametre.

Supermicrometre particles – particles larger than 1 micrometre in diametre.

Time-weighted average - These are calculations allocating a measured exposure to the interval of time during which the exposure occurred. A worker may have an elevated exposure during one interval and a lower exposure in the next time interval. The TWA is calculated using the following relationship: $TWA = \sum C_i t_i / \sum t_i$, where C_i is the concentration during the ith sampling interval, and t_i is the sampling time for the interval. By weighting the exposure concentration, C_i, for the ith sampling period, t_i, it is possible to determine a worker's estimated TWA exposure to a chemical or agent. The TWA concentration can then be compared to a workplace exposure standard, exposure limit or guidance level. Common averaging times (denominator) include 8-hours, and 15 minutes which is used to compare exposures with STELs [2].

Ultrafine particle - a particle with an equivalent diameter less than 100 nm [1].

NOTE: Most nanoparticles, defined by their geometrical dimensions, are ultrafine particles, when measured [1].

I. INTRODUCTION

Measurement Strategy

43. In general, the objectives of any measurement campaign to measure nanomaterials in air will determine the strategy and methods that will be used. Differing strategies will be used for:

- Determining the exposure process and the fate of aerosols released by a source.
- Determining the effectiveness of a control measure.
- Compliance measurements, relative to a reference value. Specific guidance, e.g. CEN and ISO standards, already exists to support compliance measurements.
- A full risk assessment, which will require a comprehensive exposure assessment.
- A risk or concern driven tiered approach, to support evidence-based decisions on actions to be taken.

44. The recommendations of this report focus on the latter objective of a measurement campaign. Thus the report undertakes an appraisal of techniques and sampling protocols for determining the concentration of manufactured nanomaterials in air using a risk or concern driven tiered approach tiered approach.

45. Large framework programs on nanosafety research in the European Union and the United States and worldwide national programs have resulted in a number of approaches to assess exposure to manufactured nanomaterials. The development of exposure measurement methods and strategies is an ongoing global process and emphasizes the need for harmonization, which is currently being progressed through the work of the Global Exposure Measurement Harmonisation Workgroup.

46. A tiered approach for risk- or concern driven assessment of exposure assessment of nanomaterials is not new. The NEAT approach developed by the US NIOSH [51] formed the basis of OECD WPNM report *Emission Assessment for the Identification of Sources and Release of Airborne Manufactured Nanomaterials in the Workplace: Compilation of Existing Guidance* [76]. Slightly different tiered approaches have also been proposed by VCI and German Research Institutes (VCI 2010) [77], NanoGEM [105] and by INRS and other institutes. This report supports the application of a tiered approach as described in previous work, builds on previous work and suggests some refinements in methodology detail.

About exposures

47. People are constantly exposed to particles both within and outside their work environment. Morawska et al [3] found that the average concentration of outdoor particles in the lower submicrometre range (average number median diameter of 40 nm) in the city of Brisbane, Australia, was 7.4 x 10^3 particles cm^{-3}. Because outdoor particles infiltrate work environments, and multiple sources of particles can be present in work areas, assessment of particle emission and exposure arising from nanotechnology processes must account for *local background particle exposure*[4].

48. Exposure to ambient $PM_{2.5}$ particles is known to be associated with respiratory and cardiovascular disease [4]. Evidence for specific health effects relating to nanomaterials is limited because the research is not as substantial as that for size distributions including supermicrometre particles. With the exception of some manufactured nanomaterials such as carbon nanotubes there is minimal scientific literature regarding the toxicology [5] of the vast range of nanomaterials. In addition, the World Health Organisation has concluded that while there is considerable toxicological evidence of potential detrimental effects of nanoparticles on human health, the existing body of epidemiological evidence is insufficient to reach a conclusion on the exposure–response relationship of nanoparticles [6].

49. However, as the ability to characterise the nanoparticle fraction of $PM_{2.5}$ has increased, so too has concern about the potential health effects of nanoparticles. This concern relates to (i) the dominance of nanoparticles in the PM mixture, constituting up to 90% of the PNC of the aerosol, (ii) the relatively large surface to volume ratio of the nanoparticles, and (iii) the resultant large total surface area of the nanoparticles to provide reactive sites with biological tissue [7]. Concerns about a potential association between the nanoparticle fraction of air pollution and cardiovascular and respiratory health effects has been reported in the literature [7-9]. Therefore a precautionary approach[5] is prudent regarding exposure to particles associated with nanotechnology where an understanding of the hazards is limited.

2. SCOPE

50. This report provides:

- a literature review on existing methods and instrumentation to measure and characterize airborne manufactured nanomaterials
- the results and data from a measurement campaign in non-industrial situations
- an examination of measures for the mitigation of the potential exposure relative to the task, and
- an evaluation of methods for measuring emissions, exposures and characteristics of airborne nanomaterials with focus on a risk or concern driven tiered approach.

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[4] See definition in glossary

[5] Underpinning the precautionary approach is the precautionary principle set out in Principle 15 of the *United Nations Rio Declaration on Environment and Development* which indicates that where there are threats of harm lack of full scientific certainty shall not be used as a reason for postponing cost-effective control measures.

3. OBJECTIVES OF THE MEASUREMENT CAMPAIGN

1. Identify and quantify particle emission sources in non-industrial workplaces that manufacture or handle manufactured nanomaterials
2. Characterise the emitted particles in terms of airborne concentration, size, and morphology at the emission point (temporal study)
3. Pilot a study of spatial particle characteristics so as to gain insight into the transport and fate of particles, and
4. Evaluate the effectiveness of workplace controls.

4. COMMON METHODS AND INSTRUMENTATION FOR TO THE CHARACTERISATION OF AIRBORNE MN

51. A selection of the scientific literature, spanning the time period 1998 to 2011, reporting the results of, and methods and instrumentation used to characterise a range of aerosols including those incidental to combustion, industrial, and nanotechnology processes is reviewed below. This review was conducted so as to identify methods and methodology pertinent to the characterisation of airborne manufactured nanomaterials.

4.1 Properties of nanomaterials that influence measurement decisions

52. Nanomaterials are structurally and chemically diverse and should not be considered as a group of similar compounds [12]. Evidence of the toxicity of nanomaterials is informed by studies of exposure to particles and fibres such as quartz, asbestos, and combustion derived particles from diesel engines and processes such as welding and smelting [10]. These studies have investigated the relationship of various particle characteristics, such as size, shape, solubility, surface area, and particle number and mass concentration, to toxicological outcomes. The findings of these toxicological studies have in turn influenced decisions regarding what particle metric/s should be measured so as to estimate exposure.

4.1.1. Particle size

53. A nanometer (nm) is one billionth of a meter (10^{-9}m) and the nanoscale has been defined by ISO as the size range of approximately 1-100nm [1]. Many terms are used to describe particles in this size range including ultrafine particle, ultrafine aerosol, nanoparticle, and nanoparticle aerosols, however some of these terms have not been rigorously defined and nor is there agreement on some definitions. Common to the various definitions of ultrafine particles is “at least one dimension less than 100 nm” [11, 12].

54. Use of the size range of less than 100 nm is simplistic when discussing health effects or emission characteristics of particles because particles seldom present as a single size [11]. The “less than 100 nm” size range is useful when defining manufactured nanomaterials because the novel and differentiating properties of nanomaterials are developed at a crucial length scale of typically under 100 nm [11, 13]. This definition is not particularly useful for particle assessment because nanomaterials are unlikely to persist in their primary particle size but rather will agglomerate or aggregate into larger sized particles, including into the micrometer size range [11, 14, 15]. Therefore,

respirable particle mass concentration measurements are also necessary for the exposure assessment of nanomaterials in workplaces [15]. However, if agglomerates or aggregates of nanomaterials either de-agglomerate or disaggregate completely following deposition in the lungs, it is conceivable that the resulting biological impact will be similar to an equivalent exposure of discrete nanomaterials [14].

55. Primary particle size and agglomeration and aggregation particle size have important implications for the effective particle penetration and deposition into the lungs, mechanisms of cellular toxicology, and measurement of airborne nanomaterials. A cut size for nanomaterials of 100 nm is not derived from particle behaviour in the respiratory tract following deposition and therefore is not a health based metric [14]. Models of particle deposition in lungs, such as the that published by the International Commission on Radiological Protection (ICRP) [16], indicate the lung particle deposition does not reach minima for the tracheobronchial and alveolar regions until the size range of 300-400nm. A health based metric needs to consider an upper size limit based upon the mechanism of particle deposition within the lung.

56. Particles in the nanometer size range have a high probability of penetrating to the alveolar regions on the lung and diffusing to the lung surface area [17]. Toxicity of nanoparticles has been shown to increase with decreasing particle size [18] and the small size of nanoparticles may allow them reach the tracheobronchial region, including the alveolar region which have large surface areas [19]. In particular this large surface area allows possibility of transfer of nanoparticles to the blood stream [19], which in turn allows the possibility of translocation [14, 17-19] from the bloodstream to cells and organelles presenting a potential systemic health hazard [14, 17].

4.1.2 The surface area and the reactivity of that surface area

57. Because of their small size, nanoparticles possess a very high surface-area-to mass ratio [17] and this has found to be a key factor in causing cell damage in conjunction with dose and surface reactivity/chemistry [17, 18, 20]. The mechanism of cell injury is one of oxidative stress [18] caused by the reactive surface area and chemistry of the particle leading to inflammatory processes [18] that can then give rise to pathologies such as airways disease, cardiovascular disease, fibrosis, or cancer [18]. The toxicological evidence for surface area as a valid dose metric is strongest for insoluble particles [19]

58. In general, particles with less biologically reactive surfaces are less toxic. However even particles with lower inherent toxicity (e.g. titanium dioxide) can cause pulmonary inflammation and fibrosis at sufficiently high surface area doses [21].

4.1.3 Solubility and biopersistence

59. A number of studies [22-28] cited by Maynard and Kuempel [17] have shown that the solubility of inhaled particles and fibres influences their toxicology. For example, poorly soluble substances retained in the lungs have reportedly caused oxidative stress leading to inflammation, fibrosis, or cancer.

4.1.4 Shape and fibres

60. Definitions of a hazardous fibre vary and include:

(a) a fibre that is thinner than 3 micrometers, longer than approximately 20 micrometers, and biopersistent in the lungs [29]; and

(b) particles with diameter < 3 µm, length > 5 µm, and aspect ratio (length to width) greater than or equal to 3 to 1 [30].

61. However, these size definitions appear to be arbitrary and are related to the need to define regulatory fibre sizes for health assessments, noting that fibres must be respirable to pose an appreciable hazard. Respirability is mainly determined by diameter and density, and with a given fibre diameter a higher specific density is associated with lower respirability [31].

62. Carbon nanotubes (CNTs) are engineered to form fibrous or rod shaped particles with high aspect ratios [32]. Physico-chemical traits of toxicological concern with CNT include the fibrous length [18, 32, 33] being too large for effective phagocytosis to occur [33], biopersistence [32, 34], functionalisation [18, 35], and metal contamination [18, 32, 36], which may lead to oxidative stress, inflammation [33, 34], fibrosis [34], granulomas [33, 37], and potential formation of mesothelioma [32, 33].

63. Takagi et al. [32] concluded, after injecting samples of 1) stiff, fibrous multi-wall carbon nanotubes (MWCNT), 2) crocidolite, and 3) fullerene into the abdominal (peritoneal) cavity of mice, that carbon-made fibrous or rod shaped micrometer particles may share the carcinogenic mechanisms postulated for asbestos.

64. Poland et al. [33] concluded, after injecting samples of 1) long, straight MWCNT, 2) short tangled MWCNT, 3) long-fibre amosite, 4) short-fibre amosite, and 5) a nonfibrous nanoparticle carbon black material into the abdominal (peritoneal) cavity of mice, that long straight nanotubes act like long straight asbestos fibres and cause mesothelial injury.

65. Limitations of both studies include whether the intraperitoneal administration of the CNTs is representative of a dose that could penetrate and deposit into the lungs of humans during airborne exposure.

66. However, an important finding of both these studies was that the long MWCNT and not the short MWCNT were implicated in damaging the mesothelial tissue in a manner similar to asbestos fibres. The conclusions from these two studies confirm what is known about fibre toxicology in general, i.e. a hazardous fibre is one that is thinner than 3 micrometers, longer than approximately 20 micrometers, and biopersistent in the lungs [29].

4.1.5 Primary particle size, aggregation, and agglomeration

67. The concept of aggregation is important when assessing the penetration and deposition of CNTs into the lung as emphasised by Donaldson et al. [18],

> "The deposition of CNT in the lungs is expected to depend on the form that the CNT take when they are aerosolised. In an aggregated form, the CNT are likely to be deposited in the lung like a particle with a similar aerodynamic diameter. However, if CNT can be aerosolised as single fibres, their deposition will be conventional, i.e. based on aerodynamic diameter and the possibility of aligning with the airstream."

4.2 Measurement of nanomaterials

4.2.1 Metrics, methods, and instruments

68. In relation to assessment of toxicological properties, there is considerable uncertainty over how exposure to nanomaterials should be measured because of the different toxicological pathways arising from the diversity of nanomaterial physico-chemical traits [38].

69. Typically, health-related aerosol evaluation has been based upon size selective sampling processes and weight (mass) or fibre counting analytical techniques. Other physico-chemical properties of nanomaterials such as number, shape, surface area, surface chemistry, solubility, and core-surface composition heterogeneity [38] are also relevant to their ability to cause disease.

However, as will be demonstrated later, mass and fibre counting techniques may still be used effectively when assessing potential nanomaterial exposure.

70. Consensus is not evident within the scientific literature regarding the use of mass to characterise nanoparticle aerosols. Nanoparticles have a higher specific surface area per unit of mass than larger particles and therefore it is possible that characterisation by mass will lead to an underestimation of health effects [39]. However, the Recommended Exposure Limits for nano-TiO_2 and fine-sized TiO_2 published by the US National Institute for Occupational Safety and Health are mass based, but are adjusted for particle size based on surface area which relates to the health endpoint [40].

71. Because of the diversity of physico-chemical properties amongst nanomaterials no single method for measuring airborne particles will suit all nanomaterials [38]. Paradoxically, the limited toxicological data on many manufactured nanomaterials, means the decision as to which nanomaterial properties to measure is not a straightforward process.

72. The paucity of toxicological data relating to the biological effects of the wide range of nanomaterial types, especially manufactured nanomaterials means that no decisions have been made as yet by health and safety regulators and other decision-makers and stakeholders as to which metric should be used for exposure assessment [14]. No single sampling method is available that will measure all the nanomaterial traits described above [12]. Therefore, it has been recommended that a wide range of measurement equipment [12] should be used to characterise workplace exposure and evaluate the effectiveness of emission controls, including equipment to measure mass, number and surface area concentrations, and for collection for physical and chemical characterisation off-line [14].

73. Commonly, the measurement of airborne toxic substances in occupational settings has been through the use of instruments that measure the mass of the toxic agent per volume of air, e.g. mg/m^3, or volume of the toxic agent per volume of air, e.g. ppm, with the regulation of airborne toxic agents using exposure standards expressed in the same terms [41]. The exception to this has been with aerosols formed from fibrous material such as asbestos where measurement is based upon fibre counting methods [14, 38]. Health-related aerosol fractions have been defined relating to the probability of penetration of airborne particles to various anatomical regions of the respiratory system and to provide specifications for the performance of sampling instruments [14].

74. There is strong agreement in the literature that mass [14, 41], or at least mass on its own, is not an appropriate measurement for nanomaterial exposure. Nanomaterial properties such as surface area and activity [14, 21, 38, 41], particle number [14, 38], fibre aspect [38], are considered to be better measurement indicators of exposure than mass.

75. However, because surface area is not well understood and is dependent upon the measurement method used, exposure to nanomaterials could be characterised against aerosol mass and number until further information is available – this will necessitate in the case of mass concentration the development of particle size inlets relevant to the target size range [14].

76. Although number concentration is relatively easy to measure above 10 nm using Condensation Particle Counters (CPC), such measurements are generally not size-specific and so it is difficult to distinguish between process and background aerosols [17]. Therefore particle number concentration is useful if measured in conjunction with other measurements [42].

77. The normal background of particles in a workplace environment can be several thousand nanoparticles per millilitre of air resulting in extremely “noisy” measurements [43] cited in Harford et al. [41]. Therefore workplace monitoring of nanoparticles should include a range of parameters [41] and should also include characterisation of any background particles [42].

4.2.2 Characterising particle emission and transport: Summary of available instruments and methods

78. Some instruments currently available and referenced in the literature for characterising particle emission and transport are described, including limitations [14, 15, 19, 38, 41, 44-49], in Table 1. Available devices are continuously evolving.

79. In summary, of 28 studies of nanomaterial measurement and methodology reviewed for this report, the following particle characterisation methodology was included:

- Particle number concentration (23 studies)
- Particle size distribution (15 studies)
- Mass concentration, using either optical particle sizer measurements, stationary and personal filtration samples, and PM_1, $PM_{2.5}$, PM_{10} samplers (8 studies)
- Collection of particles using various devices, for off-line analysis (11 studies)
- Surface area (3 studies)
- Electron microscope (10 studies)
- Chemical analysis (5 studies)
- Personal sampling (2 studies)
- Area sampling (28 studies)

80. This is consistent with the findings of the review of use of particle characterisation methods by Kuhlbusch et al. [44].

4.2.2.1 Personal samplers for time resolved nanoparticle measurements

81. Review of the literature shows minimal data on measurement of *personal* exposure to manufactured nanomaterial aerosol, with the literature dominated by area measurement results. This is because of the lack of availability of portable instruments that can be used in the breathing zone of workers.

82. Three devices designed to characterise personal exposure within the breathing zone to particles < 300nm in size were identified in the literature. The first is the Aerasence NanoTracer that can be used to provide both real-time particle concentration and average particle diameter data in the size range of 10 to 300nm.

Table 1. Instruments for characterising submicrometre particles in workplaces

Instrument/Device	**Capabilities/Notes**	**Metric**	**Brief Description of Operating Principle, plus limitations**	**literature that reported using this instrument/method**
Condensation Particle Counter (CPC)	Real-time particle number concentration measurements between approximately 10nm and a few µm, dependent upon the specific device. Some devices are hand-held and battery operated.	Number	Particles too small to scatter light to be detected by conventional optics (approx <300nm) are grown to larger size by condensation of either an alcohol or water. The larger droplets are then counted by a laser technique. Counts all particles in aerosol but not size specific. Counting efficiency decreases with particle size.	[42], [50], [51], [52], [53], [54], [55], [56], [57], [58], [59], [60], [61]
Electrical Aerosol Detector (EAD)	Measures particle concentration as a function of time, and mean diameter of aerosol (when combined with a CPC).	Total aerosol length concentration (mm/cm^3)	Particles larger than 1 µm are typically removed using a cyclone. Diffusion charging of particles than occurs, followed by detection of the particle charge via an electrometer.	[62]
Mobility particle sizers such as Scanning Mobility Particle Sizer (SMPS) and Fast Mobility Particle Sizers (FMPS)	SMPS - Real-time (electrical mobility diameter) measurement of aerosol size distribution – interpreted as number concentration or surface area concentration. Counts particles with a CPC after they have been separated into numerous size channels. Size range 2.5 to 1000nm FMPS - sort of hybrid between the ELPI and SMPS and calculates sizes and numbers based on 21 electrometers and a lot of maths.	Particle number concentration and size distribution (including count median diameter, CMD) in real-time. CMD is the geometric mean diameter of lognomal size distributions typical of aerosols [113]. Mass (Data may be interpreted in terms of aerosol mass concentration but only if particle shape and density are known)	SMPS - fastest scanning speed is approximately 3 minutes which is suitable provided that the process being monitored does not change within this timescale. FMPS have been developed but are limited to measurements at relatively high number concentrations. Size and complexity of use limit ready use at workplaces. Using particle detection principles based upon electrical mobility, variability in measurement accuracy is stated in the literature in relation to non-spherical particles [44] for these instruments. In addition, the time resolution of several minutes required for SMPS limit its application for situations where size distributions may vary over the space of seconds in time [44].	[49], [63], [64], [42], [65], [66], [50], [62], [54], [55], [44], [56] [57], [59], [60]
Aerodynamic particle sizer (APS)	Real-time aerodynamic measurements of particles.	Particle number concentration and size distribution in real-time.	For example the TSI model 3321 sizes particles from 0.5 to 20 µm, and *detects* particles from 0.37 to 20 micrometers using a light-scattering technique.	[49], [65], [59]
Brunauer–Emmett–Teller (BET) method	Method for measuring surface area based on a gas adsorption method.	Surface area	Is appropriate for relatively large quantities of powder only, but not suited to a rapid evaluation of aerosol surface area, particularly at low concentrations. Does not have on-line capabilities.	
Epiphaniometer		Aerosol surface area	Not well suited for widespread use at workplaces because of inclusion of radioactive source and the lack of effective temporal resolution.	
Electrical Low Pressure Impactor (ELPI^{TM})	Real-time size-selective (aerodynamic diameter)	Particle number concentration and	The operating principle can be divided into three major parts: particle charging in a unipolar corona charger, size classification in a cascade impactor and	[42], [44], [55]

Instrument/Device	Capabilities/Notes	Metric	Brief Description of Operating Principle, plus limitations	literature that reported using this instrument/method
	measurement of size distribution or active surface area, and particle number concentration. Sensitive to 6-7 nm to 10 µm. Size selected samples may be further analysed off-line.	size distribution in real-time. (Data may be interpreted in terms of aerosol mass concentration but only if particle shape and density are known)	electrical detection with sensitive electrometers. Because particles tend to deagglomerate with increasing pressure difference across an orifice, low pressure impactors may lead to significantly artificial change of the particle size distribution in the measuring device. Particles are collected on filters that can be analyzed gravimetrically or chemically.	
Optical Particle Counter (OPC)	Real-time number and mass concentration measurement of particles larger than approximately 300 nm to 20 µm in diameter	Number size distribution	Based on light scattering equivalent diameter.	[51], [52], [53], [58], [60], [61]
SMPS and ELPI used in parallel	Differences in measured aerodynamic and mobility diameter can be used to infer particle fractal dimension, which can be further used to estimate surface-area	Surface Area		
Impactors – micro-orifice uniform-deposit impactor (MOUDI)	Divide particles into a series of different size fractions by impacting smaller and smaller particles as the aerosol flow is passed over a substrate	Various size fractions	High flow rate and low pressure drop can cause changes in aerosol particle size, for example deagglomeration of particle agglomerates can occur.	
Diffusion Charger	Real-time measurement of aerosol active surface-area.	Surface Area	Diffusion charging of sampled particles, followed by detection of charged particles using an electrometer. There are differences between surface areas measured by diffusion chargers and the surface area by BET of a powder. These values are not necessarily the same.	[64], [55]
Nanoparticle Surface Area Monitor	Real-time measurement of the lung deposited surface area, of particles < 1000nm.	Lung deposited surface area concentration	Diffusion charging of sampled particles followed by detection of charged aerosol using electrometer. The lung deposited surface area, of particles < 1000nm is obtained by weighting the geometric surface area as a function of particle size with the deposition efficiency for a lung region, for example a reference worker for workplace exposure determination – an example of such is the human lung deposition models published by the International Commission on Radiological Protection 1995. Most accurate in size range of 20 to 400nm. Diffusion chargers [44] and Nanoparticle Surface Area Monitors (NSAM) [19, 45] are referenced in the literature as being used to characterise particle surface area and lung deposited surface area respectively. The accuracy of diffusion charger based surface area monitors, such as the TSI Nanoparticle Surface Area Monitor model 3550 and Aerotrak 9000, is stated to be in the size range of approximately 20 nm to 400 nm [19]. The upper size limit of accuracy at 400nm reflects the use of the ICRP lung deposition model to weight the instrument response where the ICRP model shows a minima of the deposition curves at the 400nm size. Particle lung deposition increases on either side of this minima on the lung deposition curve. Therefore even a small number of particles > 400	[19], [45], [62]

Instrument/Device	Capabilities/Notes	Metric	Brief Description of Operating Principle, plus limitations	literature that reported using this instrument/method
			nm can have a significant contribution to total surface area causing significant errors in the lung deposited surface area estimate of the device [19, 44]. Because a pre-separator for the 400nm cut-point is not available, only lung-deposited surface area concentrations of aerosols with no significant surface contribution above 400nm can be accurately measured using these devices [19].	
Tapered Element Oscillating Microbalance (TEOM®)	Sensitive real-time monitors such as the TEOM® may be useable to measure nanoaerosol mass concentration on-line with a suitable size selective inlet.	Mass		
Tapered Element Oscillating Microbalance (TEOM®) with Aethalometer	The Aethalometer Module will provide continuous output of carbon content of ambient particle matter (PM), while the TEOM monitor simultaneously measures the total PM mass concentration.	Mass and Carbon Black		
Electrostatic precipitators	Deposition of particles onto sampling substrate. Can efficiently sample particles > 20 nm.	Particle deposition for later morphological and chemical analysis	A subject aerosol is routed through a flow channel within which an intense electrical field has been created. Any particles that are charged, when they encounter the electrical field, drift within the electrical field toward a collection plate. Collection of particles for morphological and chemical analysis can be performed so as to provide additional data on particle emission and exposure to that provided by real-time measurements. The use of electrostatic precipitation of particles onto various substrates is an accepted method [44, 48] used to provide data on particle emission and exposure from nanotechnology operations. Most are bench top models thereby limiting their effectiveness in workplace measurements in particular within the breathing zone of workers. The exception to this was the work being conducted by Miller et al. [48] to develop a hand-held electrostatic precipitator. The ideal precipitator would achieve 100% uniform deposition of the particles onto the sampling medium. Increasing the charge of the instrument increases the deposition of larger particles and increasing the flow decreases the residence time of the particles in the device, thereby decreasing sampling efficiency for larger particles [67]. Therefore, knowledge of the likely particle charge and size will assist with choosing an appropriate flow rate and voltage so as to maximise particle capture and deposition. However, such information is commonly not known for the aerosol of interest.	[48], [68], [59]
NanoTracer	Real-time personal or area monitoring of particle number and average particle diameter in size range of 10 to 300 nm.	Number concentration and average particle diameter		[69], [66], [70]
Personal Nanoparticle Respiratory Deposition Sampler	Full-shift personal sampler designed to collect particles with efficiency matching respiratory tract deposition of particles < 300 nm in diameter.	Mass of particles < 300nm diameter	Consisting of a respirable sampler and impaction plate so as to remove particles larger than than 300 nm, and a deposition stage where the remaining particles deposit onto nylon mesh screens. 300 nm size matches the minimum deposition for submicrometer particles based upon the ICRP lung deposition curve [16]. The sampler is lightweight (60 g), fits in a standard lapel mount (model 225-1,	[49]

Instrument/Device	Capabilities/Notes	Metric	Brief Description of Operating Principle, plus limitations	literature that reported using this instrument/method
	Subsequent chemical analysis of the particles < 300nm deposited on the collection media of the NRD sampler allows for characterization of these particles apart from larger background particles.		SKC Inc., Eighty Four, PA) and operates at an airflow rate (Q) of 2.5 Lpm with a pressure drop of 3.54 kPa (14.2 in. H_2O). The sampler can be used with a commercially available belt-mounted sampling pump for the duration of a work-shift (e.g., AirCheck 2000, SKC Inc., Eighty Four, PA).	
IOSH-NCTU Personal Nanoparticle Sampler	Respirable cyclone and micro-orfice impactor for classifying respirable particle matter and nanoparticles.	Personal sampling of respirable particle mass and nanoparticles	The PNS operates at 2 L/min with a pressure drop of 125 cm H_2O by a SKC XR 5000 pump. The PNS consists of a respirable cyclone and a micro-orifice impactor (137 x 55 micrometer nozzles) in series for classifying respirable particulate matter (RPM) and NPs, respectively. The impactor plate is rotated by a stepper motor to deposit particles uniformly on the substrate. A final filter is used to collect NPs.	[15]
Cyclones		Respirable particle mass		[63]
Photometers		Mass estimate	Aerosol photometers are being used to characterise mass of manufactured nanomaterials, in particular the agglomeration phase of the particles. Measurement accuracy is reduced where the optical properties of the aerosol differs markedly to that of the particle used to calibrate the instrument [44].	[55], [58], [59], [60]
Transmission Electron microscope	Off-line analysis of particle shape, morphology, size.		Frequently used with EDX analysis for chemical characterization of the sample. Expensive, requires highly trained technicians, only small fraction of sample analysed.	[63], [64], [51], [52], [53], [59], [60], [61]
Scanning Electron microscope	Off-line analysis of particle shape, morphology, size.		Frequently used with EDX analysis for chemical characterization of the sample. Particles smaller than approximately one nanometre require use of TEM. Expensive, requires highly trained technicians, only small fraction of sample analysed.	[42], [57]
Chemical analysis			Can include EDX, or range of other methods such as *NIOSH Manual of Analytical Methods (NMAM)* Method 7303 for metals, NMAM Method 5040 was used to quantify the amount of carbonaceous material.	[42], [52], [71], [60], [61]
Phase contrast microscopy (PCM) and polarized light microscopy (PLM)	Particle.	Particle shape, size, surface characterisation		[60]
Q-Trak Plus (Temperature, relative humidity, carbon monoxide, carbon dioxide)	Carbon monoxide and carbon dioxide can be used to indicate presence of air contaminants in exhaust emissions generated from combustion-derived ultrafine particles.	Temperature º C, relative humidity %, carbon monoxide ppm, carbon dioxide %		[42], [55]
Filter membrane and a sampling pump	Collection of particles for off-line analysis.		Collection of particles for gravimetric, morphological, and chemical analysis.	[42], [51], [52], [53], [60], [61]

83. The second is the Personal Nanoparticle Respiratory Deposition (NRD) Sampler designed for full-shift personal sampling of particles with a sampling efficiency matching respiratory tract deposition of particles < 300 nm in diameter.

84. The third is the IOSH-NCTU Personal Nanoparticle Sampler decribed by Liu et al. [15] as consisting of a respirable cyclone and micro-orfice impactor for classifying respirable particle matter and nanoparticles.

85. Because these devices have only become available since 2010, there are relatively few references in the literature describing the actual use of the devices and include Marra [69], Marra et al. [72], and van Broekhuizen et al. [70] for the Nanotracer; Cena et al. [49] for the NRD; and Liu et al. [15] for the IOSH-NCTU Personal Nanoparticle Sampler.

4.2.3 Response of instruments to aerosols dominated by specific particle characteristics

86. Real-time particle instruments are calibrated using specific aerosolised substances such as NaCl. These particles are often spherical in shape, have specific solubility and hygroscopicity [19]. The response of the instrument will vary where the properties of the aerosol being studied differ significantly to that of the calibration particle. For example, spherical particles are used to calibrate the NSAM [19] and mobility particle sizers [50] and each instrument may react differently, not only to changing particle concentrations but also to different morphologies and materials [50]. CPC's with different particle size ranges will record differing PNC where there is significant difference in particle size in the non-overlapping range of the instruments [50]. Where the density and hygroscopicity of the particles being investigated differ significantly to the particles used in determining the ICRP lung deposition curves, the response of the NSAM will vary [19]. Also, differences in the counting efficiency of each instrument, coupled with different refractive indices of nanomaterials, make direct comparisons across instruments difficult [52]. Where the PNC exceeds the upper limit of a CPC, an underestimation of the true PNC will occur [52].

87. The results of studies of the performance of three CPC's concluded that the minimum detectable particle diameter of the instruments can be influenced by interaction of three variables - the relative humidity of the aerosol [73], ambient temperature [56, 73], and hygroscopicity [73] of the particles. Therefore, characterisation of relative humidity and temperature should be concurrent, and reported, when characterising particle metrics.

88. The response of a water-based CPC to both n-butanol and propanol has been the subject of several studies [56, 74, 75], all concluding that the solubility of the sampled particles to the condensation fluid played an important role in the detection efficiency of the instruments.

4.2.4 Sampling and measurement strategy issues

89. A major compounding factor in most workplaces is the large diversity of ultrafine particles found in ambient atmospheres, the dispersion of which is dependent upon the ventilation characteristics of the workplace [14]. Because no single instrument is capable of simultaneously measuring all nanomaterial traits of interest and because some instrumentation is large and bulky and not conducive to personal aerosol monitoring the following factors should be considered in a sampling strategy:

- Characterisation of the particles in the ambient environment, including the identification of all the potential nanoaerosol sources in the workplace [14];
- An understanding of the ventilation system in the workplace to determine the potential for cross contamination. This could be a significant problem for nanomaterials as they will remain airborne for considerable periods of time and be easily dispersed by the air currents in the workplace [14];

- Care taken in the siting of area samplers as aerosol characteristics can change with distance from source, leading to spatial and temporal variation of nanoaerosol size, mass, and number concentration [14, 38, 52];
- Care taken with interpretation of source and area samples as this type of sampling cannot be interpreted as representative of exposure [52];
- Cost effective determination of airborne manufactured nanomaterials at workplaces [44].

90. Mark [14] states that unless outdoor sources of nanoparticles (such as vehicle exhausts and other industrial actions) are excluded or minimised from the workplace environment (using for example clean room conditions or high efficiency filters on the inlet air ducts), these ambient particles will penetrate indoors. This could result in overestimation of the levels of nanoparticles emitted from the process under investigation. One method to overcome this problem is to carry out simultaneous measurement of background concentrations using a duplicate set of monitoring equipment to monitor outside the workplace, and to subtract the outdoor levels from those measured inside the workplace. However caution is needed when this approach is applied, since a number of nanoparticle sources can contribute to variation in outdoor levels, but not all these sources may significantly contribute nanoparticles to the process under investigation. Simply subtracting the outdoor concentration without correcting for these differences may lead to an underestimation of the level of nanoparticles emitted by the process of interest.

91. The importance of differentiating background particles from particles of interest is considered to be of paramount importance during particle characterisation [44]. One such method is The *Nanoparticle Emission Assessment Technique (NEAT) for the Identification and Measurement of Potential Inhalation Exposure to Engineered Nanomaterials* [51, 52, 76]. This method has been proposed for the workplace characterisation of airborne manufactured nanoparticle emission and exposure assessment, and for measurement of background particle concentrations. This method proposes the simultaneous use of a hand-held CPC and OPC to provide data on particle count and size in the range of 10-20 to 10,000 nm before, during, and after process operation[6]. The utility of this method for workplace use lies in the portability, relative ease of operation, and relatively low dollar cost of these hand-held instruments compared to instrumentation such as SMPS.

92. In accordance with this method, a high PNC in the CPC range in combination with a low PNC in the OPC small size range (300-500 nm) would indicate the presence of nanoscale particles. Conversely a low PNC in the CPC range in conjunction with a high PNC in the OPC large size band (> 1000 nm) would indicate the presence of large particles and/or agglomerates. An average background PNC is calculated and subtracted from measurements made during processing. In addition, filter based air samples, both area and personal sampling collected simultaneously during real-time measurements, is recommended so as to analyse particle morphology and chemical composition using SEM or TEM.

93. Kuhlbusch et al. [44] reviewed 25 peer reviewed studies from the scientific literature and concluded there is a lack of a harmonised approach concerning measurement strategies and techniques, metrics, size ranges, and data analysis procedures. These authors concluded the measurement strategy to be related to whether the study question was personal exposure related, process related, or linked to toxicological and epidemiological questions. Four basically different approaches were described –

- Time series approach
- Spatial approach

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[6] The use of CPC P-Trak would provide particle count from lower size of approximately 20nm, whilst use of CPC 3007 would provide count from lower particle size of approximately 10nm.

- Approach based on comparative studies with and without the nanomaterial
- Size resolved chemical and/or morphological analysis.

94. Kuhlbusch et al. [44] argue that tiered approaches such as NEAT are the most practical for workplace and laboratory measurements because complete measurement campaigns are very time consuming and hence cost intensive and may only be necessary if there is evidence of an increased particle concentration.

95. The following three-tiered measurement strategy has also been recently proposed [77]:

- Tier 1 – information gathered according to established industrial hygiene practices. If release of nanoscale aerosols cannot be excluded then exposure must be assessed as per Tier 2;
- Tier 2 – conduct a basic exposure assessment using a limited set of easy-to-use equipment. If significant increase over total aerosol background concentration (or occupational exposure limit if available) is detected, then potential exposure is assessed as per Tier 3;
- Tier 3 – employ the latest state-or-the-art measurement technology to assess workplace exposure to nanoscale aerosols.

96. A tiered approach provides flexibility to allow customization of measurement to the specific needs of an organization and to ensure it is appropriate for the regulatory environment.

4.3 Conclusions

97. Characterisation of aerosols in terms of particle size, number and mass concentration, surface area, morphology, and chemical composition has been conducted by environmental and occupational aerosol scientists for many decades and is the subject of a wide body of scientific literature. In particular, coinciding with the increased penetration of nanotechnology across most sectors of the world-wide economy, there has been a dramatic increase of scientific literature over the last 10 years on the subject of characterising emission of, and exposure to, particles arising from nanotechnology processes. This literature reflects the uncertainty regarding the toxicology of manufactured nanomaterials in that the particle metrics chosen by researchers for characterisation differ, as does the methodology and instrumentation used. However, given that people are typically exposed to a range of nanomaterial particle sizes with a significant fraction of agglomerates and aggregates being above 100nm in size, the literature reflects an over-emphasis on attempts to demarcate only the sub-100 nm fraction of aerosols, adding complexities to measurement methods.

98. It is also clear there is no consensus on the format of reporting of study results, including reporting sampling and analytical error; whether data should be reported as real-time data, time-integrated, or peak; and excursion criteria for demarcating particles of interest from background particles. This in turn impacts adversely on making available a public repository of data that can be used to 1) implement generic risk management for similar nanotechnology processes, and 2) inform epidemiological studies.

99. However, it is clear from the literature that in relation to characterising emission and exposure of particles within a workplace, particle number and mass concentration, along with filter sampling for particle morphology and chemical composition can be conducted relatively easily using a range of portable instrumentation already available on the market so as to provide reliable estimates of particle exposure and emission.

5. RESEARCH METHODOLOGY

5.1 General Information

100. Data characterising the emission and transport of particles associated with nanotechnology processes was collected during the operation of six processes involving manufactured nanomaterials. In order to compare and evaluate the response of different instrumentation to airborne manufactured particles, the particle measurement instrumentation and equipment was co-located and operated so as to characterise particles from each of the six processes. Temporal and spatial data were collected at likely sources of particle emission, and where possible within the breathing zone of workers both during and between operation of the processes, so as to characterise particles arising from the nanotechnology process and background particle sources. The responses of the hand-held condensation particle counter (CPC), optical particle counter (OPC) and DustTrak and also more complex instruments used to characterise particles were evaluated.

5.1.1 Operator safety

101. The potential risk associated with taking measurements was assessed for each task and appropriate controls were used. For example, given the potential for harm from inhalation when working with carbon nanotubes, the Process 5 experiment was carried out in the sealed chamber and the researchers wore P2 respirators.

5.1.2 Process summary

102. The processes for which particle measurements were conducted are summarised in Table 2. At the request of the relevant organisations the location of the processes has not been identified and so an identifier code has been allocated for each measurement event as outlined in Table 2.

Table 2. Processes included in particle measurement

Process and primary nanomaterial	**Description of process**	**Measurement identification codes**
Process 1 Modified titanium dioxide	A university laboratory process involving two stages: Stage 1-A: Functionalised Anatase TiO_2 (~80% anatase, 20% rutile) powder was added to a bowl containing Iron Stearate, oil, and polyethylene resin beads, and this was mixed by hand using a spatula. This mixture was taken to Stage 1-B in which it was added to an extruder machine[7], designed to homogenise and heat the mixture. This produced pellets of the mix that could then be used to blow photo-degradable thin film for use in agriculture. Details regarding the specific functionalisation of the anatase were classified as a proprietary secret and so were not available to the researchers.	1-A, 1-B **1-A** Stage 1-A of process **1-B** Stage 1-B of process Further details are in Appendix B.

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[7] An extruder is a machine for producing more or less continuous lengths of plastic sections. Its essential elements are a tubular barrel, usually electrically heated; a revolving screw, ram or plunger within the barrel; a hopper at one end from which the material to be extruded is fed to the screw, ram or plunger; and a die at the opposite end for shaping the extruded mass. A diagram of an extruder similar to that used in Process One can be found at Appendix A.

Process and primary nanomaterial	Description of process	Measurement identification codes
Process 2 Clay platelets	Fine, functionalised clay platelets and polyurethane plastic beads were simultaneously added to an extrusion machine[8], designed to homogenise and heat the mixture so as to form a clay-polyurethane nanocomposite material.	2-A, 2-B, 2-C Measurements taken over three days: **2-A** – Day 1 **2-B** – Day 2 **2-C** – Day 3 Further details are in Appendix C.
Process 3 Titanium dioxide	A university laboratory process investigating electron transfer and nanotechnology as applied to solar cells. Nanocrystalline titanium dioxide (TiO_2) (99% Anatase) was manually ground, using a mortar and pestle, and mixed with a diluted acidic solution. The resultant TiO_2 solution was added to a slide using a dropper.	3-A, 3-B, 3-C, 3-D, 3-E, 3-F **3-A, 3-C,3-E** Wet grinding with addition of acid solution. **3-B, 3-D, 3-F** Dry grinding with no solution added. Further details are in Appendix D.
Process 4 Clay platelets	A university laboratory process involving jet-milling of a functionalised clay powder, followed by the cleaning of the equipment; This process is carried out in order to increase the particle surface area and the powder is used in Process 2 as described above.	4-A, 4-B **Process 4-A** Reducing size of modified clay platelets. **Process 4-B** Reducing size of: unmodified clay platelets. Further details are in Appendix E.
Process 5 Single- and multi-walled carbon nanotubes	Proprietary manufactured single and multi walled carbon nanotubes in solid form were repeatedly introduced to a chamber from which the resultant aerosols were analysed for particle number and mass concentration, size, morphology, and chemical composition. The response of the instrumentation used for this process informed the instrumentation and methodology used for the particle characterisation during the laboratory carbon nanotube usage for Process 6.	5-A, 5-B **Process 5-A** Decanting of SWCNT **Process 5-B** Decanting of MWCNT Further details are in Appendix F.
Process 6 Carbon nanotubes	Chemical Vapour Deposition (CVD) manufacture of carbon nanotubes. Process 6A utilised a furnace for catalytic CNT synthesis, whilst Process 6B utilised a SabreTube^{TM} Bench Top Thermal Processing System.	6-A, 6-B **Process 6-A** CVD using a sealed furnace chamber **Process 6-B** CVD using SabreTube^{TM} Bench Top Thermal Processing System. Further details are in Appendix F.

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[8] See footnote 2

5.2 Instrumentation

- Four TSI Incorporated (St. Paul, MN) Condensation Particle Counters (CPCs) were used for measurements of total particle number concentration: a TSI Model 3781 CPC, with a sampling time of 1 second, and a size range 0.006 - 3 µm, a TSI Model 8525 hand-held P-Trak Ultrafine Particle Counter with a sampling time of 1 second in the size range 0.02 - 1 µm, a TSI 3007 Ultrafine Particle Counter with a sampling time of 1 second in the size range 0.01 - 1 µm, and a TSI Model 3022 CPC with a sampling time of 5 seconds in the size range 0.006 – 3 µm, were used to measure total particle number concentration.
- Particle size distribution (including count median diameter) in the nanometre range was measured by a Scanning Mobility Particle Sizer (SMPS) comprising of a TSI Model 3080 Electrostatic Classifier (EC) and a TSI Model 3781 CPC or TSI 3025 CPC, with a scan time of 180 s and size range of approximately 4 - 160 nm.
- Particle size distribution in six channels between 0.3 µm to 10 µm was measured by a TSI Model AeroTrak 9306 hand-held optical particle counter (OPC).
- A TSI 3550 Nanoparticle Surface Area Monitor (NSAM) with a size range of 0.01 µm to 1.0 µm (noting instrument response for particles larger than 400nm is not fully quantified as described in Table 1) was used to obtain surface area equivalent dose of inhaled particles for the alveolar lung region.
- Particle mass concentration was measured by a TSI Model 8520 DustTrak Aerosol Monitor fitted with a 2.5 µm impactor.
- Particles were collected electrostatically onto carbon-coated **200-mesh copper Transmission Electron Microscope (TEM) grids** using a TSI 3089 Nanometre Aerosol Sampler. Samples were also collected using 37 mm diameter open-face, polytetrafluoroethylene, quartz, and mixed cellulose ester filters connected to air sampling pumps operating at approximately 5 L/min.
- Air temperature, relative humidity (RH) and carbon dioxide (CO_2) concentration were monitored using a TSI Q-Trak Plus Indoor Air Quality Monitor.
- Air velocity of extraction systems was measured by a TSI Velocicheck hot-wire anemometer.

103. The research work was undertaken with TSI instruments. However, other equipment manufacturers can also supply similar instrumentation with potentially similar performance.

5.3 Experimental design

104. The nanotechnology processes selected for aerosol particle characterisation were chosen following discussion with nanotechnology researchers at two universities located in Brisbane, Australia. The final selection of the processes reflected (i) the willingness of the researchers to participate in the study, (ii) the desire to include both fibrous and non-fibrous particles in the study, and (iii) the desire to include both low and high particle emitting processes.

5.4 Analysis

5.4.1 TEM, SEM and Energy-dispersive X-ray spectrometry

105. The transmission electron microscope (TEM) grids were examined using a Philips CM200 TEM, and individual particles on the films were analyzed for elemental composition using energy-dispersive X-ray spectrometry (EDX) with the instrument operated in the TEM microprobe mode. The polytetrafluoroethylene filters were examined using an FEI Quanta 200 Environmental Scanning Electron Microscope (ESEM) operated in high vacuum mode. The filters were coated with a thin

layer of evaporated carbon to provide electrical conductivity under the beam, and individual particles on the films were analyzed for elemental composition using an EDX microanalysis system.

5.4.2 Thermal optical analysis of elemental carbon

106. Carbon Nanotube aerosol was sampled onto quartz fibre filters using sampling pumps at a flow rate of 3.6 LPM. The organic, elemental, and total carbon mass of each filter was analysed using Evolved Gas Analysis by a thermal-optical analyser in accordance with the NIOSH Method 5040 [71] and the elemental carbon concentration as $\mu g\ m^{-3}$ was calculated.

5.4.3 Processing and Analysis of Data

107. A level of significance of $p = 0.05$ was used for all statistical procedures.

108. The inter-instrument Pearson’s Correlation matrix for particle source/type was determined. This information was used to reach conclusions regarding the relative strengths and weaknesses of each instrument when challenged with different particle sources. In particular, this allowed us to determine if a P-Trak, OPC, and DustTrak as a minimum set of instruments were able to characterise the investigated aerosols in terms of estimating personal exposure and identifying sources of particle emission, or if a more expansive approach was required.

6. QUALIFYING THE SIGNIFICANCE OF THE RESULTS OF PARTICLE MEASUREMENT

109. This section discusses the relationship between particle measurement results and triggers for the implementation of particle emission and exposure controls.

6.1 Particle control values

110. Underpinning the use of measurement results is the need for a *particle control value* that would guide the decision making in regard to controlling particles arising from nanotechnology processes.

111. There are a number of different types of *particle control values* that might be used for nanomaterial aerosols (described in 6.1.1 to 6.1.4 below). Ease and speed of measurement are factors in deciding which particle control values are used.

6.1.1 Examples of national exposure standards and limits for nanomaterials

112. With regard to nanomaterials, Australian Workplace Exposure Standards (WES) have been set for a small number of chemicals for which the primary particle size is nanoscale, i.e., they are nanomaterials. These WES, which are eight-hour time-weighted average standards are [78]:

- Carbon black – 3 mg m^{-3}, and
- Fumed silica – 2 mg m^{-3}.

113. The United States National Institute for Occupational Safety and Health (NIOSH) has established the following (ten-hour time-weighted average) mass-based Recommended Exposure Limits (RELs)[9] [40]:

- for fine[10] TiO_2 of 2.4 mg m^{-3}, and
- ultrafine[11] TiO_2 of 0.3 mg m^{-3}.

114. For comparison, the Australian WES for TiO_2 [78] is:

- 10 mg m^{-3} (inhalable fraction of PM_{10}) [eight-hour time-weighted average standard].

6.1.2 Proposed workplace exposure limits

115. In the 2010 draft Current Intelligence Bulletin *Occupational Exposure to Carbon Nanotubes and Nanofibers*, the US NIOSH proposed a REL of 7 $\mu g/m^3$ elemental carbon (EC) 8-hr TWA for carbon nanotubes and nanofibres, which was set at the upper limit of quantitation (LOQ) for NIOSH Method 5040 [79]. In view of quantified health risks at 7 $\mu g/m^3$ and ongoing improvements in sampling and analytical methodologies, NIOSH is now proposing a REL of 1 $\mu g/m^3$ EC as an 8-hr TWA respirable mass concentration using NIOSH Method 5040 [111], noting that efforts should be made to reduce airborne concentrations to carbon nanotubes and nanofibres as low as possible.

116. Japan's National Institute of Advanced Industrial Science and Technology (AIST) has published risk assessments and proposed workplace exposure limits [eight-hour time-weighted average standard] for the following nanomaterials [80]:

- TiO_2 – 0.6 mg m^{-3}
- fullerenes (C_{60}) – 0.39 mg m^{-3}
- carbon nanotubes (CNTs) – 0.03 mg m^{-3}

117. These AIST proposed workplace exposure limits are based on a subchronic exposure period of 15 years [80].

6.1.3 Benchmark Exposure Level

118. An alternative approach, in the absence of an exposure standard or limit, or proposed exposure limit, is to set Benchmark Exposure Levels (BELs) for groups of nanomaterials, based on consideration of health effects for those groups. Such an approach was first proposed in the British Standards Institution (BSI) document – Nanotechnologies: Part 2: Guide to safe handling and disposal of manufactured nanomaterials [81]. Other authors have since examined the use of BELs [82, 83, 96] and this will be discussed further in section 9.1.

6.1.4 Local Particle Reference Value

119. An alternative precautionary approach, in the absence of in-house limits, national exposure standards or limits, proposed workplace exposure limits, and BEL for a nanomaterial, could include

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[9] TWA concentrations for up to 10 hours/day during a 40-hour work week

[10] With *fine* defined as all particle sizes collected by respirable particle sampling

[11] With *ultrafine* defined as the fraction of respirable particles with primary particle diameter < 100nm

reference to the *local background particle exposure*[12] of the workers. This is then used as the basis of a *local particle reference value*[13] to guide decision of when excursion from this value is unacceptable.

120. This concept was utilised by McGarry et al. [58, 84] in describing exposure to particles arising from the operation of laser printers, and evidence for the application of this concept to manufactured nanomaterials is provided in section 9 of this report.

6.2 Criteria for assessing excursion above the particle control values

121. Where feasible, 8 hr TWA results can be used as reference values. However, further evaluation can be undertaken by utilising the normal occupational hygiene protocol for determining when excursion from a *particle control value* is unacceptable. Based upon the guidance principles on excursions of atmospheric contaminants within the occupational environment as outlined by both the *Australian National Occupational Health and Safety Commission* (now Safe Work Australia) [85] and the *American Conference of Governmental Industrial Hygienists* [86], a nanotechnology process could be considered to require further assessment if:

(a) short term exposures exceed three times the *particle control value* for time periods that add up to more than a total of 30 minutes per eight-hour working day, or
(b) if a single short term value exceeds the *particle control value* by five times.

122. These excursion criteria are useful in that they allow for normal variations in background particle values and also allow for inaccuracies that exist in all instrumentation, and sampling and analysis methods. Accuracy of instrumentation is discussed in section 6.3.

123. These excursion criteria are applicable to *particle control values* in general. This report explores in detail the use of excursion criteria relative to *local particle reference values*.

6.3 Factors to considered when comparing and interpreting particle measurement data

124. When interpreting and comparing particle measurement data at least four factors need to be considered and accounted for:

1. The minimum and maximum particle measurement size ranges may differ between different instruments. For example, the P-Trak with its size range of approximately 20 to 1000nm will characterise a lower PNC than a CPC 3025 with it larger size range of 6 to 3000 nm for the same aerosol.
2. Particles may exhibit significant differences in solubility and therefore detectability between water and alcohol operating fluids utilised by CPC's.
3. Fluctuations in background particle concentration - to ensure these are not interpreted as being related to the process under investigation.
4. The particle concentration accuracy of the instruments. This information can be obtained from the instrument specification data supplied by the manufacturer. Data for the instruments used in this study are contained in Table 3.

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[12] See glossary for definition

[13] See glossary for definition

Table 3. Instrument particle concentration accuracy data - provided by instrument manufacturers

Instrument	Particle concentration accuracy
TSI Model 3781 CPC	±10% at 5 x 10^5 particles cm^{-3}
TSI Model 8525 hand-held P-Trak	±20% of the reading*
TSI Model 3022 CPC	±10% at 5 x 10^5 particles cm^{-3}
TSI Model 3025 CPC	±10% at 5 x 10^5 particles cm^{-3}
TSI Model 3550 NSAM	±20% or 0.5 $\mu m^2/cm^3$ Alveolar
TSI Model 8520 DustTrak	±0.1 % of reading or ±0.001 mg/m^3, whichever is greater
TSI Model 9306 AeroTrak OPC	±5%#
SMPS	±10% at 5 x 10^5 particles cm^{-3}

* although concentration accuracy is not specified by the manufacturer, a study by Matson et al comparing response of P-Trak and 3007 concluded both CPCs have proven to be reliable and yield comparable results of the UFP number concentrations

although manufacturer doesn't specify the accuracy, the flow rate is specified at +/-5% and is a key determinant of accuracy

125. As can be seen from the data in Table 3, differences of up to 20% in measurement values may be related to accuracy of the instrument. Although it is difficult to verify the information provided by the instrument manufacturers, the essential point is that all instrumentation has accuracy issues.

126. Asbach et al (2009) reported an inter-comparison study for SMPS devices [97], which showed that comparable measurement results within about 30% accuracy can achieved, noting that this work was conducted by experienced researchers and workplace hygienists under controlled conditions.

127. When collecting sequential temporal and spatial data, the same instrumentation should be used. If different instruments of the same class (e.g. CPC model 3781 and P-Trak) are to be used for either temporal or spatial data collection, differences in particle concentration accuracy, size range, and operating fluid between the instruments should be accounted for. In this case, instruments should be co-located and operated simultaneously to characterise an aerosol source, allowing a correction factor for one of the instruments to be calculated. The correction factor can then applied to the field data.

128. The discussion in this report of particle measurement results considers factors that influence accuracy.

7. PARTICLE EMISSION, TRANSPORT, MORPHOLOGY, AND CHEMICAL COMPOSITION FOR SIX MN AEROSOLS: RESULTS OF THE CHARACTERISATION

129. The results of particle measurement data have been organised in the following manner:

- Firstly, provide time-series plots including particle number concentration, $PM_{2.5}$ concentration, particle count median diameter, and particle alveolar deposited surface area.
- Secondly, analyse data on the peak and mean particle metrics to evaluate whether the nanotechnology process contributed to increases over *local background particle metrics*. Such an analysis accounts for the impact of normal fluctuations in *local background particle exposure* and known accuracy of the instruments when determining if particle measurement values are significant.
- Thirdly, evaluate the influence of particle emission controls on particle emission and transport.
- Finally for three processes, describe particle morphology and chemical composition for particles collected using filters and TEM grids, and analysed using both SEM and TEM, and for one process to describe the results of the analysis of elemental carbon.

130. The detailed results of the six Case Studies, summarised in Table 2 (section 5.1), are presented in Appendices B-G.

131. The plotted measurement values reflect both the source and background particles, and in specific cases estimated worker exposure to particle concentrations during these nanotechnology operations, so as to illustrate temporal and spatial particle behaviour.

7.1 Mean particle metrics for all six nm aerosols

132. The means of the PNC, CMD, alveolar deposited surface area, and $PM_{2.5}$ concentration that reflect process operation and *local background particle exposure* were calculated and are presented in Table 4. The data in this table is discussed in detail as part of the analysis of each process in Appendices B-G.

133. Differences of between 10 and 20% in the spatial PNC was recorded by the two 3781 CPC's operating simultaneously at 7 metres apart, as evidenced by the data in Table 4. These differences can likely be accounted for by a combined effect of the particle concentration accuracy of the instrument (+/- 10% at 5×10^5 particles cm^{-3}) and the effect of spatial variation in PNC over the 7 metre distance.

134. From nanomaterial-related processes, three types of particles can be emitted; (a) manufactured nanomaterials, (b) particles formed by condensation in the processes (e.g. condensation of vapours produced by heating, such as laser printer emissions), and (c) particles produced from the operation of machines (e.g. copper nanoparticles produced from electrical equipment).

135. For the processes examined in this study, potentially, condensed particles may be emitted from Processes 1B, 2 and 6 and particles could be emitted from machine operation in Process 4. Measurements indicate that some of the particles emitted are not manufactured nanomaterials, but in relation to decision-making about process control, the quantity is not significant when compared with manufactured nanomaterials emissions.

Table 4. Summary of mean particle metrics reflecting the nanotechnology process in operation and the LBPC

	At nanomaterial emission source																**Spatial data at 7m from emission source**	
	Mean PNC 6 to 3000nm [particles cm^{-3}] **CPC 3781**		Mean PNC 20 to 1000nm [particles cm^{-3}] **CPC P-Trak**		Mean PNC 300 to 3000nm [particles cm^{-3}] **OPC**		Mean PNC 300 to 10000nm [particles cm^{-3}] **OPC**		Mean $PM_{2.5}$ Up to 2500nm [µg m^{-3}] **DustTrak**		Mean CMD Over range 4 to 160nm [nm] **SMPS**		Mean alveolar surface area 10 to 1000nm [µm^2 cm^{-3}] **NSAM**		Elemental Carbon NIOSH Method 5040 [µg m^{-3}]	Mean PNC 6 to 3000nm [particles cm^{-3}] **CPC 3781**	
Process	During	LBPC	During	LBPC	During	LBPC	During	LBPC	During	LBPC	During	LBPC	During	LBPC	During	During	LBPC
1A	6.4 x 10^3	6.3 x 10^3	5.3 x 10^3	5.2 x 10^3	#	#	#	#	8.6	6.5	55	54	18	18	#	7.8 x 10^3	7.9 x 10^3
1B	2.3 x 10^4	1.5 x 10^4	#	1.1 x 10^4	#	#	#	#	8.7	7.4	54	37	104	31	#	1.9 x 10^4	1.8 x 10^4
2*	8.5 x 10^3	1.0 x 10^4	4.8 x 10^3	6.6 x 10^3	#	#	#	#	8	4.6	35	31	15	20	#	1.0 x 10^4	1.1 x 10^4
3^	6.8 x 10^3	5.9 x 10^3	4.0 x 10^3	2.7 x 10^3	#	#	#	#	12	10	37	37	18	15	#	#	#
4^{Δ}	#	#	1.2 x 10^4	5.5 x 10^2	4.0 x 10^2	< 1	< 1	< 1	450	1	#	#	#	#	#	#	#
5A	#	#	7.1 x 10^3	7.0 x 10^3	26	15.7	<1	< 1	56	14	64	60	56	50	1474☐	9.1 x 10^3	8.9 x 10^3
5B	#	#	4.3 x 10^3	3.9 x 10^3	34	37	< 1	< 1	35	25	82	80	32	30	< 2	5.4 x 10^3	4.3 x 10^3
6A	#	#	8.2 x 10^3	4.0 x 10^3	86	3	#	#	420	7	#	#	#	#	#	#	#
6B	#	#	3.4 x 10^4	3.1 x 10^3	3	3	#	#	19	3	#	#	#	#	#	#	#

local background particle concentration (LBPC)

Note: measured simultaneously at the nanomaterial emission source and 7 m from source for six nanomaterial aerosols

Instruments used:
Process 1A – CPC 3781; P-Trak, DustTrak, SMPS, NSAM, SEM
Process 1B - CPC 3781; DustTrak, SMPS, NSAM
Process 2 - CPC 3781; P-Trak, CPC 3022, DustTrak, SMPS, NSAM, SEM, TEM. Local extraction ventilation operating
Process 3 - CPC 3781; P-Trak, DustTrak, SMPS, NSAM
Process 4 – CPC P-Trak; DustTrak, OPC
Process 5 - CPC 3781; P-Trak, DustTrak, SMPS, NSAM, SEM, TEM, Elemental Carbon
Process 6 - CPC P-Trak; DustTrak, OPC
not measured
☐ Result is qualitative only because analyst noted "filter overloaded and uneven particulate distribution"
* mean results over measurements 2A, 2B and 2C
^ mean results over measurements 3A to 3E s
Δ values reflect jet milling phase only, and do not include cleaning phase differences in both spatial and temporal absolute PNC recorded by the different CPC's operating simultaneously can be explained the differing particle measurement ranges and operating fluids.

8. COMPARISON AND EVALUATION OF THE RESPONSE OF DIFFERENT INSTRUMENTATION AND MEASUREMENT METHODOLOGY TO A RANGE OF AIRBORNE MN

8.1 Methodology

136. In order to evaluate the correlation between instrument responses the inter-instrument Pearson's Correlation matrix for different particle sources was calculated and the resultant r-values are summarised in Tables 17 to 23 at Appendix H.

137. Using the Fisher r-to-z transformation, a value of z is calculated that can be applied to assess the significance of the difference between two correlation coefficients, r_a and r_b, found in two independent samples. If r_a is greater than r_b, the resulting value of z will have a positive sign; if r_a is smaller than r_b, the sign of z will be negative.

138. Where repeated particle measurements were taken for a process the data has been pooled into one data set and the Pearson's correlation has then been calculated. For the purposes of this discussion an r-value of between -0.4 and 0.4 is considered a poor correlation, -/+0.5 to -/+0.7 a weakly positive correlation, and -/+ 0.8 to -/+1.0 a strong correlation.

8.2 Discussion

139. The calculated r-values indicate that the correlation between the various CPCs, OPC, DustTrak, SMPS, and NSAM was highly variable and partly source dependent. This is likely due to differences in counting efficiencies and ranges of the different instruments. In addition, the differing particles generated from each source, would result in different refractive indices (for DustTrak and OPC) of the particles. For example, during the operation of processes 4 and 5, the P-Trak showed a weakly positive to strong positive linear correlation to the OPC (particle bin sizes 300 to 1000nm), the DustTrak showed a weakly positive linear correlation to the OPC (bin sizes 300 to 1000nm) and DustTrak showed a weakly positive linear correlation to the P-Trak. However the OPC (particle bin sizes > 1000nm) showed a poor linear relationship to both the DustTrak and the P-Trak. This suggests the aerosols were dominated by submicrometre particles and that a positive correlation can only be expected where the aerosol particle size is within the particle size parameters of the respective instruments.

140. Where the aerosol was primarily composed of submicrometre sized particles, such as with processes 1A and 2, in most cases a weakly positive linear relationship existed between all CPCs, including the P-Trak, and the NSAM located at the emission source.

141. The NSAM and the P-Trak exhibited a consistent positive linear relationship (weakly positive to strong positive) across a range of aerosols composed of particles with the size range 20 to 1000nm. This result is expected considering the particle size parameters of each instrument are the same, i.e. 20 to 1000nm.

142. The SMPS exhibited a mostly a weakly positive linear relationship with all CPC's for nanoparticle measurements (processes 1 to 4), but a poor relationship for process 5 which predominantly emitted large agglomerates of CNTs. The SMPS exhibited a poor positive to weakly positive linear relationship with the NSAM for nanoparticle measurements (processes 1 to 4) and a poor relationship for process 5.

143. The SMPS exhibited a poor positive to weakly positive linear relationship with the DustTrak for nanoparticle measurements (processes 1 to 4) and a poor relationship for process 5. This is consistent with the SMPS particle size range of 5 to 160nm being at the lower limit of the DustTrak. The SMPS exhibited a poor linear response with the OPC which is as expected considering the SMPS particle size range is below the minimum particle size of the OPC.

144. These Pearson's correlation r-values indicate the P-Trak, OPC, DustTrak, and NSAM exhibit relationships to one another across a variety of nanomaterial aerosols, including fibrous and non-fibrous particles, which are consistent with emitted particle size and instrument measurement range. These results indicate a P-Trak, OPC, NSAM, and DustTrak if used as a suite of instruments are sufficient to characterise the variability inherent in the investigated aerosols.

9. CHARACTERISATION AND REPORTING OF TEMPORAL AND SPATIAL CONCENTRATIONS OF AIRBORNE MN: RECOMMENDATIONS

145. The results clearly indicate that when used as a complementary set of instruments, a P-Trak, OPC, and DustTrak are able to characterise temporal and spatial particle number and mass concentration when evaluating emission sources, breathing zone exposure of process operators, incidental and background particles, and effectiveness of particle emission controls. In addition, if required, filter based samples can be collected with relative ease for analysis by electron microscopy.

146. The results also clearly indicate the DustTrak $PM_{2.5}$ mass concentration correlates positively with the PNC in size range of 300 to 2500 nm. These instruments are particularly good tools to characterise relative changes in airborne particle concentrations.

9.1 Utilise Particle Control Values when evaluating particle emission and exposure

147. In Section 6.1, *Particle Control Values* that might be used for nanomaterials were described. A company or laboratory may set its own in-house control limits, but these must be equal to or lower, i.e. more stringent, than applicable national regulatory limits.

148. A small number of exposure limits have been recommended by companies for use of their products:

Material	**Recommended Exposure Limits, mg m^{-3}**	**Company**
Carbon nanotubes	0.0025	Nanocyl
Carbon nanotubes	0.05	Bayer Material Science

9.1.1 Hierarchy of Particle Control Values for nanomaterials

149. Examples of various standards or limits are presented in this section. In general, for detailed analysis particle control values might be used in the following order of priority, using the highest available in the list:

1. A country's national exposure standards or limits, e.g. Recommended Exposure Limits (US NIOSH) or Australian Workplace Exposure Standards
2. National exposure standards or limits from another country
3. Proposed workplace exposure limits – from research results
4. Benchmark Exposure Levels (BEL) – which include some consideration of health effects
5. Local particle reference values based on background nanomaterial levels

150. However ease and speed of analysis is also a factor. For fast screening analysis, measurements with CPC, OPC and photometer can be compared with local particle reference values based on background nanomaterial levels.

1. National Workplace Exposure Standards or Limits

Material	National Exposure Standard or Limit, mg m^{-3}	Source
Carbon black	3 (8 hr TWA)	Australian WES
Fumed silica	2 (8 hr TWA)	Australian WES
Ultrafine TiO_2	0.3 (10 hr TWA)	US NIOSH REL

2. Proposed workplace exposure limits

Nanomaterial	Proposed exposure limit, (8 hr TWA), mg m^{-3}
Carbon nanotubes and nanofibres (US NIOSH)	0.001
Fullerenes (Japan AIST)	0.39
TiO_2 (Japan AIST)	0.6
Carbon nanotubes (Japan AIST)	0.03

3. Benchmark Exposure Levels

151. An alternative approach, in the absence of an exposure standard or limit, or proposed exposure limit, is to set Benchmark Exposure Levels (BELs) for groups of nanomaterials, based on consideration of typical hazard severity for those groups. Both mass concentration-based and number concentration-based BELs have been proposed.

152. Such an approach was first proposed by the British Standards Institution (BSI) [81]. Four groups of nanomaterials were defined and BELs were proposed for the four groups:

1. Fibrous nanomaterials : BEL = 0.01 fibres/cm^3
2. Nanomaterials classified as Carcinogenic, Mutagenic, Asthmagenic, or Reproductive Toxins (CMAR): BEL = 0.1 x Workplace Exposure Limit (WEL) of the bulk material
3. Insoluble nanomaterials: BEL = 0.066 x WEL of the bulk material
4. Soluble[14] nanomaterials: BEL = 0.5 x WEL of the bulk material.

153. For insoluble nanomaterials, a particle number concentration BEL was proposed of 20 000 particles/ml, discriminated from the ambient environmental particle concentration.

154. BELs were intended to be used as precautionary benchmarks to assess workplace exposures by measurement.

155. Benke et al [82] examined the BEL groups and reported that they appear to be practical groupings of nanomaterials. This report recommended that the BEL for insoluble or poorly soluble fibrous nanomaterials should be 0.1 fibre/cm^3, rather than the 0.01 fibre/cm^3, as there is no evidence that these nanomaterials are more toxic on a fibre-by-fibre basis than asbestos. Also, a higher number of fibres will be counted by electron microscopy which is needed to resolve fine fibres, e.g. carbon nanotubes.

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[14] The BSI document [81] does not define soluble vs insoluble; however the solubility of nanomaterials may be examined in a number of solutions. In the Globally Hamonized System of Classification and Labelling of Chemicals (GHS) [106], water solubility is considered in relation to aspiration hazard and environmental hazards. Osmond et al [107] examined the durability of carbon nanotubes in Gamble's solution (simulated lung fluid).

156. The relationship between number concentration and mass concentration for the BELs has been examined by the German IFA [83]. In this work, particle size and density variation were considered, and the number concentration required for a mass concentration of 0.1mg/m^3 was calculated for a number of manufactured nanomaterials (Appendix I, Table 24).

157. IFA proposed the following recommended benchmark levels as increases over the background exposure during an entire shift (8 hours), for monitoring the effectiveness of protective measures in the plants. These recommended benchmark levels are geared to minimizing the exposure in accordance with the state of the art, and are not substantiated toxicologically.

- For metals, metal oxides and other biopersistent granular nanomaterials with a density of > 6 000 kg/m^3, a particle number concentration of 20 000 particles/cm^3 measured between 1 and 100 nm should not be exceeded. If the density is below 6 000 kg/m^3, a particle number concentration of 40 000 particles/cm^3 in the measured range between 1 and 100 nm should not be exceeded.
- For carbon nanotubes, a provisional fibre concentration of 0.01fibres/cm^3 (same as [81]) is proposed for assessment. But given sampling and analysis issues, for a transitional period, a particle number concentration of 20,000 particles/cm^3 should not be exceeded.
- For ultrafine liquid particles (such as fats, hydrocarbons, siloxanes), the applicable maximum workplace limit (MAK) or workplace limit (AGW) values should be employed owing to the absence of effects of solid particles.
- The recommended benchmark levels stated above should not be applied to incidental ultrafine particles (e.g. in welding fumes), where other limits apply.

158. A group from the Netherlands evaluated the IFA values, and accepted the benchmarks of 20,000, 40,000 for biopersistent nanomaterials and 0.01 fibres/cm^3 for rigid biopersistent nanofibres as Nano Reference Values (NRVs) [96], and in addition recommended that for non-biopersistent granular nanomaterials the applicable OEL should be used [96].

159. Considering what might be an appropriate default mass-based BEL for insoluble nanoscale particles, it is noted that the US NIOSH’s REL for TiO_2 is 0.3mg/m^3 (10hr TWA). This value of 0.3mg/m^3 might be used as a default value in the absence of other data and it is noted that this value has also been proposed as a reduced general threshold value for respirable dusts in Germany [103].

160. The 8–hour TWA Nano Reference Values were considered to be a comprehensible and useful instrument for risk management [96], with the use of particles/cm^3 being an accepted metric. These values avoid the issue associated with use of the BSI BELs in that a significant number of manufactured nanomaterials do not have macroscale equivalents with exposure standards. However, number concentration-based benchmarks that are defined for particles in the range 1-100nm require the use of relatively complex instruments such as SMPS for measurement.

4. Local Particle Reference Values

161. National exposure standards and limits and proposed workplace exposure limits are in place for only very few nanomaterials. In the absence of these limits, BELs may be used. Measurement may also be focussed on identifying relative changes in particle concentration using *local particle reference values* derived from characterising background particle levels. This approach allows assessment of emission and exposure relative to the local background particle concentration.

162. Local particle reference values should be assigned in bands based upon particle number and mass concentration. For example, the following three bands can be assigned: (a) $PNC_{20\text{-}1000nm}$, (b) $PNC_{300\text{-}3000nm}$, (c) Mass concentration, e.g. PM_1, $PM_{2.5}$, respirable dust size fraction (PM_4), or PM_{10} (inhalable) - the respirable or inhalable dust fraction is the currently used administrative/regulatory size fraction for most compounds.

163. The upper range of 3000nm has been used for the PNC because from the research results, all background and nanomaterial aerosol concentrations > 3000nm were <1 particle cm^{-3} and therefore insignificant. However, in the event that background PNC and/or nanomaterial aerosol are dominated by particles >3000nm then a relevant particle reference band, such as $PNC_{3000-10000nm}$, could be assigned. Also in such circumstances, the PM_{10} rather than $PM_{2.5}$ particle size impactor could also be used for the DustTrak.

164. Use of a three-tiered assessment approach is recommended in this report:

- Tier One - comprehensive survey of the process environment
- Tier Two - comprehensive characterisation of real-time particle number and mass concentration
- Tier Three - utilise sampling methods for off-line analysis of particle morphology, chemical composition, and mass concentration and compare with measurement by real-time instruments

165. In the Tier Two assessment, particle concentrations can be compared with the three different *local particle reference values*, i.e. $PNC_{20-1000nm}$, $PNC_{300-3000nm}$ and mass concentration. Exceeding the excursion criteria for any of these, for either source emission or breathing zone concentrations, may be sufficient to consider undertaking a Tier Three assessment.

9.2 Utilise real-time particle number and mass concentration data to identify sources of particle emission and spatial variation, and to validate effectiveness of engineering controls in containing particle emissions

166. The number of particle metrics characterised should be minimised to make assessment as straightforward as possible. The metrics characterised should be those necessary to inform risk assessment and will normally be particle number and mass concentration. In this research, particle number and mass concentration measurements clearly identified points of particle emission.

167. The DustTrak was found to be a useful instrument in estimating airborne mass concentrations. Noting the DustTrak is calibrated using Arizona road dust (ISO 12103-1, A1 test dust), which is representative of a wide range of ambient aerosols, a custom calibration using the aerosol of interest may be needed for the DustTrak to be used for accurate real-time mass concentration monitoring.

168. The observed correlations of the CPC's and DustTrak with for example SMPS and NSAM are valid for the scenarios investigated, but may differ in other scenarios e.g. with higher background concentrations.

169. As part of the assessment of Process 4 (see Appendix E), a P-Trak, OPC, and DustTrak were utilised to characterise sources of particle leakage during operation of the jet-milling machine. Use of this instrument combination showed clearly that the aerosol emission was dominated by sub-1000 nm sized particles with the P-Trak able to characterise these particles. The particle signature from the process includes particles within the 300 to 1000nm size range as characterised by the OPC, and mass concentration less than 2500nm is characterised by the DustTrak. The data obtained from the P-Trak, OPC and DustTrak showed that both sub and supermicrometre particles are emitted from this process and that these measurement methods combined are capable of characterising particles.

170. Particle number and mass concentration are reliable in validation of the effectiveness of particle containment controls such as enclosure and extraction ventilation. It is clear from Figure 15 that turning off the extraction ventilation for Process 2 resulted in an immediate and significant increase in PNC. From Figure 41 it is clear the fume cabinet was able to effectively minimise the escape of particles to the laboratory environment as evidenced by the orders of magnitude lower concentration of particles within the laboratory compared to within the fume cabinet.

171. The data in Figures 24 and 25 demonstrate that particle number and mass concentration measurements are reliable in estimating particle exposure within the breathing zone of workers. Particle number and mass concentration measured at point C (breathing zone) are significantly lower than at the particle emission points, B and D.

172. Therefore, particle number and mass concentration data should be utilised in identifying if a nanotechnology process is a significant emitter of particles to the local environment. Specifically this should include simultaneous measurement of the sub and supermicrometre particle size range. Instrumentation that is currently available and recommended for this work includes:

- A portable CPC with a particle measurement range that includes the ultrafine particle range (<100nm), for example a P-Trak
- An OPC with a particle measurement range of submicrometre to 10 µm
- A photometer with a mass concentration range that overlaps with the portable CPC and OPC, for example a DustTrak.

173. The relative portability of these instruments allows for them to be moved easily and quickly so as to obtain temporal and spatial particle data. Careful analysis of the data from each instrument and an understanding of the overlap in particle measurement bands of the three instruments will allow sound conclusions to be made as to the dominant particle signature. For example, a significant PNC in the range of 500 to 3000nm should correlate with significant $PM_{2.5}$ concentration. A significant PNC characterised by the P-Trak at same time as insignificant PNC characterised by the OPC would suggest a particle signature dominated by sub-300nm sized particles, though not necessarily nanoscale particles. Subtracting OPC and CPC measurement results from one another is not recommended because of the fundamental differences in operating principles of both instruments.

Use of NSAM and SMPS

174. Although the NSAM data from Processes 1B and 3 indicated significant peaks in alveolar deposited surface area, it cannot be concluded that the NSAM values reflect true alveolar lung deposited surface area. This is because, as described in Table 1, the accuracy of the NSAM is stated to be only in the range of aerosol particles of size range 20 to 400 nm and significant peaks in $PM_{2.5}$ concentration were evident during operation of Process 1B. Even a small number of particles > 400 nm can have a significant contribution to total surface area causing significant errors in the lung deposited surface area estimate of the device [19, 44]. Despite this it is evident the NSAM is useful in identifying the occurrence of particle emission from a source.

175. The SMPS with for example an upper particle size of 160nm as used in this research, can be used to identify the contribution of ultrafine particles to the total aerosol particle size distribution. However, particle number and mass concentration varied across a size measurement band between 20 nm and 3000 nm. Thus, characterising ultrafine size range is only one part of identifying particle emission and spatial distribution and is not sufficient on its own.

9.3 Comprehensively characterise background particle number and mass concentration

176. Both sub and supermicrometre particles are ubiquitous in the environment. Therefore, these background particles and sources of such background particles need to be identified and fully characterised in order to accurately assess emissions of particles from a process of interest.

177. Background concentrations can be examined and accounted for in two ways:

- Simultaneous measurement at; (a) emission source, and (b) away (isolated) from the source.
- Before and after measurement with process operating.

178. For example, it is clear from Figure 16 that there was significant variability in background PNC prior to operation of Process 2. It is also clear from Figure 21 that variation in background PNC was similar to that when Process 3 was operation. Conversely, it is clear from Figure 3 that PNC varied significantly during the operation of Process 1B when compared to the relatively small PNC variability in background when this process was not in operation. A similar pattern in particle variability is evident in Figure 24 for Process 4A.

179. The contribution of particles to the work area from both the process of interest and incidental sources should be characterised by utilising a spatial measurement process, such as that utilised to obtain the data contained in Figure 15 in Appendix C.2.2. This Figure provides data from two CPC's operated simultaneously during the operation of Process 2C. One CPC was located at the process particle emission point, whilst the second was located approximately 7 m away. Two things are evident from this data, first the particle emission from the process in general was not strong enough to influence the background away from the immediate emission point, and secondly the strength of process emission was enough to influence background PNC at 7 m when the extraction ventilation was stopped.

180. Figures 1 and 2 demonstrate that incidental sources of particles, such as nearby welding, need to be identified and characterised. In this case, the welding process was a stronger source of particles than the process of interest.

Figure 1. Particle number concentration both during and after the introduction of CNTs to the chamber

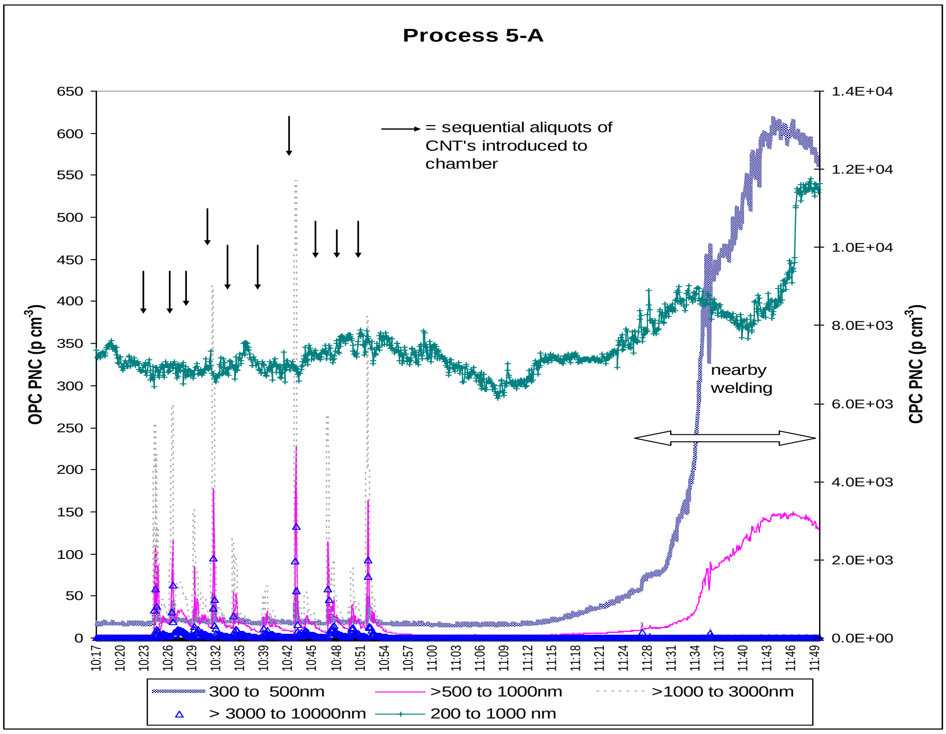
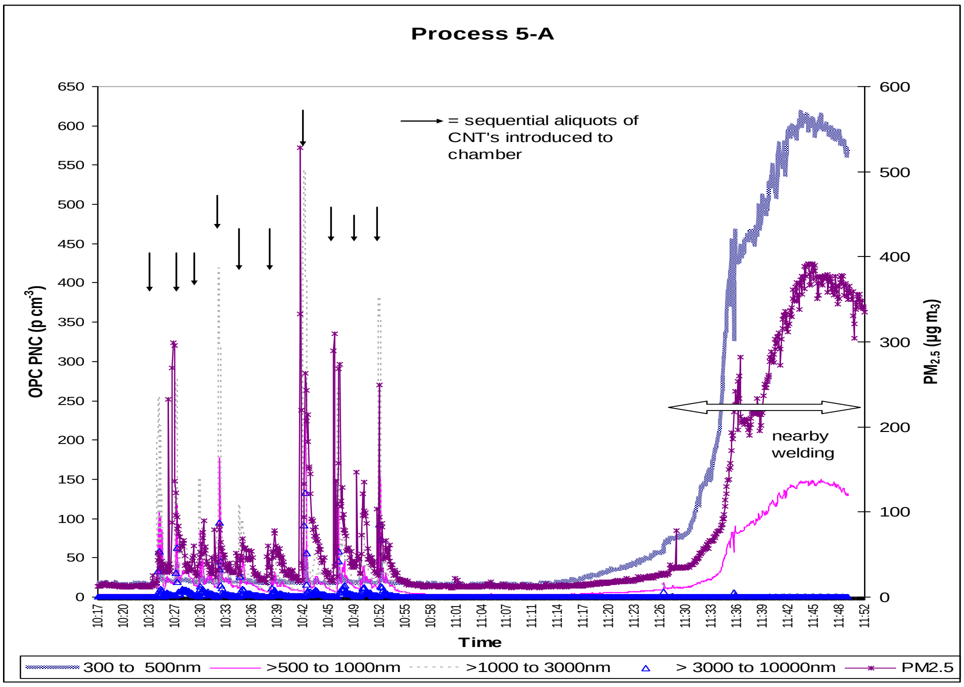
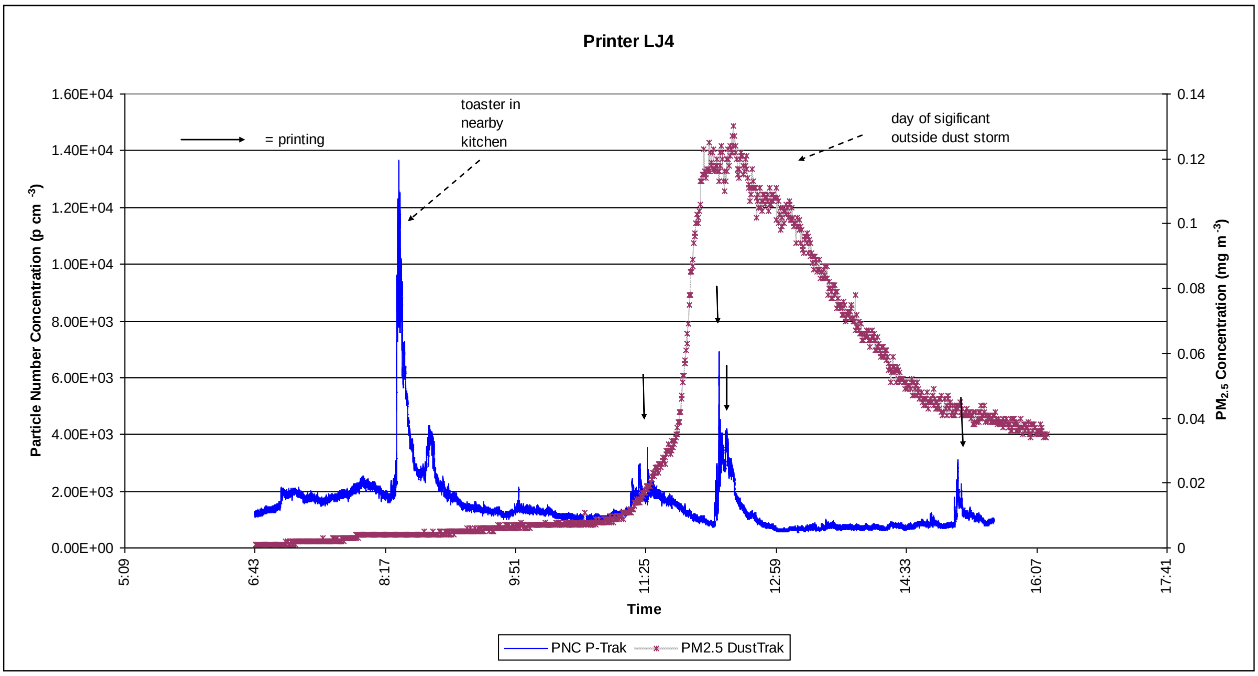


Figure 2. Particle number and mass concentration response of OPC and DustTrak to carbon nanotube aerosol and nearby welding



181. The influence of incidental particle sources is further illustrated in the data contained in Figure 3. This Figure includes the time-series plot for particle number and PM$_{2.5}$ concentration, including P-Trak responses to printer emissions and incidental particles arising from nearby operation of a toaster, plus DustTrak response to a significant outside dust storm [84].

Figure 3. Particle number and mass concentrations associated with incidental background particle sources



182. This data illustrates two concepts, firstly, the P-Trak and DustTrak are able to respond rapidly to significant changes in incidental background particle number and mass concentrations, respectively; and secondly, awareness of changes in background particles is essential for the accurate evaluation of particle sources of interest.

183. The procedures used in the present report demonstrate how to characterise background particle levels in non-industrial situations. This issue can be more complex in industrial situations, where a simple nano- non-nano activity comparison without any additional sources of particles is less frequently achievable.

9.4 Utilise excursion guidance criteria to evaluate temporal and spatial particle variation in relation to risk assessment

184. As described in Section 6.2, *excursion guidance criteria* can be utilised to inform decisions as to whether particle concentration emission and exposure relative to particle control levels are acceptable or require further assessment.

185. A nanotechnology process can be considered to require modified controls or further assessment if, for example, the:

(a) eight-hour TWA exposure > *particle control value*, or
(b) short term emissions or exposures exceed three times the *particle control value* for time periods that add up to more than a total of 30 minutes per eight-hour working day, or
(c) a single short term value for emission or exposure exceeds five times the *particle control value*.

186. These are based on guidance on excursions above an exposure standard for chemicals generally, and are the conditions when a process is not considered to be under reasonable control [109]. A number of countries have similar administrative rules which can be adopted in those countries to develop excursion criteria for nanomaterials.187. The length of time the single short term value represents will be determined by the minimum sampling of the equipment used. As described in Section 5.2, the CPCs used in this study had a sampling time of between 1 and 5 seconds.

Use of particle control values when applying excursion criteria

188. When applying excursion criteria, particle control values should ideally be based on absolute concentrations. Workplace exposure standards, exposure limits, benchmark exposure levels and nano reference values are all of this form.

189. Though variable, the background particle number concentration, i.e. the *local particle reference value* can also be used as the particle control value. It cannot be used to make conclusions about exposure related health effects, but provides for replicable decision making regarding control of emissions.

190. However, there are situations where applying excursion criteria when using the background particle number concentration, i.e. the *local particle reference value* as the *particle control value* can be problematic. In cases with low background (e.g., clean-room like air), the critical ratio may be much higher than the ratios recommended above. In the case where background concentrations are relatively high, the ratio of even 3 or 5 will be unacceptable, especially when dealing with high toxicity and toxicologically classified substances. Hence, absolute concentrations need to be taken into consideration.

Low background concentration – Options for local particle reference value

191. The Tier 2 assessment is a screening assessment and therefore concentrations should be easily measurable, i.e. by CPC, OPC or photometer. This infers that the use of BELs, which have been specified for the range 1-100nm, are not applicable as this instrumentation does not measure this range of values.

> ***Proposed approach*** *- If background concentration < 1000 particles/cm^3 as measured by CPC, then apply excursion criteria based on a background concentration of 1000 particles/cm^3 as measured by CPC.*

High background concentration – Options for particle control values

192. Similar to above:

> ***Proposed approach*** *- If background concentration > 20000 particles/cm^3 as measured by CPC, then apply excursion criteria based on a background concentration of 20000 particles/cm^3 as measured by CPC.*

193. The advantage of using background particle number concentrations as the benchmark is this assessment can be done quickly and easily using a CPC, OPC and Dust Trak. Thus it is generally suitable for Tier 2 assessments. The measurements associated with other particle control values either require sampling or use of more complex instruments to determine number concentration in the range 1-100nm and are thus sutitable for Tier 3 assessments.

194. In order to make a decision regarding acceptability of particle emission and exposure, the following four steps should be utilised:

1. *Particle control value* identified
2. Real time data of particle number and mass concentrations should be graphed – as measured in the breathing zone of process operators, and at emission points located as close as possible to the process.
3. TWA, short term and peak values of emissions and exposure are examined using the *excursion guidance criteria*.
4. Examine:
    a) the particle *exposures* in relation to particle control values, and
    b) the particle *source emissions* in relation to particle control values.

9.4.1 Application of excursion guidance criteria to research data contained in this report using local particle reference values

195. Table 5 has been divided along the lines of “Tier Two” and “Tier Three” assessment to reflect the three-tiered particle assessment process recommended in Section 9.5.

196. Analysis of the Tier Two data allows a determination to be made as to whether the *excursion guidance criteria* have been exceeded by peak values at both the potential points of emission and in the breathing zone of workers. The comparison of peak values to the *local particle reference values* allows decisions to be made as to the acceptability of a process as a particle emitter to the workplace environment and whether further assessment of particle emission is required.

197. The *excursion guidance criteria* have been applied to Processes 1A, 1B, 2, 3, 4, 6A, and 6B, as shown in Table 5. In relation to the *local particle reference value*, where the excursion criteria have been exceeded, the relevant cell within Table 5 has been shaded to signify that this is a Tier Two assessment finding needing further examination. Options available for further assessment as part of Tier Three assessment are also presented, such as analysis of particle size and morphology, and the application of National Exposure Standards or similar.

198. As part of the Tier Two assessment, *local particle reference values* have been assigned in following three bands: (a) $PNC_{20\text{-}1000nm}$, (b) $PNC_{300\text{-}3000nm}$, (c) $PM_{2.5}$. The upper range of 3000nm was used for the PNC because all background and nanomaterial aerosol concentrations > 3000nm were <1 particle cm^{-3} and therefore do not make a substantive contribution to the PNC. However, in the event that background PNC and/or nanomaterial aerosol are dominated by particles >3000nm then a relevant particle reference band could be assigned. In such circumstances, the PM_{10} rather than $PM_{2.5}$ particle size impactor should be used for the DustTrak.

9.4.2 Examination of findings in relation to background particle reference values

199. As can be seen in Table 5, for the processes studied in this work, the combination of *local particle reference values*, excursion criteria of "> 3 times the particle reference value for more than 30 minutes in an eight hour period" and "any single value > than five times the particle reference value" were relevant in identifying process particle emissions that required control and/or further assessment.

200. As noted earlier, there can be problems with applying excursion criteria when using the background particle number concentration as the *local particle reference value* in cases with low background concentrations or where background concentrations are relatively high. Nevertheless, use of the *local particle reference value* based on background concentrations offers a screening method which can be applied using a CPC, OPC and DustTrak.

201. Alternative approaches could be considered for screening. For example:

1. Mass concentration screening assessment based on measurement by photometer and comparison with exposure standards/limits if available or mass concentration-based BELs. Photometer measurements can vary from gravimetric measurements, but for screening that may not be an issue in practice.
2. Number concentration-based BELs may be defined based on measurement by CPC. Different CPCs measure over different size ranges, but this need not be an issue for screening. This means that particles are measured over a wider size range than 1-100nm, e.g. over the range of 20-1000nm, but this is toxicologically relevant as particles in the range 20-1000nm are respirable.
3. Deriving excursion guidance criteria and local particle reference values from background particle concentrations using a statistical approach that takes into account the variability in background concentrations.

Table 5. Summary of assigned local particle reference values and calculation of excursions above such at the point of particle emission and within breathing zones

Tier Two assessment						Tier Three assessment	
PROCESS	Local Particle reference values a) PNC$_{20\text{-}1000nm}$ [p cm^{-3}] b) PNC$_{300\text{-}3000nm}$ [p cm^{-3}] c) PM$_{2.5}$ [µg m^{-3}]	Application of excursion criteria using measured particle concentrations relative to local particle reference values				Tier Three assessment conducted for the nanomaterial	Particle control values for Tier Three Assessment - using national exposure standards or limits, proposed exposure standards or limits, or Benchmark Exposure Levels (BELs)
		Is *source emission* > 3 times the particle reference value for more than 30 minutes in 8 hour day?	Is any single *source emission* peak value > 5 times the particle reference value?	Is *breathing zone* value > 3 times the particle reference value for more than 30 minutes in 8 hour day?	Is any *breathing zone* peak value > 5 times the particle reference value?		
1A	a) 5.2 x 10^3	no	No	No	no	SMPS data – no substantive difference in count media diameter during or between process operation at emission point	REL Ultrafine TiO$_2$ 300 µg m^{-3} (10-hour TWA)
	b) #	n/a	n/a	n/a	n/a		
	c) 6.5	no	yes = 50 µg m^{-3}	No	no		
1B	a) 1.2 x 10^4	no	yes = 1.6 x 10^5 p cm^{-3}	no	no	Electron microscopy and EDX of emission particles indicated morphology and chemical composition similar to raw nanomaterial.	REL Ultrafine TiO$_2$ 300 µg m^{-3} (10-hour TWA)
	b) #	n/a	n/a	n/a	n/a		
	c) 7.4	no	No	no	no		
2*	a) 6.6 x 10^3	no	yes = 6.0 x 10^4 p cm^{-3}	#	#	Electron microscopy and EDX of emission particles indicated morphology and chemical composition similar to raw nanomaterial	BEL Default insoluble: 300 µg m^{-3}
	b) #	n/a	n/a	n/a	n/a		
	c) 4.6	no	yes = 400 µg m^{-3}	#	#		
3^	a) 2.7 x 10^3	no	yes = 1.4 x 10^4 p cm^{-3}	no	no	SMPS data – no substantive difference in count media diameter during or between process operation at emission point	REL Ultrafine TiO$_2$ 300 µg m^{-3} (10-hour TWA)
	b) #	n/a	n/a	n/a	n/a		
	c) 10	no	yes = 70 µg m^{-3}	No	no		
4^{Δ}	a) 5.5 x 10^2	yes = 1.2 x 10^4 p cm^{-3}	yes = 1.5 x 10^5 p cm^{-3}	No	no	no data collected	BEL Default insoluble: 300 µg m^{-3}
	b) < 1	yes = 4.0 x 10^2 p cm^{-3}	yes = 8.0 x 10^2 p cm^{-3}	yes = 50 p cm^{-3}	yes = 100 p cm^{-3}		

Tier Two assessment						Tier Three assessment	
PROCESS	Local Particle reference values a) $PNC_{20\text{-}1000nm}$ [p cm^{-3}] b) $PNC_{300\text{-}3000nm}$ [p cm^{-3}] c) $PM_{2.5}$ [µg m^{-3}]	Application of excursion criteria using measured particle concentrations relative to local particle reference values				Tier Three assessment conducted for the nanomaterial	Particle control values for Tier Three Assessment - using national exposure standards or limits, proposed exposure standards or limits, or Benchmark Exposure Levels (BELs)
		Is *source emission* > 3 times the particle reference value for more than 30 minutes in 8 hour day?	Is any single *source emission* peak value > 5 times the particle reference value?	Is *breathing zone* value > 3 times the particle reference value for more than 30 minutes in 8 hour day?	Is any *breathing zone* peak value > 5 times the particle reference value?		
	c) 1	yes = 450 µg m^{-3}	yes = 16000 µg m^{-3}	no	yes = 170 µg m^{-3}		
6A	a) 4.0 x 10^3	No	yes = 5.7 x 10^4	no	no	no data collected	Proposed REL 1 µg m^{-3}
	b) 3	yes = 86 p cm^{-3}	yes = 550 p cm^{-3}	no	no		
	c) 7	yes = 420 µg m^{-3}	yes = 18000 µg m^{-3}	no	no		
6B	a) 3.1 x 10^3	No	yes = 2.1 x 10^5 p cm^{-3}	no	no	no data collected	Proposed REL 1 µg m^{-3}
	b) 3	No	No	no	no		
	c) 3	yes = 19 µg m^{-3}	yes = 550 µg m^{-3}	no	no		

- no values are able to be calculated because measurements in this particle size range were not conducted
n/a - not applicable because particle reference values were not calculated
* mean between process value is of 2A, 2B, 2C combined values, whilst peak values are highest for 2A, 2B, 2C
^ mean between value is of 3A to 3E combined values, whilst peak values are highest for 3A to 3E
Δ values reflect jet milling phase only, and do not include cleaning phase because cleaning phase did not emit particles above background values

9.5 Utilise a three-tiered particle evaluation process

202. The results of this measurement campaign support the use of a three-tiered measurement approach. Similar approaches have previously recommended by OECD WPMN [76], US NIOSH [51], IUTA, BAuA, BG RCI, VCI, IFA, TUD [77] and nanoGEM [105].

203. A tiered-approach requires criteria on which the decision is taken to enter the next tier, and these are described later in section 9.6. The tiered approach recommended in this report is focussed on informing decision-making about controls used. Therefore:

- The assessment results for each tier are used to assess controls effectiveness and exposure
- It may not necessary to utilize all three tiers. Tier One assessment alone, or Tier One plus Two assessments may be sufficient.

204. A three tiered assessment process is recommended in order to:

1. Identify particle emission points from the process of interest and sources of incidental particle emission to the work area
2. Estimate particle exposure of workers
3. Validate effectiveness of engineering controls such as forced dilution ventilation, extraction ventilation, and enclosures
4. Review control strategies

205. Thus, the assessment process will examine both task-based emissions and exposure levels. The importance of task-based analysis for emissions assessment was highlighted by Brouwer et al [98]. In relation to exposure assessment, the most critical dataset are the personal exposure data and these should always be measured. Simultaneous number and mass concentration measurements at emission point as well as at the perimeter of the process and LEV is often difficult to perform at the same time without interfering with the environment.

206. The three-tiered particle evaluation process proposed in this report is one approach that can be utilized. Other approaches, e.g other three-tiered approaches [51,76,77,105] can also be used.

9.5.1 Tier One - comprehensive survey of the process environment

207. The Tier One step involves a standard industrial hygiene survey of the process area and is predominantly focussed upon the gathering of qualitative information. Quantitative data is gathered only to the extent of direct instantaneous particle number and mass measurements to identify likely points of particle emission relative to the background.

208. If actual or potential nanomaterial emissions from the process are identified then the recommended actions are either:

- Improve controls if evidence indicates this is needed and/or
- Undertake Tier Two assessment

9.5.1.1 Qualitative survey

209. A survey of the process, from its beginning to end, should be conducted and involves observations and interviewing of appropriate process personnel. Information gathered includes:

- Materials used – type, quantity, form
- Process operation
- Number and roles of workers associated with process
- Work patterns of workers including shift duration, work tasks, work location
- Maintenance schedule and process
- Likely points of particle emission from the process
- Likely sources of incidental particle emission
- Current particle emission and exposure controls used such as enclosures, ventilation, and personal protective equipment
- Ventilation assessment including measurement of flow rates, air velocities and pressure

9.5.1.2 Quantitative survey

210. Portable Instrumentation should be used to gather instantaneous temporal and spatial peak particle number and mass concentration data at likely emission sources (both the process being investigated and incidental sources of particles), in the breathing zone of workers, and at background locations.

211. The P-Trak, OPC, and DustTrak should be placed onto a tray or similar holder so as to 1) co-locate their aerosol inlets, and 2) to facilitate ease of movement of the instruments when required. Figure 5 (section 9.8) contains a picture of such set-up of instruments.

212. The time series data described in Appendix E for Process 4, and Appendix G for Process 6, illustrate how to conduct and document the quantitative survey. Figures 24, 25, 41, and 42 provide examples of time series of particle number and mass concentration obtained at the emission source, in breathing zone of worker, and at background locations. Figures 41 and 42 depict similar information plus information on assessment of the capacity of the process enclosure and extraction ventilation to contain particle emission. Note the specific times and locations of the measurements have been correlated to the measurement data within these figures.

213. The information gained from the Tier One assessment is used to inform Tier Two.

9.5.2 Tier Two – comprehensive characterisation of real-time particle number and mass concentration

214. Tier Two assessment must be relatively easy to implement and also be able to reliably identify sources of particle emission. The measurement method will vary according to whether the aim is to characterise emission sources, to estimate exposure, or validate particle emission controls. Tier Two measurement should utilise direct reading instruments for particle number and mass concentration, and the calculation of *local particle reference values*. In order for Tier Two assessment to be relatively easy to implement, the more complex sampling and analytical methods have been assigned to Tier Three.

215. The Tier Two assessment undertaken in this work was undertaken successfully with a CPC, OPC and photometer. However, other widely used handheld instruments like the DISCmini or NanoTracer can also be used, but these should be used concurrently with the OPC and photometer.

9.5.2.1 Characterisation of particle source emission

216. Where the goal of particle measurement is to characterise particle emission from the process of interest, plus the particle background, instruments should be positioned as close as possible to the particle

emission point and also at locations representative of spatial particle variation. Instrumentation should be used over periods of time that capture typical variation in particle concentrations, with measurement repeated over multiple days, to fully characterise variations in particle number and mass concentration over time.

217. Measurements should be commenced prior to start-up of the process of interest so as to characterise the background. Measurements should continue following shut-down of the process, to characterise any residual impact on the background following shut-down of the process of interest.

218. In addition to measurements at the emissions sources, ideally, a second suit of instruments of the same make and model should be located at a distance from the emission sources so as to characterise any impact on the general workplace atmosphere and therefore potential exposure of workers. Figure 15 illustrates the time series data obtained from using two CPC's.

219. Further information on the utility of multiple photometers and CPC's to obtain spatial data, at laser printer emission points and at the air intake of office buildings, is also described in two publications authored by McGarry et al. [58, 84].

Differentiating from particle sources arising from equipment operation

220. There are two types of nanomaterials that workers can be exposed to as a result of processes involving manufactured nanomaterials; (a) manufactured nanomaterials emitted from the process and (b) incidental nanoparticles, e.g. combustion particles, resulting from operation of the process equipment. Both of these sources may result in emission of hazardous particles, so it is important to know about both sources of emissions.

221. To characterise the manufactured nanomaterial emissions, it is necessary to differentiate between these and incidental nanoparticles. This can be achieved by running process equipment in the absence of manufactured nanomaterials and seeing if this impacts on background particle measurements.

9.5.2.2 Estimation of exposure

222. Exposure monitoring must occur within the breathing zone of the person. The breathing zone is generally defined as the area near the worker's nose/mouth [94]. Ideally, personal exposure monitoring should be conducted using a portable monitoring device with the sampling orifice located within the breathing zone of the worker.

223. Particle number and mass concentration within the breathing zone of workers can be estimated during operation of the process and compared relative to the background using a CPC, OPC, and photometer. Such results should be reported as *estimated* exposure and not as actual exposure unless; 1) the instrument has been calibrated using an aerosol that reflects the likely density, morphology, refractive index, and solubility of the nanomaterial aerosol, and 2) measurements have been conducted within the breathing zone for a continuous period representative of usual tasks, work practices, and movement around the work area.

224. Particle exposure concentration can be estimated as follows. The P-Trak, OPC, and DustTrak should be placed onto a tray or similar so as to 1) co-locate their aerosol inlets, and 2) to facilitate ease of movement of the instruments when required. Figure 5 (section 9.8) contains a picture of such a set-up of instruments.

225. Peak particle number and mass concentration exposure can be reliably obtained using instruments such as a P-Trak, OPC, and DustTrak. These peak values are compared to the mean particle number and mass concentration calculated from measurements conducted of the background when the process of interest was not in operation. Peak particle number and mass concentration data obtained from the breathing zone of workers is summarised in Table 6.

Table 6. Peak particle number and mass concentrations in process operator breathing zone during process operation compared to the LBPC

Process	PNC – 20 to 1000 [particles cm^{-3}] **CPC P-Trak**		PNC – 300 to 3000nm [particles cm^{-3}] **OPC**		PM$_{2.5}$ [µg m^{-3}] **DustTrak**	
	Peak during	LBPC	Peak during	LBPC	Peak during	LBPC
1A	5.4 x 10^{3}	5.2 x 10^{3}	#	#	8.9	7.6
1B	4.5 x 10^{4}	1.2 x 10^{4}	#	#	8.4	7.6
2	#	#	#	#	#	#
3*	5.0 x 10^{3}	2.7 x 10^{3}	#	#	14	10
4[Δ]	5.0 x10^{2}	5.0 x 10^{2}	100	< 1	170	1
5A & 5B	#	#	#	#	#	#
6A	4.5 x 10^{3}	4.0 x 10^{3}	4	3	7	7
6B	4.0 x 10^{3}	3.1 x 10^{3}	5	3	3	3

not performed

^ “value listed for Process 3 is mean of 3A to 3E, whilst peak values are highest value recorded for each of 3A to 3E

Δ values reflect jet milling phase only, and do not include cleaning phase

local background particle concentration (LBPC)

9.5.2.3 Validation of effectiveness of particle emission controls

226. The goal of this measurement is to validate if engineering controls such as enclosure and extraction ventilation are allowing leakage of particles to the general work area. A portable CPC, OPC, and photometer can be used to validate the effectiveness of particle emission controls as evidenced below. In all cases, the background particle concentration must first be fully characterised during the period when the process is not operating so as to identify particle concentration excursion significantly greater that normal fluctuations in background particle concentrations.

227. Figures 15, 24, 25, 41 and 42 contain information obtained from using the instruments to assess the effectiveness of enclosures, mechanical dilution ventilation, and extraction ventilation in containing and entraining particles.

Local extraction ventilation

228. Figure 15 contains data from a CPC located at a particle emission point over several hours. When the extraction ventilation was momentarily turned off, the CPC was clearly able to characterise a significant increase in PNC, indicating the extraction ventilation was effective in capturing emitted particles.

Mechanical dilution ventilation

229. A P-Trak, OPC, and DustTrak were used to evaluate the effect of mechanical dilution ventilation to disperse particles from the breathing zone of the operator of the jet-milling machine used for Process 4. Figures 24 and 25 provide the time-series plots of the PNC and $PM_{2.5}$ concentration. Comparison of the PNC at locations B and D (both within 0.2m of particle emission points of the jet milling machine) to location C (the breathing zone) of the machine operator, shows a spatial reduction in PNC exposure of up to two orders of magnitude for sub-300 nm particles, and approximately an eight-fold reduction in super-300 nm particle exposure. The spatial reduction in PNC between the particle source and the operator breathing zone reflects the configuration of the mechanical dilution ventilation to the work area as described in Appendix E.2.2.

Enclosures

230. A P-Trak, OPC, and DustTrak were used to assess the ability of chambers enclosing two Chemical Vapour Deposition (CVD) processes, and the associated fume extraction cabinet to prevent particle leakage into the laboratory atmosphere. The time-series plots for particle number and mass concentration from these measurements are contained in Figures 41 and 42 (Appendix G.2.1). It is clear from these figures that both sub and supermicrometre particles are generated in significant concentrations within the CVD chambers (orders of magnitude higher than the laboratory work area), and that the three instruments were able to characterise these particles. In addition, the three instruments were able to validate that both process enclosures and the fume extraction cabinet prevented measurable concentrations of particles escaping to the laboratory work area.

Historic performance levels of engineering control options for airborne dusts

231. Historic performance levels of engineering control options for airborne dusts in the pharmaceutical industry were summarised by Schulte et al [94], and are shown in Table 7. The research data indicate that performance levels shown in Table 7 can be achieved using engineering controls for processes involving nanomaterials and that it is feasible in practice to achieve acceptable airborne concentrations.

Table 7. Historic performance levels of engineering control options for airborne dusts in the pharmaceutical industry [94]

Control technology	Historic performance (mg m^{-3})
Open handling with engineered local exhaust ventilation (LEV)	<1
Directional laminar flow with LEV and vacuum conveyance	0.01–1
Closed systems	0.001-0.01
High-containment	<0.001

9.5.2.4 Summarising overall findings of Tier Two assessment in this study

232. From Tables 5 and 6, a comparison of short term and peak emissions and breathing zone concentrations with the corresponding *local particle reference values* is discussed below.

- Process 1A. Peak emissions for $PM_{2.5}$ exceed the excursion criteria, but the peak in the breathing zone is not significantly higher than background (LBPC). No further assessment or controls is required.
- Process 1B. Peak emissions for $PNC_{20\text{-}1000nm}$ exceed the excursion criteria. The peak in the breathing zone is 4xLBPC. This does not exceed the excursion criteria (5xLBPC), but is sufficiently high that further assessment may be considered.
- Process 2. Peak emissions for both $PM_{2.5}$ and $PNC_{20\text{-}1000nm}$ exceed the excursion criteria. The evidence of Figure 15 and of measurements taken 7m away from source is that emissions are contained using LEV. However, breathing zone measurements were not taken and thus, further assessment may be considered.
- Process 3. Peak emissions for both $PM_{2.5}$ and $PNC_{20\text{-}1000nm}$ exceed the excursion criteria but the peaks in the breathing zone are not significantly higher than LBPC. No further assessment or controls is required.
- Process 4 is a strong emitter and $PM_{2.5}$, $PNC_{20\text{-}1000nm}$ and $PNC_{300\text{-}3000nm}$ exceed the excursion criteria, $PM_{2.5}$, and $PNC_{300\text{-}3000nm}$ significantly exceed the excursion criteria in the breathing zone, which suggests that this process requires a Tier Three assessment and further controls.
- Process 6A is a strong emitter of CNTs and $PM_{2.5}$, $PNC_{20\text{-}1000nm}$ and $PNC_{300\text{-}3000nm}$ exceed the excursion criteria. However, process enclosure is shown to be highly effective as peaks in the breathing zone are not significantly higher than LBPC. Given the potential hazards associated with CNTs and hence potential risk associated with low airborne concentrations, further assessment may be undertaken by sampling in the breathing zone to further examine potential exposures.
- Process 6B is also an emitter of CNTs and $PM_{2.5}$ and $PNC_{20\text{-}1000nm}$ exceed the excursion criteria. However, process enclosure is again shown to be highly effective as peaks in the breathing zone are not significantly higher than LBPC. As for Process 6A, further assessment may be undertaken by sampling in the breathing zone to further examine potential exposures.

9.5.3 Tier Three - utilise sampling methods for off-line analysis of particle morphology, chemical composition, and mass or fibre concentration and compare with measurement by real-time instruments

When to use a Tier Three assessment

233. The *excursion guidance critieria* should be utilised in deciding if emission or likely exposure is significant. Therefore, where analysis of the results of the Tier Two assessment indicate that, for example:

- short term emissions or exposures exceed three times the *local particle reference value* for more than a total of 30 minutes per eight-hour working day, or
- if a single short term value for emission or exposure exceeds five times the *local particle reference value,*

either:

a. review and implement particle control strategies, or
b. conduct a Tier Three assessment with more comprehensive particle sampling in order to inform the review of controls.

234. Three different *local particle reference values* i.e. for $PNC_{20\text{-}1000nm}$, $PNC_{300\text{-}3000nm}$ and $PM_{2.5}$ or PM_4 may be used. A decision on whether to consider undertaking a Tier Three assessment should be based on examining all Tier Two evidence.

- Exceeding the excursion criteria for any of these *local particle reference values* for breathing zone concentration is sufficient to consider undertaking further assessment.
- Exceeding the excursion criteria for any of these *local particle reference values* for source emissions may be sufficient to consider undertaking further assessment, depending on; (a) the corresponding breathing zone concentration and (b) the toxicity of the nanoparticle, with higher (or uncertain) toxicity favouring further assessment.

235. Also, given that a strategy of reducing exposures as far as reasonably practicable by containing emissions at source is generally recommended, further assessment may help achieve this goal.

236. Use of a Tier Three assessment is also recommended when examining processes that can potentially emit high toxicity chemicals. A specific example is processes that can emit fibres or structures of fibres of pathogenic fibre dimensions, e.g. according to the WHO definition. In the case of low emitting processes, on-line measurement techniques may not detect significant increases in airborne concentrations, but these emissions can be detected by sampling techniques.

237. Depending on manufacturer and/or production process, different fibre structures and morphologies may be produced, e.g. single fibres, open clusters or fibre agglomerates. The different morphological relevant fibres may cause different effects in humans and sampling and analysis, with methods capable of capturing single fibres.

About Tier Three assessment

238. A Tier Three assessment involves the repeat of the Tier Two measurements but this time with simultaneous collection of particles for off-line analysis of mass or fibre concentration, particle morphology and chemical composition. The results of the off-line analysis can also be compared to real-time measurement results.

239. Aerosols can be collected onto a filter membrane connected to a sampling pump or TEM grid within an electrostatic precipitator, with analysis using SEM/XRD and TEM/XRD respectively. Sections 9.5.3.1 and 9.5.3.3 (for carbon nanotubes) include a description of successful use of the above particle sampling and analysis methods.

240. Chemical analysis can be necessary for proper quantification of the exposure levels to specific nanomaterials. Such methods should be specifically selected to quantify the compound(s) known to be in the exposure. Certain online methods may be appropriate for direct measurement in the airborne state, e.g. for carbonaceous matter.

241. Measurement results are then compared with particle control values to determine whether controls are sufficiently effective or need to be improved. Wherever possible, the Tier Three assessment should involve use of national or international standards in relation to equipment and methodology that are known to be able to measure and quantify the exposure.

242. Where a Workplace Exposure Standard, Recommended Exposure Limit, proposed workplace exposure limit or benchmark exposure level have been established for the nanomaterial, the sampling and analytical method recommended for that standard or limit should be utilised as part of the Tier Three assessment.

Differentiation between aggregates, agglomerates and primary particles

243. On-line measurement techniques do not directly differentiate between agglomerates, aggregates and primary particles. Sampling and analysis by TEM can determine whether particles are; (a) primary particles or (b) agglomerates/aggregates, but does not differentiate between agglomerates and aggregates. Surface area analysis, e.g. by BET, can be used to help differentiate between agglomerates and aggregates, Agglomerates typically have specific surface areas (i.e, area/unit mass) similar to primary particles, whereas aggregates have lower specific surface areas.

Using additional more complex real-time instrumentation

244. If further information on size distribution is needed, a number of other measuring instruments may potentially be used in a Tier Three assessment. SMPS, NanoSpectrometer and ELPI can be used for particle size distributions and for size-resolved aggregated sampling other devices are on the market, e.g. NanoID and Wide Range Aerosol Sampler. If information is needed on the size distribution of particles above 300nm in size (e.g. agglomerates), then an Aerodynamic Particle Sizer (APS, sizes over the range 500 – 20,000nm) or Optical Particle Sizer (OPS, range 300-10,000nm) can be used. The newly developed personal nanoparticle samplers, with capability of measuring respirable particulate mass e.g. PENS [99] and Personal Nanoparticle Respiratory Deposition (NRD) Sampler [49] can extend the suite of devices for Tier Three assessment.

245. An SMPS with a lower size measurement point within the ultrafine particle size range and as small as possible could be utilised for the Tier Three assessment. The count median diameter (CMD) of the aerosol particles generated during operation of the process relative to the background should be assessed. Significant differences between the count median diameter during the process compared to the local background particle concentration may be due to the nanotechnology process emitting particles, but can also be caused by a change in background particles during operations. These particles may be within the ultrafine size fraction but could also be of larger particle sizes due to agglomeration of particles, where an SMPS could be used in combination with APS or OPS. While suitable for Tier Three assessment, SMPS is not recommended for Tier Two assessment as sufficient information can be obtained from the CPC and the SMPS is more operationally complex. Similarly, the OPC and photometer provide suffuicient information about larger particles for Tier Two assessment.

246. Number concentration-based Benchmark Exposure Levels have been proposed for use with nanomaterials (see Recommendation 1). These are defined for particles in the range 1-100nm. Because of this size range, use of instruments such as SMPS and ELPI is required for comparison with these particle control values.

Tier three assessment in this study

247. The results of the off-line analysis of particles in this study provided greater confidence that the elevated particle concentration identified by the real-time measurement were associated with emissions from the processes being investigated. These results are described below.

9.5.3.1 Collection of particles at emission point

248. As part of the assessment of Process 2 (see Appendix C), a P-Trak and DustTrak were used to characterise the particle number and $PM_{2.5}$ concentration at the point of particle emission, both during and between operation of the process. It is clear from the data presented in Appendix B and Appendix C that filter membranes within open-faced cassettes attached to sampling pumps, and TEM grids utilised within electrostatic precipitators can entrain airborne manufactured nanomaterials originating from process emission points. Subsequent TEM/SEM and EDX analysis was able to clearly distinguish particles with morphology and chemistry consistent with the nanomaterial associated with the process.

249. For example in Process 1A, the results of real-time particle concentration measurement revealed the particle emission to be weak and analysis of the emission aerosol by SEM and EDX showed airborne particles to have a morphology and chemical composition broadly consistent with that of the raw material. Therefore using the data obtained from the P-Trak, DustTrak, particle collection, and electron microscope analyses it can be concluded that both sub and supermicrometre particles, albeit in insignificant concentrations, are emitted from this process and that the measurement methods are valid for characterising particles.

250. As part of the assessment of Process 1B (see Appendix B), the aerosol at the point of particle emission was collected onto a filter membrane connected to a sampling pump, and analysed using SEM and XRD. The filters were located ~ 20 cm from the point of powder crushing. The SEM and XRD analysis indicated a particle morphology and chemical signature consistent with the predominantly TiO_2 component of the raw material.

251. Process 2 is an example of where real-time measurement results indicate a process to be a likely emitter of significant peak concentrations of particles. Both SEM-EDX and TEM-EDX analysis of aerosol particles clearly verified the process was an emitter of particles to the work area atmosphere.

252. In addition, NIOSH Method 5040 for the analysis of elemental carbon concentration was successfully utilised to identify significant concentrations of carbonaceous particles arising from a CNT process (Process 5A) at the point of emission.

9.5.3.2 Collection of particles in the breathing zone of workers

253. The decision to assess exposure by collecting particles within the breathing zone of workers for subsequent analysis should be informed by the results of the Tier Two assessment.

254. As outlined in section 6.1 exposure standards/proposed exposure limits, all mass based, are in place for six nanomaterials. To utilise these exposure standards/proposed exposure limits, sampling and analytical methods are recommended for each nanomaterial. For example:

- in utilising the NIOSH proposed REL of 0.001 mg m^{-3}, Carbon Nanotube aerosol should be sampled onto quartz fibre filters using sampling pumps operating within a defined flow rate. The organic, elemental, and total carbon mass of each filter is then be analysed using Evolved Gas Analysis by a thermal-optical analyser in accordance with the NIOSH Method 5040.
- In utilising the default insoluble nanomaterial BEL of 0.3 mg m^{-3}, the aerosol can be sampled and analysed in accordance with Australian Standard 2985 – 2009: *Workplace atmospheres – Method for sampling and gravimetric determination of respirable dust*.
- In utilising the NIOSH REL for ultrafine TiO_2 of 0.3 mg m^{-3}(10-hour TWA), an initial exposure assessment should include the simultaneous collection of respirable dust samples with one sample using a hydrophobic filter (as described in NIOSH Method 0600) and the other sample using a mixed cellulose ester filter (MCEF). If the respirable exposure concentration for TiO_2 (as determined by NIOSH Method 0600) is less than 0.3 mg m^{-3}, then no further action is required. If the exposure concentration exceeds 0.3 mg m^{-3}, then additional characterization of the sample is needed to determine the percentage of ultrafine TiO_2 (respirable particles with primary particle diameter < 100nm). To assist in this assessment, the duplicate respirable sample collected on a MCEF should be evaluated using transmission electron microscopy (TEM) to size particles and determine the percentage of ultrafine TiO_2.

255. Photometers should not be used as a substitute for the sampling and analytical method recommended for an exposure standard, REL, or proposed exposure limit. This is because the sampling and analytical method of operation of photometers is fundamentally different to that of the off-line methods. Photometers do not provide true gravimetric mass concentration data, but rather provide an estimate based upon the measured response to light scattering of particles. The light scattering detected by the instrument is a function of particle size, shape, and refractive index which may differ significantly amongst different sources of aerosols.

256. In recent work, Zhu et al (2011) used a DustTrak and gravimetric samplers to measure average in-cabin $PM_{2.5}$ concentrations for drivers [100]. Results indicated that the association between average real-time and gravimetric $PM_{2.5}$ measurements on moving trucks was fairly consistent (Spearman rank correlation of 0.63), with DustTrak measurements exceeding gravimetric measurements by approximately a factor of 2. This ratio differed significantly only between the industrial Midwest cities and the other three sampled cities scattered in the South and West of the United States.

257. Where exposure standards/proposed exposure limits have not been established, samples collected in the breathing zone can also be analysed using electron microscopy so as to assess if the morphology of the aerosol particles is consistent with that of the nanomaterial.

9.5.3.3 Case study of tier three assessment

258. As part of the assessment of Processes 5A and 5B (discussed in detail in Appendix F), a P-Trak, OPC, and DustTrak were used to characterise particle number and mass concentration arising from the generation of single and multi-walled carbon nanotube (CNT) aerosols. The three instruments were used for area monitoring with their sampling orifices located ~ 6 cm from the CNT sources. The aerosol at the point of particle emission was also simultaneously collected onto (1) MCE, quartz, and PTFE filter membranes connected to sampling pumps, and analysed using SEM and XRD, (2) a TEM grid within an electrostatic precipitator, and analysed using TEM and XRD, and (3) a quartz filter connect to a sampling pump and analysed for elemental carbon mass using Evovled Gas Analysis by thermal-optical analyser.

259. Figures 26, 27, 28, and 29 provide the time-series plots of this data. It is clear from these figures that the P-Trak and OPC, when paired as a sampling set, were able to provide the following data on particle characteristics – (1) significant peaks in PNC in the particle bin sizes of between 300 and 3000nm were associated with both the single- and multi-walled CNT aerosols, with stronger peaks for the single walled CNT. It is also clear from these figures that the $PM_{2.5}$ concentration response of the DustTrak mirrored the OPC response in the bin sizes 300 to 3000nm. The Pearson’s correlation r-values, calculated in section 8, confirmed an overall positive correlation for these two instrument particle responses.

260. Analysis of the filter membranes and TEM grid revealed the aerosol particles to have a morphology and chemical composition consistent with CNTs. Therefore using the data obtained from the P-Trak, DustTrak, particle collection, and electron microscope analyses it can be concluded that the aerosol emitted from this process was composed of both sub and supermicrometre CNT particles.

261. This case study illustrates how emissions that potentially contain fibres or fibre-like structures of pathogenic dimensions can be assessed and characterised.

9.5.4 Summary of three-tiered approaches

262. A summary of various three-tiered approaches is presented in Table 8 below. Overall, the approaches are all similar, but there are some differences the detail e.g.:

- Estimation of mass concentration by use of photometer is recommended in the current study.

  - In Tier 1 in the current study, measurements are used to support the industrial hygiene survey. Other approaches do not use measurements in Tier 1.

  - The excursion criteria used in Tier 2 to determine whether increase over background particle number concentration is significant are different in each approach. The Global Exposure Measurement Harmonisation Workgroup is planning to examine this issue.

- One of the projects proposed by CEN TC137 Working Group 3 in response to EU Mandate M/461 on Standardization of Nanotechnologies is on developing guidance to assess inhalation exposure to nanomaterials. This project will focus on proposed tiered-approaches and will explicitly address the decision criteria proposed to proceed to next tier or to refrain from further actions. Statistical soundness, robustness and accuracy will be investigated. The project will involve the Global Exposure Measurement Harmonization Workgroup to get feedback.

- The Business and Industry Advisory Committee (BIAC) has proposed an OECD WPMN project on a harmonized tiered approach to measure and assess the airborne exposure to engineered nano-objects (up to 100nm in size) and their agglomerates and aggregates (above 100nm in size) in workplaces. This project was approved at the WPMN 11 meeting in February 2013. The project will progress the development of pragmatic in-field methodology, including concepts and strategies for occupational exposure measurement and assessment, aimed at a harmonized approach towards exposure characterization. The pragmatic approach will be designed to ensure both adequate and efficient risk management for workforces across the widest variety of occupational environments and situations to enable effective risk management in small, medium and large enterprises

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Table 8. Summary of three-tiered approaches

	This study [58,84,101]	**NEAT/OECD WPMN [51,76], JNIOSH [108]**	**IUTA, BAuA, BG RCI, VCI, IFA, TUD [77]**	**nanoGEM [105]**
Tier 1 Method	Standard industrial hygiene survey of the process area. Information is gathered on: ▪ Materials ▪ Process & maintenance operation ▪ Workers tasks ▪ Likely sources of incidental particle emission ▪ Likely points of particle emission from the process ▪ Particle emission and exposure controls ▪ Ventilation Quantitative data is instantaneous particle number and mass measurements to identify likely points of particle emission.	The overall purpose of this step is to develop a list of target areas and tasks that will be evaluated with the particle analyzers. The initial assessment involves • Process review • Literature review to gain an understanding of the manufactured nanomaterials being produced or used, • Observational walkthrough survey • Examination of operations and controls	At Tier 1 a decision has to be made, whether or not a release of nanoscale aerosols from ENMs into workplace air can be reasonably excluded. Information gathering conducted according to established best practices in industrial hygiene.	The task in Tier 1 is to clarify, e.g. through on-site inspection, whether nanomaterials are used in the respective workplace and if they can be released from the corresponding processes.
Tier 1 Instruments	CPC, OPC, Photometer			
Decision based on Tier 1	If actual or potential nanomaterial emissions from the process are identified then the recommended actions are either: • Improve controls if evidence indicates this is needed and/or • Undertake Tier Two assessment	Determines where emissions may occur – identifies targets for Tier 2 assessments.	If release of nanoscale aerosols from ENMs into workplace cannot be reasonably excluded, undertake Tier 2 assessment.	If a release cannot be excluded, the potential exposure has to be determined in Tier 2.
Tier 2 Method	Comprehensive characterisation of real-time particle number and mass concentration. Must be relatively easy to implement and also be able to reliably identify sources of particle emission. Measurement method varies according to	Particle number concentration sampling to identify processes, locations, and personnel for filter-based air sampling • Background measurements	Basic exposure assessment using a limited set of easy-to-use equipment. Assess measurement results against substance-specific, binding, health-based OELs for ENMs.	The simplified exposure measurements conducted using particle size integrating, easy-to-use devices, measuring e.g. the total particle number concentration. Options:

	whether the aim is to characterise emission sources, estimate exposure, or validate particle emission controls. Involves use of direct reading instruments for particle number and mass concentration. Concentrations are compared with background concentrations (local particle reference values) using excursion criteria to determine significance.	• Area sampling Measurements of airborne particle concentrations at locations near the suspected or likely emission source before, during, and after each task.	If OELs not available, determine whether • the interference value (lowest value, which can be measured with sufficient reliability) is exceeded, • a significant increase over total aerosol background concentration is detected	Screening Temporary monitoring Permanent monitoring Measurements compared with background concentrations.
Tier 2 Instruments	CPC, OPC, Photometer	CPC, OPC used simultaneously alongside each other	Direct Reading, Counting Devices: CPC, Nanoparticle monitors using electrical detection principle	Typical instruments are handheld condensation particle counters (CPCs) and diffusion charger based devices (miniDiSC, nanoTracer, Aerotrak 9000).
Decision based on Tier 2	Where results of the Tier Two assessment indicate that: • short term emissions or exposures exceed three times the particle control value for more than a total of 30 minutes per eight-hour working day, or • if a single short term value for emission or exposure exceeds five times the particle control value, either: a. review and implement particle control strategies, or b. conduct a tier three assessment in order to inform the review of controls.	Confirms where manufactured nanomaterial emissions occur. Are particle number concentrations with production system *On* 10% higher than those with the system *Off*? If no, controls appear to be adequate, no further testing. If yes, undertake Tier 3 assessment.	If the interference value is exceeded and a significant increase over total aerosol background concentration is detected, then the potential exposure has to be investigated according to Tier 3 (Expert Exposure Assessment).	If tier 2 measurements reveal a concentration level which is significantly increased over the background, a potential exposure exists and has to be assessed in Tier 3. An emission/exposure concentration is significantly above background if C(net-bg) > 3 x s_{DBI} . s_{DBI} is the standard deviation of background concentration C(net-bg) is the emission/exposure concentration – background.
Tier 3 Method	Repeat of the Tier Two measurements with simultaneous collection of particles for off-line analysis of mass or fibre concentration, particle morphology and chemical composition. If further information on size distribution is	Conduct Filter-based Area and Personal Air Sampling. Collect co-located open-face air filter samples for TEM and analytical analysis at locations of possible emissions identified by	Expert exposure assessment applying latest knowledge and technology to confirm and expand on findings from Tier 1 and Tier 2 and determine if there is evidence is available for the chemical identity of the	Tier 3 measurements are intended to provide clear evidence for the presence or absence of the nanomaterials in the breathing air in a workplace. Measurements require an extended set of measurement and

	needed, a number of other measuring instruments may potentially be used in a Tier 3 assessment. Concentrations are compared with particle control values to determine significance.	CPC and OPC. Collect additional set of co-located open face air filter samples for background, away from the process. Optional: Surface sampling. Air samples include one sample analyzed for elemental mass and one sample analyzed by electron microscopy. JNIOSH [108] measure gravimetric respirable mass concentration for decision making if further measurement is necessary.	filter samples indicating that the source is the ENM. Use of direct reading instruments & in parallel sampling systems.	sampling equipment for evaluating a possible exposure to manufactured nanomaterials in workplaces. Measurements always include the determination of the particle background in the workplace, either through simultaneous measurement at a representative background location or through consecutive measurements at the respective workplace prior to and after the process under investigation. In the latter case, the background can also be determined with the identical process ongoing but prior to and after use of the nanomaterial.
Tier 3 Instruments	CPC, OPC, photometer. Aerosols collected onto a filter membrane connected to a sampling pump or TEM grid within an electrostatic precipitator. Subsequent analysis by SEM/XRD or TEM/XRD. If further information on size distribution is needed – SMPS or ELPI.	Filter-based air sampling cassette. In the event that measurements made by the OPC indicate a large fraction (over 50%) of particles exceeding 1000 nm in size, the use of a personal cascade impactor or respirable cyclone sampler in tandem with a filter-based air sampling cassette may be required for both the elemental mass and TEM/SEM analysis to eliminate large particles, that may interfere with analysis and be of limited interest. SEM, TEM with EDX. NIOSH Method 5040 for elemental carbon. Surface wipe samples (if needed).	Equipment may include: Direct Reading, Counting Devices: CPC, SMPS, FMPS, NSAM, Aerosol Spectrometer Electrostatic and filtration sampler using grids for electron microscopy. Filtration sampler using gold coated membrane filters. Filter samples can be analyzed by ICP-AES, SEM or TEM.	Typically used direct-reading measurement instruments include Scanning or Sequential Mobility Particle Sizers (SMPS), CPC, NSAM) These measurements are accompanied by particle sampling systems, collecting airborne particles for consecutive analysis by SEM, TEM, ICP-AES or TXRF.

Decision based on Tier 3	Measurement results are compared with particle control values to determine whether controls are sufficiently effective or need to be improved.	Quantified emissions measurements to inform decision making on controls. JNIOSH [108] measure gravimetric respirable mass concentration and compare with probable OELs, such as the values recommended by the AIST [80].	Take additional risk management measures to mitigate exposures accordingly.	If particle release is determined definitively in Tier 3, measures need to be taken for exposure mitigation and the potential exposure needs to be re-assessed according to Tier 2.

9.6 Calculate impact of instrument accuracy on measurement results

263. Table 3 contains a list of the manufacturer specified instrument particle concentration accuracy data. It is important to apply this accuracy data to each peak, average, or media field data value so as to obtain confidence intervals around each value. For example, the P-Trak data from Processes 5A and 5B was inconclusive for the following reason. The P-Trak recorded increases in PNC on average of 500 and 200 p cm^{-3} at each aliquot of SWCNT and MWCNT respectively. Because such increases were similar to normal fluctuation in background and smaller than the manufacturer stated accuracy of the instrument (< ±20% of the background), it could not be concluded with confidence that these increases in particle concentration were associated with the process.

264. As reported previously in section 9.2 in relation to use of the NSAM, the accuracy of the NSAM is stated to be only in the range of aerosol particles of size range 20 to 400 nm. Even a small number of particles > 400 nm can have a significant contribution to total surface area causing significant errors in the lung deposited surface area estimate of the device [19, 44].

9.7 Calibrate equipment

265. The fundamental point of the ratio of particle emission to background being the relevant factor for the excursion model has direct relevance to calibration of the real-time measurement equipment.

266. The CPC, OPC, and photometer should be calibrated and adjusted to measurement standards yearly. Prior to and following field measurements all equipment should be field calibrated by being co-located and operated simultaneously to characterise an aerosol source for a time period of at least 8 hours. For example, in the absence of a purposely generated aerosol, the instrumentation can be subjected to the outside ambient environment.

267. For each instrument being used to gather particle data, a second instrument of the same make and model should be co-located during the field calibration process. This allows the ratio of these two instruments to be calculated. Therefore, regardless of the absolute particle values of the ambient environment pre and post field measurement, the ratio between the two instruments should be within the manufacturer stated accuracy range for that instrument. If the ratio pre and post is significantly different the field values may need to be discarded and repeated.

268. Knowledge of the typical values of particle concentrations of the ambient environment used for field calibration can also be used to judge if the instrumentation is operating correctly. This then requires records of the particle characteristics of this ambient aerosol to be maintained. Significant variations in particle metrics compared to what is expected for any given time of the day or weather condition should result in the accuracy of the instrument being questioned.

9.8 Avoid the use of sample tubing or minimise the amount used

269. If a number of instruments are used, all instruments should sample from a common sampling point. A relatively large number of instruments will require the aerosol inlets of each instrument to be joined to a common sampling point by sampling tubing. The use of sample tubing introduces the possibility of particle loss to the tubing, with theoretical increased loss directly relative to the tubing length. According to Timko et al. [92] the most prevalent mechanisms for particle loss include diffusional loss, inertial loss, and electrostatic loss. Jankovic et al., [93] investigated sample loss from rigid graphitic and flexible Tygon tubing attached to SMPS and compared mean particle concentration and size paremeters from samples collected with and without tubing. It was concluded that number concentration decreased and mean particle size increased for both tube types at lengths of approximately 0.7m.

270. A range of formulas are available for calculating particle loss in sample tubing. Particle loss would be especially relevant where particle emissions were at low concentration and within the manufacturer stated accuracy of the instruments. Figure 4 contains a picture of a complex array of measurement instrumentation, including relatively long lengths of sample tubing joined to common sampling point by way of manifold. Figure 5 contrasts this with minimalist approach that does not require use of sample tubing.

Figure 4. Complex instrument method

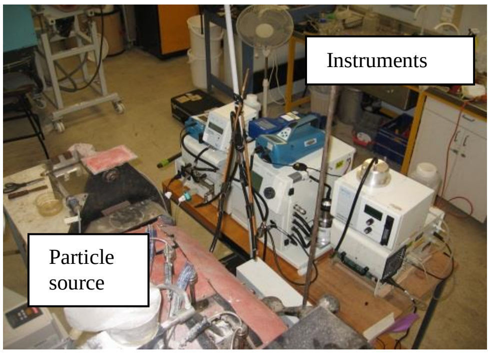
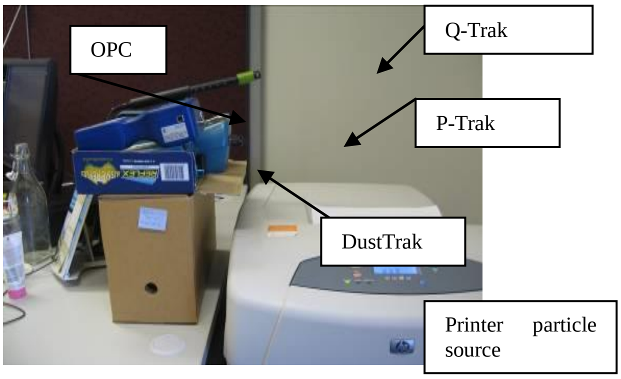


Figure 5. Minimalist instrument method



9.9 Utilise same equipment for on-going measurement of same process

271. Figures 13 and 16 provide real-time data for co-located CPC's of different make and model. As expected, the PNC results from co-located water and alcohol based CPC differed significantly for at least two reasons; (1) the minimum and maximum particle measurement size ranges differ between different instruments, and (2) particles may exhibit significant differences in solubility between water and alcohol. Therefore, when collecting sequential temporal and spatial data the same model of CPC should be used.

9.10 Record and report the relative humidity and temperature of the work area

272. Increases in relative humidity can cause an increase in particle size, associated with condensational growth of hygroscopic components of the aerosol [95]. Therefore, it is possible the concentration measurement of light scattering instruments such as the DustTrak and OPC can increase with relative humidity.

273. The results of studies of the performance of three CPC's concluded that the minimum detectable particle diameter of the instruments can be influenced by interaction of three variables - the relative humidity of the aerosol [73], ambient temperature [56, 73], and hygroscopicity [73] of the particles. Therefore, characterisation of relative humidity and temperature should be concurrent, and reported, when characterising particle metrics. Recording of such data will allow consideration of the influence of temperature and relative humidity where sudden and unexplained changes occur in particle number or mass concentration for a given process.

9.11 Include a minimum data set in all reports of assessment of nanomaterial aerosol

274. Data from the characterisation of nanomaterial aerosols is likely to be generated by researchers, industry, and regulators. In order to provide a minimum dataset that can be shared and utilised by researchers, industry, and regulators the following data should be reported following characterisation of nanomaterial aerosols.

275. NANEX provided a list of the minimum amount of data that exposure scientists should report when describing the results of an exposure assessment study [104]. It is similar to the list below.

276. **Tier One assessment** data including:

- Materials used – type, quantity, form
- Process operation
- Number and roles of workers associated with process
- Work patterns of workers including shift duration, work tasks and duration, work location
- Maintenance schedule and process
- Likely points of particle emission from the process
- Likely sources of incidental particle emission
- Current particle emission and exposure controls used such as enclosures, ventilation, and personal protective equipment
- Ventilation assessment including measurement of flow rates, air velocities and pressure.

277. **Tier Two Assessment** data including:

- Background and process particle number and mass concentration.
- Calculated averages of the measured particle number and mass concentration. Arithmetic mean is sufficient as the data is used for assessing relative concentrations.
- Time series plots of the data – identify median peak particle concentration values. Exclude particle values that are within ± of the manufacturer stated inaccuracy for the instrument, i.e. peak values that are within ± of the local particle reference value.
- Description of the peak particle number and mass concentrations relative to the local particle reference value.
- Identification of data assessment location - for example, at point of emission and in breathing zone of workers.

278. **Tier Three Assessment** data including:

- The results of the off-line particle morphology and chemical composition analysis such as:
- Aerosols collected onto a filter membrane connected to a sampling pump or TEM grid within an electrostatic precipitator, with analysis SEM/XRD and TEM/XRD respectively.

- Sampling and analysis against a Workplace Exposure Standard, Recommended Exposure Limit, proposed workplace exposure limit, or benchmark exposure level have been established for the nanomaterial.
- Detail of specific the sampling and analytical methods used.
- Data from other assessment methods such as scanning mobility particle sizer, including data on the setup parameters of the instruments.

279. In relation to Tiers 2 and 3 data including:

- Locations, times and duration of personal sampling, and similar details of area/static sampling.
- Details of aerosol controls in place at time of sampling, such as type (e.g. LEV), flow rates and other parameters of ventilation controls and personal protective equipment being used.
- Details of environmental and area conditions, for example room dimensions and sources of natural ventilation.

280. Providing this information will help overcome issues identified by the NANEX project during the review of exposure information for manufactured nanomaterials [104]. In relation to information on study context, such as frequency and duration of an activity, operational conditions, and presence of ventilation, most or all of this information was missing in nearly every study reviewed [104]. It was also noted that many studies lacked information on sampling strategy, such as where and how many samples were taken, how samples were processed, and how data were analyzed following the study.

281. Regarding airborne concentrations/estimates of exposure, it was found that concentration measurements were reported using a diverse set of metrics collected by a variety of instruments, including total particle number, particle number binned into particle size ranges, and mass per unit volume (mg/m^3) [104]. The measurements between different studies were not directly comparable because of differences in principles of operations and thresholds for detection between instruments [104].

282. A more streamlined minimum dataset, consistent with the above dataset is defined in the preliminary recommendations for measurement and data analysis from the 2010 harmonisation workshop [98]. However, these recommendations are defined for the purpose of exposure characterisation, not for sharing of information. The recommendations [98] are:

Minimum dataset

1. Statistically representative number concentration, and particle size distribution or particle number concentration with information about surface area or particle number concentration for at least two size bins (<100 and >100 nm)
2. A (qualitative) morphologic and element identification of the manufactured nano-object
3. 'Wet' mass concentration of respirable fraction (if applicable)

Type of measurement

1. Real-time task-based and peak measurements + time/task registration or
2. Real-time measurements averaged over a shift (repeated sampling is to be encouraged.)

Background distinction

The approach for background aerosol distinction should be clearly described and documented.

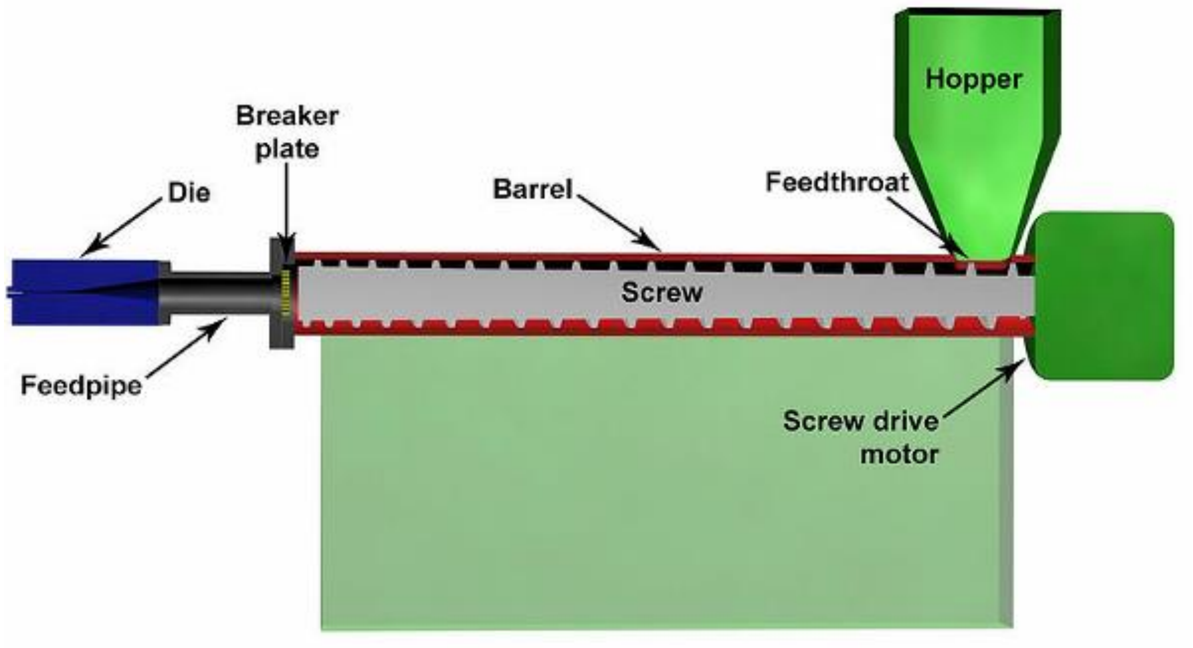
- Describe the presence of other sources of nanoparticles, e.g. compressors, fork lifts, etc.
- Contrasting of statistically representative size distributions of background and process is encouraged.

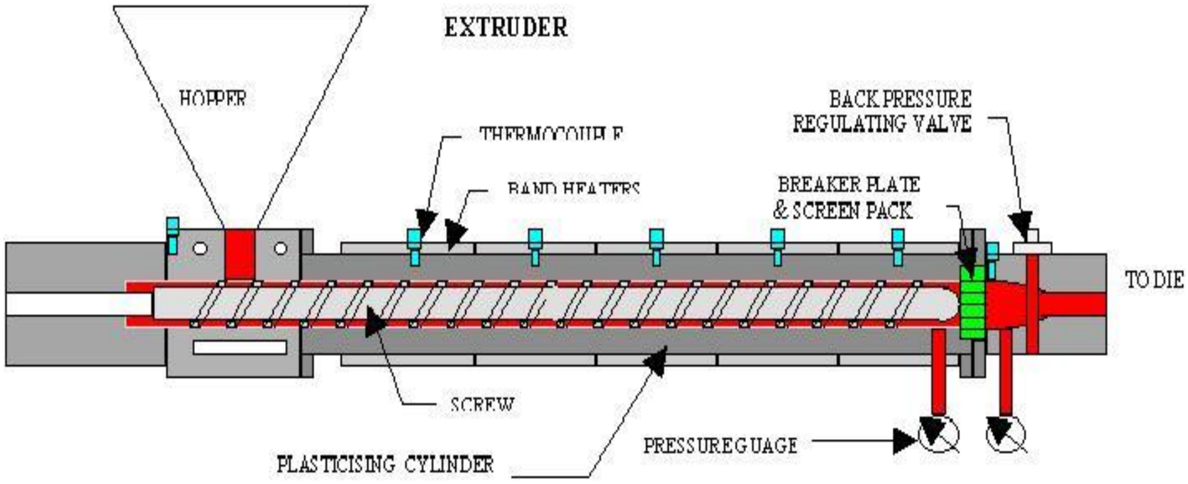
Data processing/analysis

1. Check if data are (log)-normally distributed.
2. Look at (partial) autocorrelation and stationarity (e.g. autoregressive integrated moving average). Autocorrelation in time series measurements is discussed in Appendix H.
3. Calculate AM/GM and (G)SD and other summary statistics, e.g. 95% confidence interval, highest value, etc. using appropriate methods.

APPENDIX A. PROCESSES FOR PARTICLE MEASUREMENT: EXTRUDER MACHINE

Schematics of extrusion machine [5]





APPENDIX B. PROCESS ONE – GRINDING AND EXTRUSION OF MODIFIED TiO2

B.1 Experimental Design and Conditions

283. This nanotechnology process utilised functionalised nano titanium dioxide (TiO_2) (anatase) in two discrete stages, Stage 1-A and 1-B, as described in Table 2.

284. A P-Trak, CPC 3781, SMPS, NSAM, and DustTrak sampled through a manifold from a common point located within ~20cm of the particle emission source during both stages of the process. Spatial PNC, including operator exposure, was also measured using a P-Trak at four locations proximate to the particle source, and by a CPC 3781 located approximately seven metres from the particle source. The dimensions of the work area included a floor area and room volume of approximately 100 m^2 and 400 m^3, respectively. Mechanical ventilation (forced dilution or extraction) was not used during either stage of this process. Instead, natural ventilation was provided through one open door.

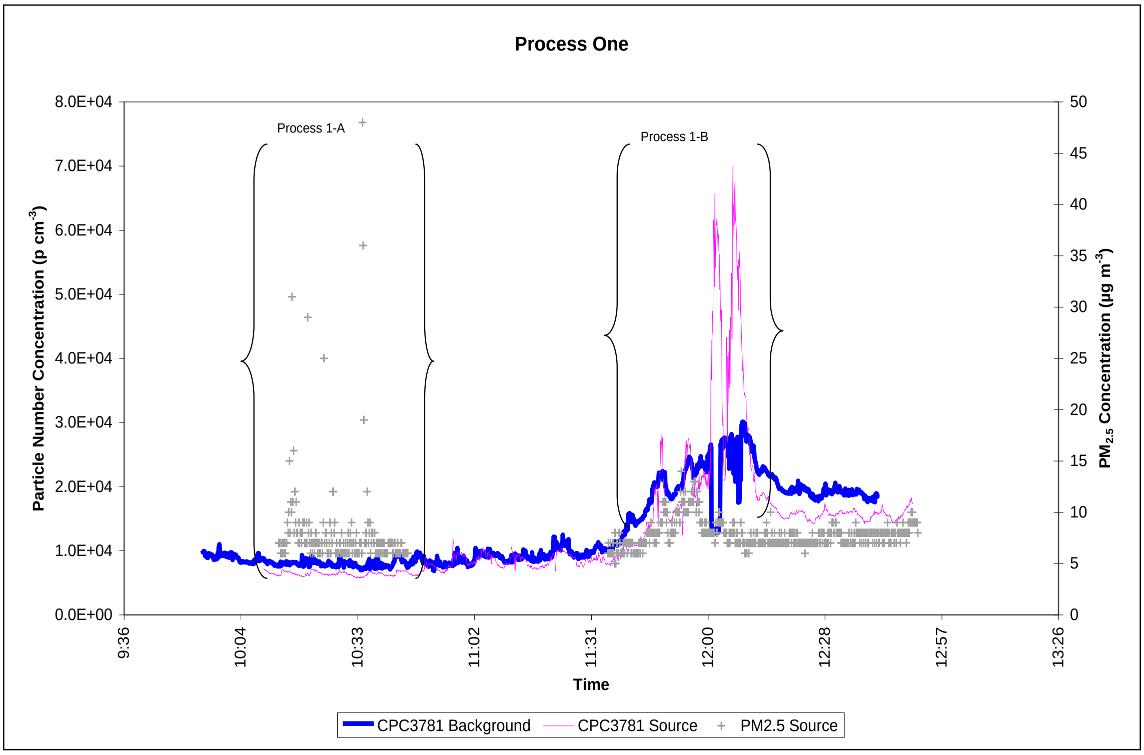
B.2 Results

B.2.1 Time series of particle number and mass concentration, count median diameter, and alveolar deposited surface area

285. Shown below are several time-series plots of the PNC and $PM_{2.5}$ concentration, particle count median diameter, and alveolar deposited surface area for Process 1. The plotted measurement values reflect both the *local background particle concentration* and particles being emitted from Processes 1A and 1B.

286. Figure 6 compares the particle number and mass concentration during process operation and the *local background particle concentration* associated with Processes 1-A and 1-B. Note that stage 1-A is not a strong particle source as evidenced by the PNC remaining steady at a concentration of about 1.0 x 10^4 p cm^{-3}, which is similar to the PNC before and after. However stage 1-B is a much stronger source of particles than background sources and influences PNC both at the point of emission and at a distance approximately seven metres from the source, and continues to have an influence on the PNC after the completion of stage 1-B. Peak $PM_{2.5}$ concentrations that have no clear association to the process are evident during both Process 1-A and 1-B.

Figure 6. Comparison of PNC and PM2.5 concentration during Processes 1-A and 1-B and the local background particle exposure.



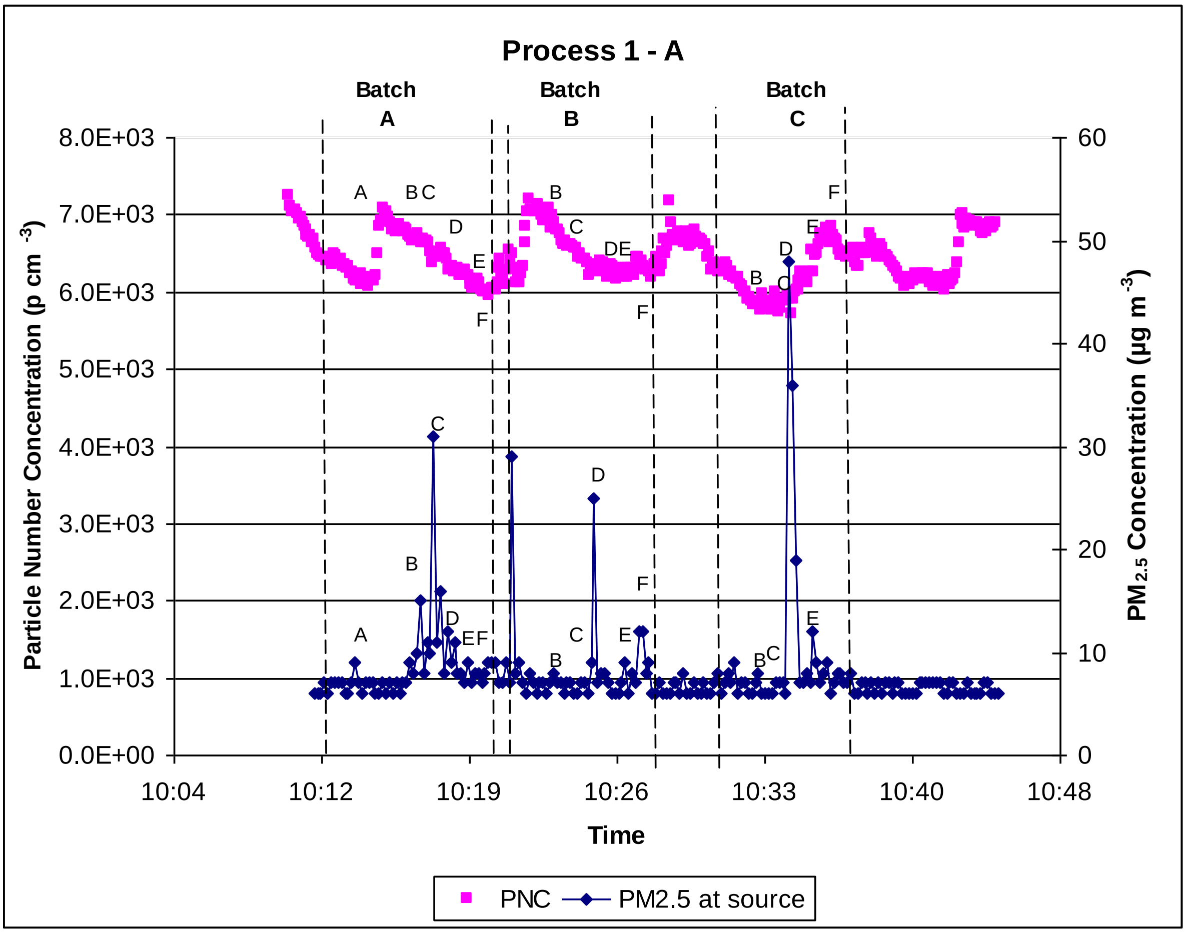
The background CPC was situated approximately 7m from the process particle source and the source PM2.5 and CPC were situated approximately 0.2m from particle emission point.

287. Figure 7 compares the time series of particle number and mass concentration during specific tasks that were undertaken during stage 1-A. No extraction or mechanical dilution ventilation was in operation during any batch.

288. During each batch the PNC at the source appears to increase above the background PNC compared to that between batches, however there is no obvious correlation to the various tasks, and the increase is relatively small when the accuracy of the instruments is considered as outlined in Table 3.

289. Peak $PM_{2.5}$ concentration associated with specific tasks is also evident in Figure 7. At least one peak in $PM_{2.5}$ concentration when compared to the background $PM_{2.5}$ concentration was associated with each of tasks A to F. In absolute terms the maximum peak $PM_{2.5}$ value of 47 µg m^{-3} was only 42 µg m^{-3} above the background of 5 µg m^{-3} and therefore of limited significance in practical terms (the US NIOSH's REL for ultrafine TiO_2 is 300 µg m^{-3}). However, the peaks in $PM_{2.5}$ concentration above background are significant in terms of process emission because they are greater than the normal background fluctuations and also greater than the inaccuracy of the instrument (in this case, the greater value of 0.01% or 1 µg m^{-3}). This also indicates the use of the DustTrak is valid and sensitive for characterising relatively low particle emission from this process.

Figure 7. Difference in particle number and mass concentration for Process 1-A.

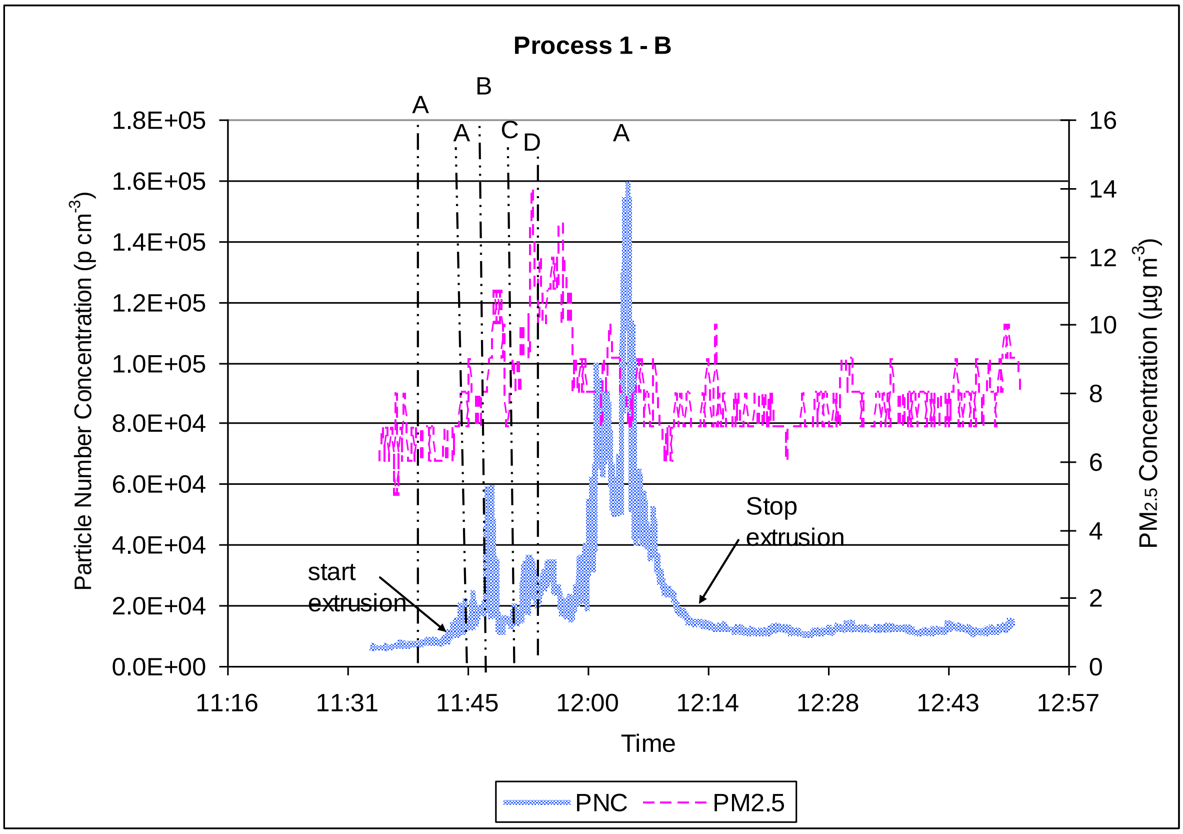


This was repeated over three batches. For each batch the main tasks are labelled A to F, with Task A = Crushing Fe Stearate; Task B = Weighing out Fe Stearate; Task C = adding oil and mixing; Task D = Adding P25 TiO2; Task E = Mixing the above using spatula; Task F = Pouring the above into another container.

290. Figure 8 presents the results of spatial measurements for stage 1-B obtained with a P-Trak and DustTrak, including from the breathing zone of the process operator during the process operation. Measurement locations are signified on the graph and no extraction or mechanical dilution ventilation was in operation during this stage. Similar to the concentrations presented in Figure 6, PNC and PM$_{2.5}$ concentrations were elevated above background during the operation of stage 1-B. The increase in PM$_{2.5}$ concentration at locations C and D likely reflect particles arising from the depositing of the end product into a receiving hopper located several metres to the left of the extruder machine.

Figure 8. Difference in particle number and mass concentration at different locations during the extrusion process, Process 1-B. .

PNC obtained using a P-Trak, and PM2.5 concentration using a DustTrak. Measurement locations are signified on graph as follows: A = at extruder control panel 0.5 m from source in breathing zone of the operator, B = 2.4 m to right of extruder machine, C = 2.4 m to left of extruder machine, D = at receiving hopper for final product



291. The time series of the count median diameter (CMD) and the alveolar deposited surface area of the particles as characterised at the emission point of Process 1-A are presented in Figure 9. Peaks in the CMD of approximately 58 nm are associated with each of the three batches, compared to a CMD of between 51 and 53 nm between the batches. Corresponding to the increase in CMD are peaks in the alveolar deposited surface area during each batch when compared to that between batches. However these peaks are relatively small when compared to background, considering the accuracy of the instruments as outlined in Table 3.

292. The CMD and the alveolar deposited surface area of the particles as characterised at the emission point of stage 1-B is presented Figure 10. Note, that compared to the background, there are obvious peaks in both the CMD and the alveolar deposited surface area of the particles. These peaks

are significant when compared to the background when the accuracy of the instruments is considered (Table 3).

Figure 9. Count Median Diameter and alveolar deposited surface area of particles at the emissions source for Process 1-A.

Common process steps are notated on the figure as follows: A = Crushing Fe Sterate; B = Weighing out Fe Sterate: C = adding oil and mixing; D = Adding P25 TiO2; E = Mixing the above using spatula; F = Pouring the above into another container.

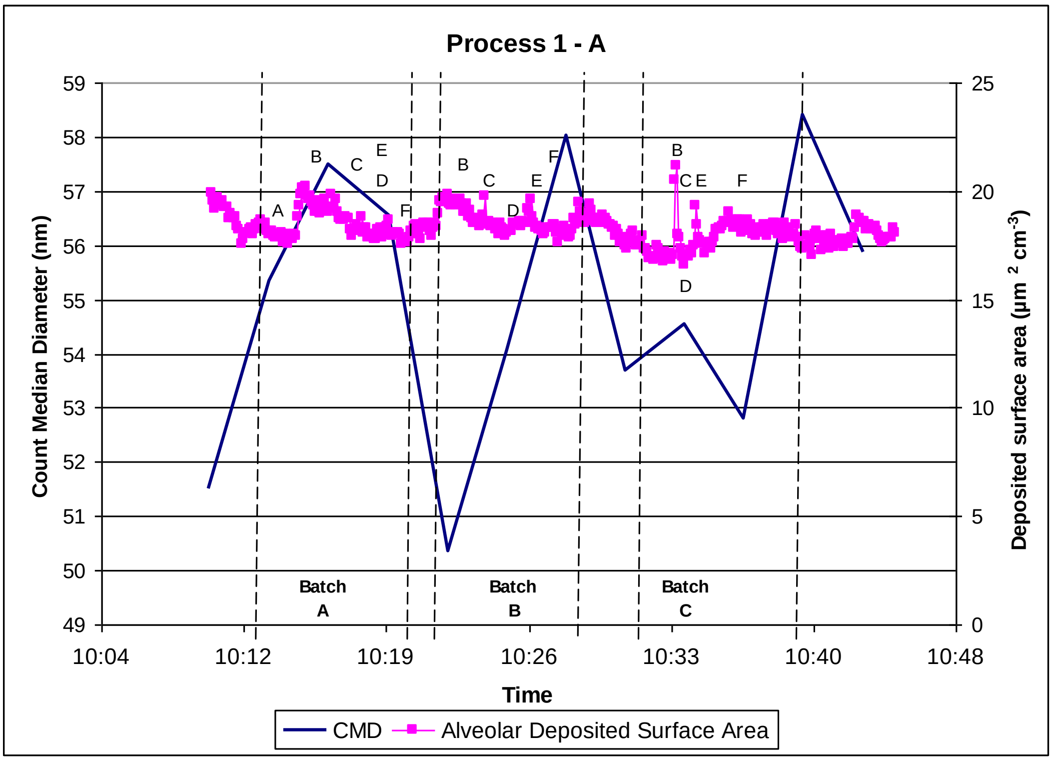
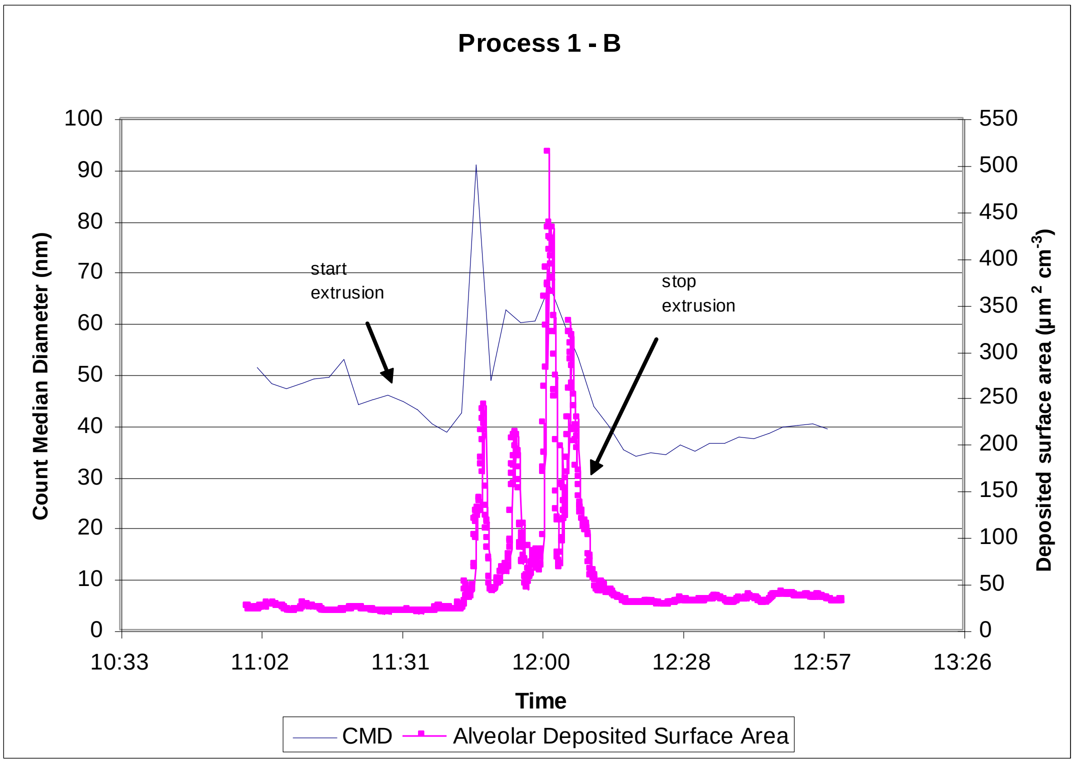


Figure 10. Count Median Diameter and alveolar deposited surface area of particles at the emission source for Process 1-B.



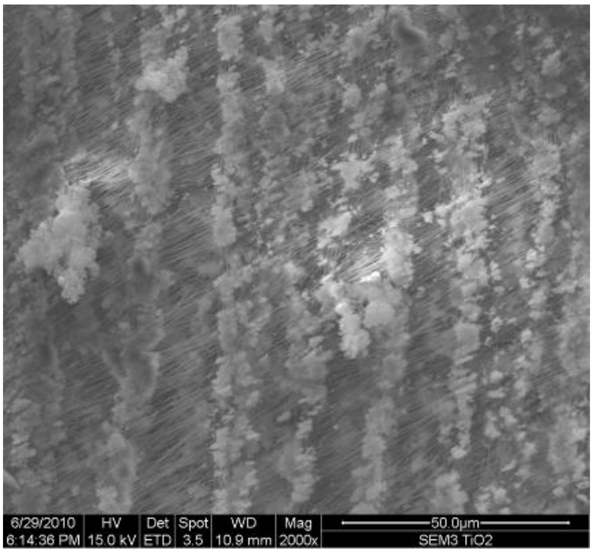
B.2.2 Electron microscope

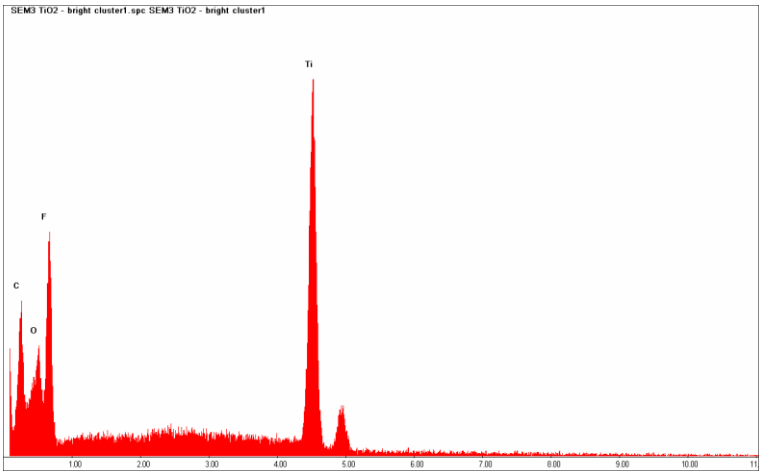
293. Figure 11 depicts the SEM and energy dispersive X-ray spectroscopy results for aerosol particles collected using 37 mm PTFE filter, open face cassette, and pump method during Process 1A. These filters were co-located with the real-time measurement instruments described above.

294. The 37mm filter was examined using an FEI Quanta 200 Environmental Scanning Electron Microscope (ESEM) operated in high vacuum mode, and elemental composition was assessed using an EDX X-ray microanalysis system. The results revealed that the open face cassette and filter with a sampling pump successfully impacted particles onto the filter, and these particles had a morphology and chemical signature consistent with the predominantly titanium dioxide component of the raw nanomaterial. Noting that the carbon and fluorine peaks in Figure 11 are due to use of the PTFE filter, the spectrum has very similar characteristics (e.g Ti/O peak ratios) to EDX spectra for nano TiO_2 in Pal et al [102], which indicates that there was little cross-contamination during sampling and subsequent sample analysis.

Figure 11. SEM image and energy-dispersive X-ray spectroscopy of particles sampled from Process 1-A.

The open face cassette used for this sampling was located at same point as that of the real-time particle measurement instruments used for Process 1-A.





B.3 Discussion

295. The data from Figures 6 to 10 is reflective of the process operation and the *local background particle exposure*, and has been used in Table 9 to examine the peak PNC, mass concentration, CMD, and alveolar deposited surface area associated with Processes 1A and 1B.

Table 9. Summary of peak particle metrics at emission source during process operation compared to the peak associated with LBPC

Process	PNC [p cm^{-3}] 20 to 1000nm **CPC P-Trak**		PNC 300 to 3000nm [p cm^{-3}] **OPC**		PNC >3000 to 10000nm [p cm^{-3}] **OPC**		PM$_{2.5}$ [µg m^{-3}] **DustTrak** [µg m^{-3}]		CMD [nm] **SMPS**		alveolar deposited surface area [µm^2 cm^{-3}] **NSAM**	
	Peak during process	Peak of LBPC	Peak during process	Peak of LBPC	Peak during process	Peak of LBPC	Peak during process	Peak of LBPC	Peak during process	Peak of LBPC	Peak during process	Peak of LBPC
1A	7.0 x 10^3	7.0 x 10^3	#	#	#	#	50	9	58	53	24	19
1B	1.6 x 10^5	1.2 x 10^4	#	#	#	#	14	10	92	53	520	35

local background particle concentration (LBPC)

not measured

296. It is evident from DustTrak measurements in Table 9 that Process 1A is a peak emitter of supermicrometre particles, whilst Process 1B is a peak emitter of both sub and supermicrometre particles, with the differences in metric values during the process and the background being greater than the manufacturer stated accuracy of the P-Trak and DustTrak.

297. For Process 1A, differences in CMD and alveolar deposited surface area between the process and the background are not significant as this is not a strong emitter if submicrometer particles. In contrast, for Process 1B there are significant differences in CMD and alveolar deposited surface area between process and background and this reflects: 1) the influence of the stronger submicrometre particle emission, and 2) the particle size being predominantly within the submicrometre measurement range of the SMPS and NSAM respectively.

298. For Process 1B, the mean of the PNC, CMD, and alveolar deposited surface area during the process operation are significantly different to that of the background (p-values < 0.0001 and 0.0005 respectively), indicating the process is a strong source of submicrometre particles. However, the spatial mean PNC values (Table 4) indicate the particle source is not strong enough to significantly influence the mean *local background particle concentration* as measured at 7 meters from the point of emission.

299. Both the water and alcohol based CPCs, plus the SMPS and NSAM were able to characterise Process 1-B as an emitter of particles when compared to background mean and peak values.

300. The results of the off-line analysis of the aerosols indicates that sample pumps, filters, open face cassettes to capture particles, SEM and EDX are valid techniques for characterising particles even where the strength of the particle source is low, as was the case for Process 1A.

APPENDIX C. PROCESS TWO – MANUFACTURE OF CLAY-POLYURETHANE NANOCOMPOSITE MATERIAL

C.1 Experimental Design and Conditions

301. This nanotechnology process involved instilling a clay product into a polyurethane polymer to form a composite using an extrusion process, as described in Table 2. The work room was the same as for Process 1 (floor area and volume of approximately 100 m^2 and 400 m^3, respectively) but this time was ventilated entirely by a local extraction ventilation system consisting of mechanical extraction vents, operating at a total flow rate of approximately 6.9 x 10^3 m^3 h^{-1}, or 17 air changes per hour, which kept the room under a constant negative pressure. The most likely point of particle emission from the extruder was identified by the operators as above the centre of the screw barrel. A P-Trak, CPC 3781, SMPS, NSAM, and DustTrak sampled through a manifold from a common point located within ~20cm of centre of the extruder machine, whilst the room *local background particle concentration* was characterised using a CPC 3781 located ~7 m away. Figure 12 illustrates the configuration of the sampling rig.

Figure 12. Configuration of measurement equipment, with sampling manifold, relative to the location of the extruder machine.

302. Measurements were repeated over three days during the processing of varying concentrations of the functionalised nanomaterial, with and without local extraction ventilation operating. The data for each of the three days is identified as Process 2-A, 2-B, and 2-C respectively for the purposes of this report.

C.2 Results

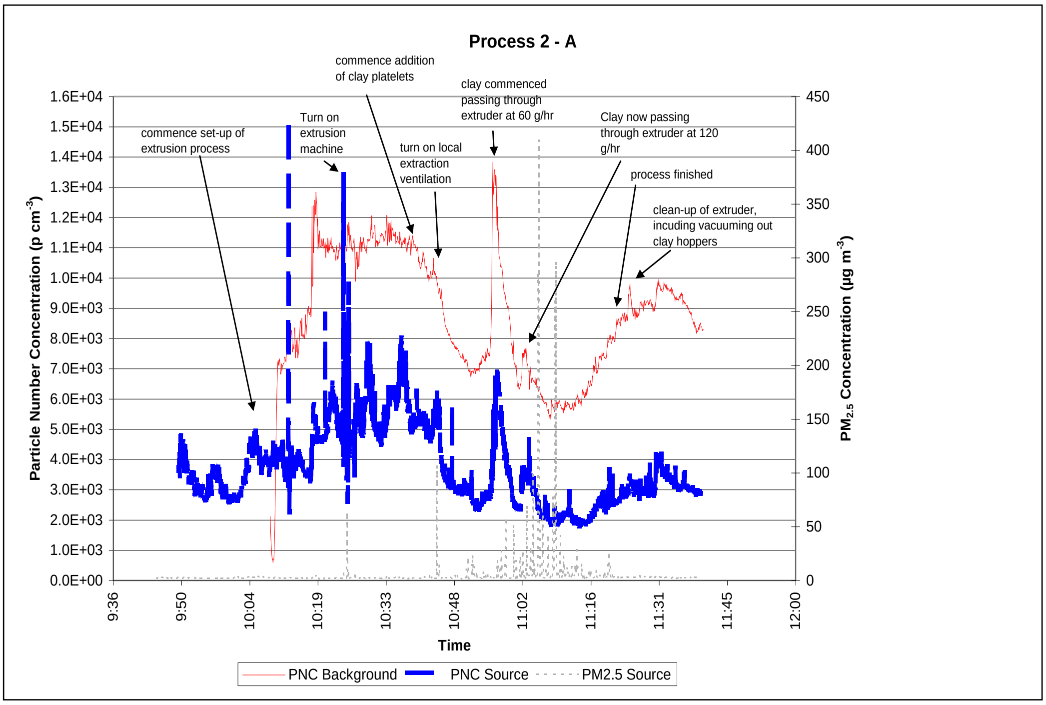
C.2.1 Time series of particle number and mass concentration, count median diameter, and alveolar deposited surface area

303. Shown below are time-series plots of PNC, $PM_{2.5}$ concentration, count median diameter, and alveolar deposited surface area for Process 2-A. The plotted measurement values reflect both the *local particle background exposure*, and particle metrics associated with the process that were typical for the three days of particle measurement. Selected events and tasks have been notated upon the plot in Figures 13 and 14.

304. Figure 13 compares both the PNC and $PM_{2.5}$ concentration at the extrusion process particle source and the background at seven metres from the source. Note there is a clear trend between particle concentration and key events/tasks such as: (i) when the extrusion machine is turned on at approximately 10:10 hours there is a peak in PNC and a sustained rise in PNC compared to background, (ii) when the extraction ventilation is turned on the PNC displays an obvious reduction (both background and at source) at approximately 10:40 hours, (iii,) when the clay commences passing through the extruder at approximately 10:55 hours there is a peak in the PNC at both measurement locations, (iv) when the clay extrusion rate is increased to 120 grams per hour at approximately 11:02 hours there is another peak in PNC at both measurement locations plus a peak in $PM_{2.5}$ concentration at the extruder machine.

Figure 13. Comparison of PNC at extruder source (CPC P-Trak) and at background 7 metres away (CPC 3781), plus particle mass concentration (DustTrak).

Note the effect of turning on the local extraction ventilation at approximately 10:40 hours. The difference in PNC between the two CPC's can be explained by a combination of the difference in particle size measured plus the location of the CPCs relative to the source.



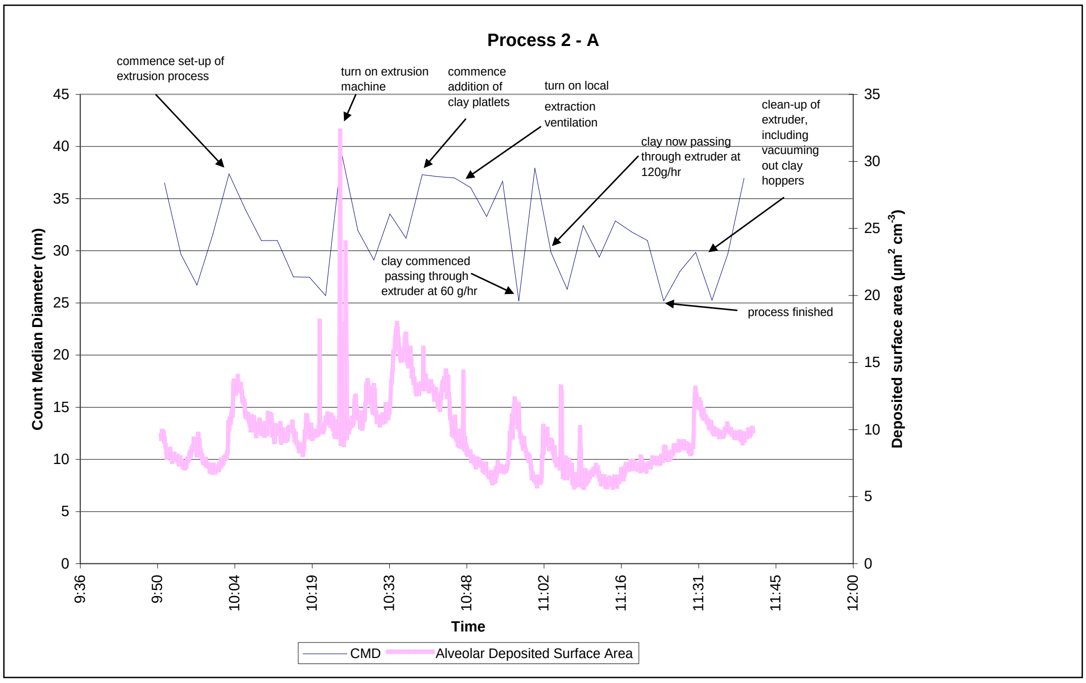
305. The PNC results from the water based CPC located at 7m from the source, and the alcohol based CPC located at the particle source differed significantly. There are three possible reasons:

(1) The minimum and maximum particle measurement size ranges differ between different instruments and therefore the lower particle measurement limit of the water based CPC (the CPC 3781 used for background measurement) allowed a greater PNC to be characterised.
(2) Particles may exhibit significant differences in solubility between water and alcohol.
(3) The location of the CPC's relative to the source.

306. These results show that when collecting spatial data, the same model of CPC should be used. However despite the differences in the CPC's, both were able to characterise similar patterns in particle variability associated with specific process events.

307. The CMD and the alveolar deposited surface area of the particles as measured at the emission point of Process 2-A are presented in Figure 14. Note that both lines display a similar trend in peaks and troughs associated with specific process stages, for example, turning on the extruder machine and addition of clay platelets, for which an elevation in PNC was also noted in Figure 13.

Figure 14. Count Median Diameter and alveolar deposited surface area of particles at the extruder emissions source of Process 2-A



308. Patterns in particle number and mass concentration, particle diameter, and alveolar deposited surface area are discernable for specific events/tasks when compared to those immediately prior. The following observations should be noted:

1. Switching on the extrusion machine results in a brief peak in PNC both at the source and seven metres away, and an increase in the particle alveolar deposited surface area at the source.

2. Switching on the local extraction ventilation results in a decrease in PNC both at the source and seven metres away, presumably because sufficient quantities of outside air with lower PNC is drawn into the work area.
3. Switching off the local extraction ventilation results in an increase in PNC both at the source and seven metres away.
4. Tipping clay powder into the extrusion machine hopper results in an increase in PNC at the source, and an increase in the particle alveolar deposited surface area at the source.
5. When the clay and polyurethane are passing through the extruder there is an increase in PNC both at the source and seven metres away, and an increase in $PM_{2.5}$ concentration and particle alveolar deposited surface area at the source.
6. When the extrusion stops there is a decrease in PNC both at the source and seven metres away and a decrease in $PM_{2.5}$ concentration at the source.

C.2.2 Influence of local extraction ventilation upon the particle concentration within the work area

309. Figures 15 and 16 show the particle number and mass concentration as measured during the operation of Process 2, with and without local extraction ventilation (LEV) in operation. The influence of LEV in reducing PNC can clearly be seen when the LEV is switched off at 12:43 hours and back on at 12:50 hours in Figure 15, and again in Figure 16 when the LEV is switched on at 12:40 hours.

Figure 15. Comparison of PNC at extruder source and at background 7 metres away.

Note effect on PNC of turning local extraction ventilation off at approximately 12:43 hours and back on at approximately 12:50 hours (circled area).

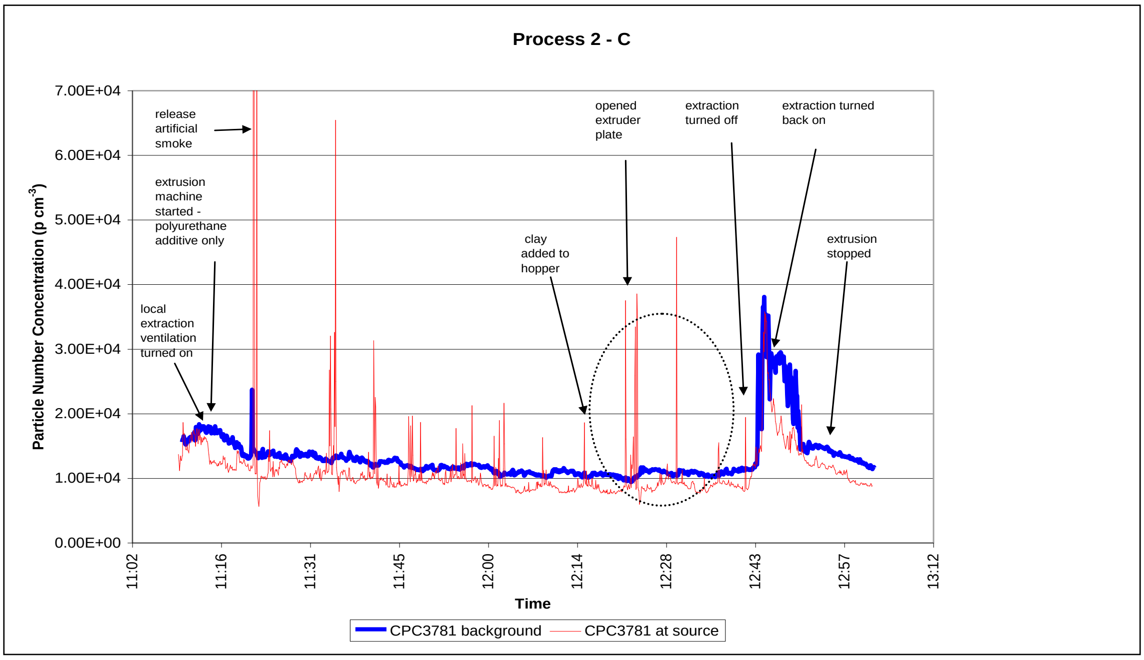
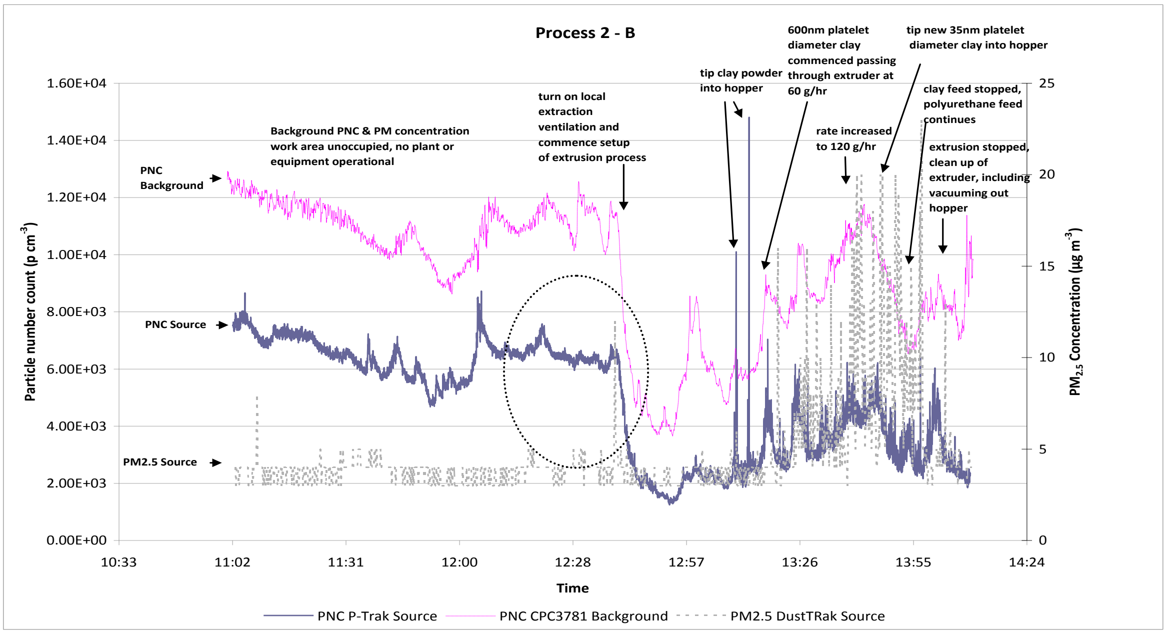


Figure 16. Comparison of PNC at extruder source (CPC P-Trak) and at background 7 metres away (CPC 3781), plus particle mass concentration (DustTrak).

Note effect of switching on local extraction ventilation at approximately 12:40 hours (circled area).



310. Further evidence of the effect of LEV on reducing the PNC is the lower mean PNC measured at the point of particle emission for Process 1B compared with Process 2, as shown in Table 4. Both these processes used the same extruder process.

Description of the local extraction ventilation servicing the extruder machine

311. The extruder machine was located within a room with a floor area and room volume of approximately 100 m^2 and 400 m^3, respectively. A closed door at one end of the room allowed access directly to a car park, whilst another closed door was used as the main entry/exit to the work area. The room was serviced by seven local extraction vents, with vent dimensions of 0.45 x 0.45 metres. Each vent had flanges in situ with dimensions of each 1m x 1m. The seven vents were positioned on the ceiling at a height of 3 metres from the floor. Outside air to the work area entered via gaps under and around the doors, and either by infiltration or actively through the effect of negative pressure created when the LEV was in operation.

312. Extraction vent C was positioned on the ceiling 0.7 metres to one side of the extruder and on the ceiling at a height of three metres from the floor resulting in the face of the vent being positioned at 45^{o} to the extruder and 2 metres straight line from the centre of the extruder machine. The average velocity across the face of extraction vent B, as determined using grid pattern measurements, was 1.7 m s^{-1}, with a range of 1.1 to 2.4 m s^{-1}. Vent B was positioned on the ceiling at 45^{o} to the extruder and 3 metres straight line from the centre of the extruder machine.

313. When artificial smoke was released at the extruder machine (at particle measurement point) the smoke was rapidly extracted into vent C and at a slower rate into vent B. The smoke was not observed to be extracted into any of the other vents, and this is because of the relatively large distances between these

vents and the extruder machine. The average velocity across the face of extraction vent C, as determined using grid pattern measurements, was 1.8 m s^{-1}, with a range of 1.1 to 2.2 m s^{-1}.

314. Using equation 1, applicable for a flanged opening hood, the effective air flow rate generated by the LEV can be calculated so as to achieve a desirable capture velocity rate at the point of particle generation.

$$Q = 0.75v(10x^2 + A) \qquad \text{Equation 1}$$

Q = air flow rate in m^3 s^{-1}, v = capture velocity in m s^{-1}, x = distance from hood to source, in metres, A = area of vent hood/face, m^2.

315. Rearranging equation 1 allows calculation of the effective capture velocity that was generated at the extruder machine on the days that particle monitoring took place:

$$v = \frac{Q}{0.75(10x^2 + A)} \qquad \text{Equation 2}$$

316. The estimation, using equation 2, of the effective capture velocity, v, generated by the combined effect of vents B and C at the particle emission point was 0.1 m s^{-1}. Air velocity measured using a hot wire anemometer positioned at the extruder machine with the LEV in operation, ranged between 0.1 and 0.2 m s^{-1}.

317. Although the PNC values plotted in Figure 13 clearly indicated that the LEV effectively captured particles arising from the extrusion process, the LEV was not effective in capturing all particles as evidenced by the peak in PNC measured at a distance of 7 metres from the extrusion machine (when clay particles began passing through the extruder machine at approximately 11:00 in Figure 13).

318. The likely reasons for the incomplete capture by the LEV of the particles arising from the extruder is that the effective capture velocity of between 0.1 and 0.2 m s^{-1} generated by the LEV system is too low to consistently overcome interference to the airflow velocity such as that caused by operator movement and random air currents in the work area. Approximate recommended capture velocities for different processes have been published in Industrial Ventilation texts. The minimum recommended capture velocity for the extrusion process is 0.25 – 0.5 m s^{-1} so as to overcome local interferences and the intrinsic release velocity of the contaminant [87]. This assumes that the condition of dispersion of the contaminant is that it is released with practically no velocity into quiet air.

319. The effective capture velocity would be increased if the vents were placed closer to the extruder machines emission sources.

320. Using equation 3, the mechanically inducted air changes per hour (AC/h) was estimated for the work area:

$$AC/h = \frac{(m^3\ s^{-1} \times 3600)}{RV} \qquad \text{Equation 3}$$

Where, m^3 s^{-1} = air flow rate in cubic metres per second, 3600 = conversion for seconds (from m^3 s^{-1}) to hours (for AC/hr), RV = room volume in m^3.

321. Therefore the work room (floor area and volume of approximately 100 m^2 and 400 m^3, respectively), ventilated entirely by 7 mechanical extraction vents, was operating at a total flow rate of approximately 6930 m^3 h^{-1}, or 17 air changes hour per hour, which kept the room under a constant negative pressure. The positioning of the LEV vents relative to the location of the extruder operator promoted a

relatively clean air flow (that was not contaminated with particles from the process), to flow from behind the operator toward the emission points of the extruder.

C.2.3 Electron microscopy analysis of particles

322. Figures 17 and 18 show the TEM and SEM images respectively, along with energy-dispersive X-ray (EDX) spectroscopy analysis spectra for aerosols arising from Process 2A. Figure 19 shows an image of particles and the nominal chemical formula for the functionalised clay platelets used during Process 2A, and this differs to that used during Processes 2B and 2C.

323. Comparison of Figures 17, 18, 19 indicates the following. Firstly, it is evident that the electrostatic precipitator impacted numerous particles onto the TEM grid film, and the use of the open face cassette, filters and pump also captured particles. Secondly, sampled aerosol particles have a chemical composition consistent with that of the raw material. Thirdly, the morphology of the aerosol sample was broadly consistent with that of the raw material, consisting of mainly plate like particles together with a few fibres.

324. The weight percent of the elements identified in the CM200 TEM EDX spectra of the collected nanomaterials was calculated and compared to that of the raw material used for Process 2A. Because some particles were very small, the X-ray spectra were generally weak and dominated by the carbon peak from the support film substrate. For the calculations below, the carbon peak was fitted but not included with the sample inorganic elements. These results, shown in Table 10, were then compared to the predicted composition of the known raw material. It appears from these results that the aerosol particles were mostly compatible with the raw mineral.

The substrate carbon peak has been omitted from these calculations

Table 10. Calculated elemental weight percent composition of raw material and aerosol particles for Process 2A analysed in the TEM

	O	F	Na	Mg	Si	Fe
Nominal raw material was $NaMg_{2.5} Si_4 O_{10} (F)_2$ which equates to the following Wt% concentrations:	**40.6**	**9.6**	**5.8**	**15.4**	**28.5**	not applicable
Analysis 403: Cluster of particles impacted onto grid	41.9	9.2	0.2	17.4	28.6	2.8
Analysis 404: Cluster of particles impacted onto grid	44.7	8.4	0.6	16.8	29.0	0.3
Analysis 402: Fibre particles impacted onto grid	43.3	4.1	4.9	18.0	29.4	0.3
Note that the values for O are slightly overestimated since there is a small O contribution from the support film. The small Fe contribution most likely results from residual contamination of the extruder machine or from other processes, or from spurious X-rays in the TEM specimen area.						

Figure 17. TEM image and energy-dispersive X-ray spectroscopy of particles sampled from Process 2-A.

The aerosol sampling inlet of the electrostatic precipitator used for this sampling was located at same point as that of the real-time particle measurement instruments used for Process 2-A.

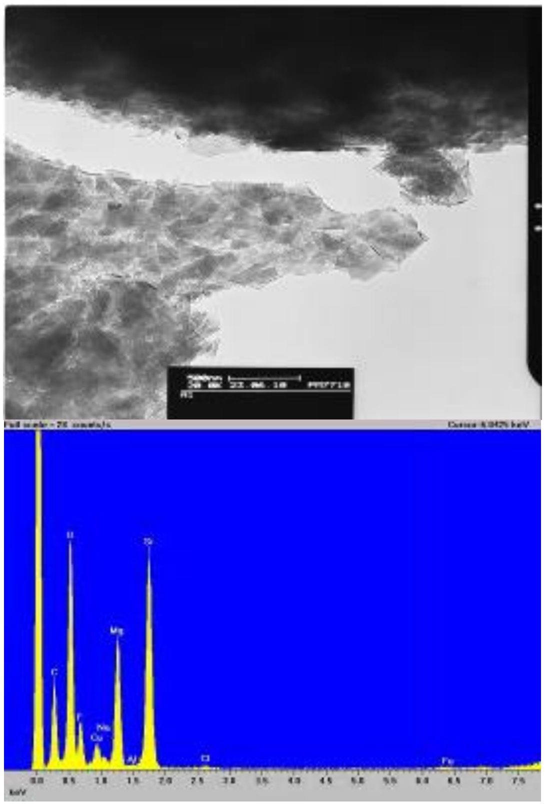


Figure 18. **SEM image and energy-dispersive X-ray spectroscopy of particles sampled from Process 2-A.**

The open face cassette used for this sampling was located at same point as that of the real-time particle measurement instruments used for Process 2-A.

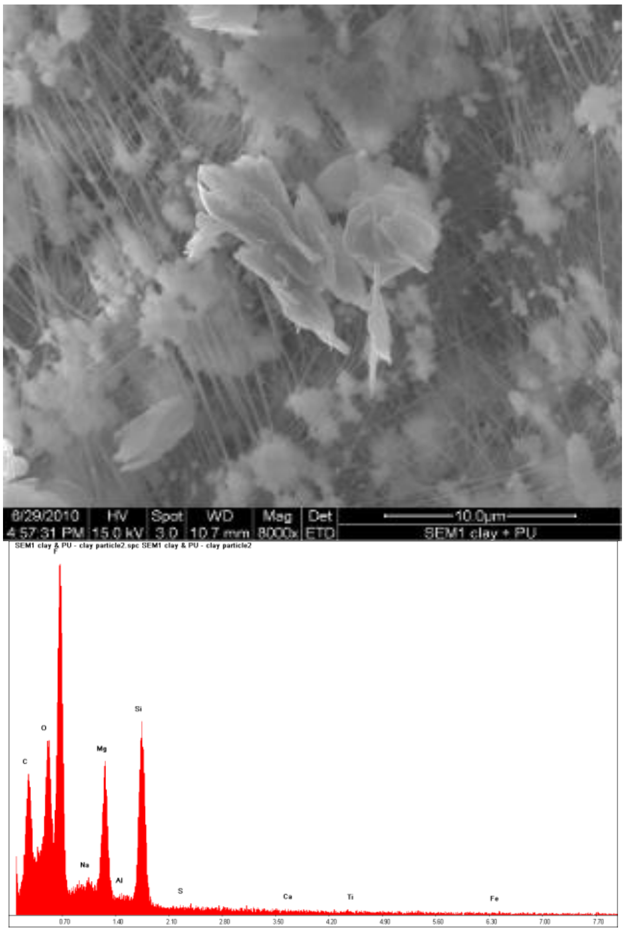
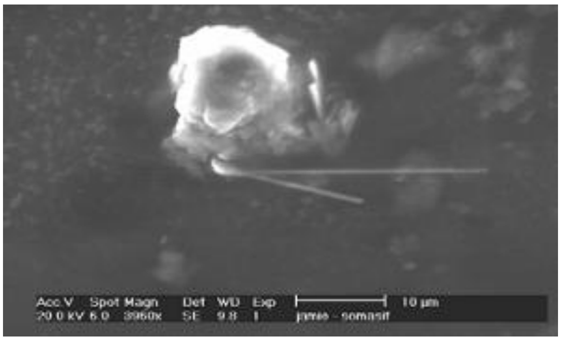


Figure 19. **SEM image of particles contained in the raw material used in the nanotechnology Process 2-A.**



325. Chemical formula[15] of raw material $[Na_{0.66}Mg_{2.68}(Si_{3.98}Al_{0.02})O_{10.02}F_{1.96}]$.

326. Similar analyses for Processes 2B and 2C, where the surface functionalisation of the clay particles differed to that of Process 2A, revealed that the elemental composition of the aerosol particles included only oxygen and silicon; the other elements present in the sample from Process 2A (F, Na and Mg) were not detected in these samples.

C.3 Discussion

327. The data from Figures 13 and 14 is reflective of the process operation and the *local background particle exposure*, and has been used in Table 11 to examine the peak PNC, mass concentration, CMD, and alveolar surface area associated with Process 2.

Table 11. Summary of peak particle metrics at emission source during Process 2 operation compared to the peak associated with

PNC [p cm^{-3}] 20 to 1000nm **CPC P-Trak**		PNC 300 to 3000nm [p cm^{-3}] **OPC**		PNC >3000 to 10000nm [p cm^{-3}] **OPC**		PM$_{2.5}$ [µg m^{-3}] **DustTrak** [µg m^{-3}]		CMD [nm] **SMPS**		Alveolar surface area [µm^{2} cm^{-3}] **NSAM**	
Peak during	Peak of LBPC	Peak during	Peak of LBPC	Peak during	Peak of LBPC	Peak during	Peak of LBPC	Peak during	Peak of LBPC	Peak during	Peak of LBPC
6.0 x 10^4	6.6 x 10^3	#	#	#	#	400	11	50	45	90	33

not measured
local background particle concentration (LBPC)

328. The data in Table 11 clearly indicates that Process 2 results in emission of both sub and supermicrometre particles with the difference in PNC, PM$_{2.5}$, and alveolar surface area all being outside the manufacturer stated accuracy of the instruments and much greater than the normal fluctuation in background particle values.

329. However, examination of the mean of the particle metrics during the process and the background, as summarised in Table 4, shows the strength of the peak particle emissions from Processes 2A, B, and C are weak with insignificant impact upon mean particle metrics when compared with the background. This is likely due to the influence of the local extraction ventilation on particle concentration. In Appendix C.2.2 it was shown that particles arising from a nanotechnology process can be entrained into a LEV system if the system is designed so that the capture velocity at the particle emission point is sufficient. To achieve this it is recommended that the minimum capture velocity be maintained at 0.25 m s^{-1}, and the LEV hood/s are positioned close to the particle source and relative to the position of local workers so as to move the particles away from the breathing zone of process workers.

330. The results of the off-line analysis of aerosol indicates sample pumps, filters, open face cassettes, and an electrostatic precipitator to capture particles, SEM, TEM, and EDX are valid techniques for characterising particles even where the strength of the particle source is low, as was the case for Process 2.

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[15] High aspect ratio fluoromica (Somasif ME100). EDX spectra not available for the raw material

APPENDIX D. PROCESS THREE – GRINDING OF TITANIUM DIOXIDE POWDER

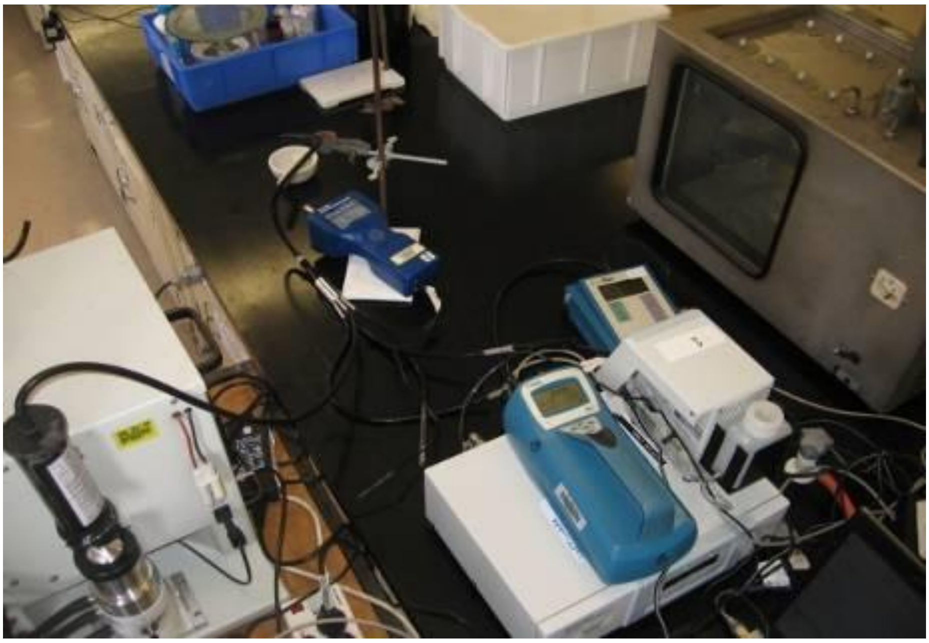
D.1 Experimental Design and Conditions

331. This process involved the grinding of titanium dioxide powder in a mortar with pestle on a laboratory bench top. The weighing out (step 1) took approximately 30 seconds to complete, the grinding (step 2) of the powder took approximately 3 minutes to complete, and the pasting of the powder onto the slides (step 3) took approximately 30 seconds. These tasks were measured over six discrete time intervals on the same day, three utilising the addition of a dilute acetic acid solution and three without (the addition of the dilute acetic acidic solution is the usual process however for comparative particle emission purposes the task was also performed without the addition of the acetic acid solution).

332. A P-Trak, CPC 3781, SMPS, NSAM, and DustTrak sampled through a manifold from a common point located ~12 cm from the mortar and pestle (particle generation point), as illustrated in Figure 20 below. The laboratory's floor area and volume were ~160 m^2 and ~500 m^3, respectively. Ventilation in the room was via natural means with the exception of a fume cupboard, located at the opposing end of the laboratory to the measurement location, that ran continuously with a total exhaust flow rate of approximately 2400 $m^3 h^{-1}$, resulting in 4.8 air changes hour $^{-1}$ for the laboratory. PNC outside the building was also measured using a TSI 3007 Ultrafine Particle Counter so as to characterise the influence of incidental background particle concentration upon the laboratory environment.

Figure 20. Photograph showing the measurement instrumentation configuration

SMPS, Ptrak, CPC 3781, DustTrak, OPC, NSAM, plus the mortar and pestle at the particle generation source



D.2 Results

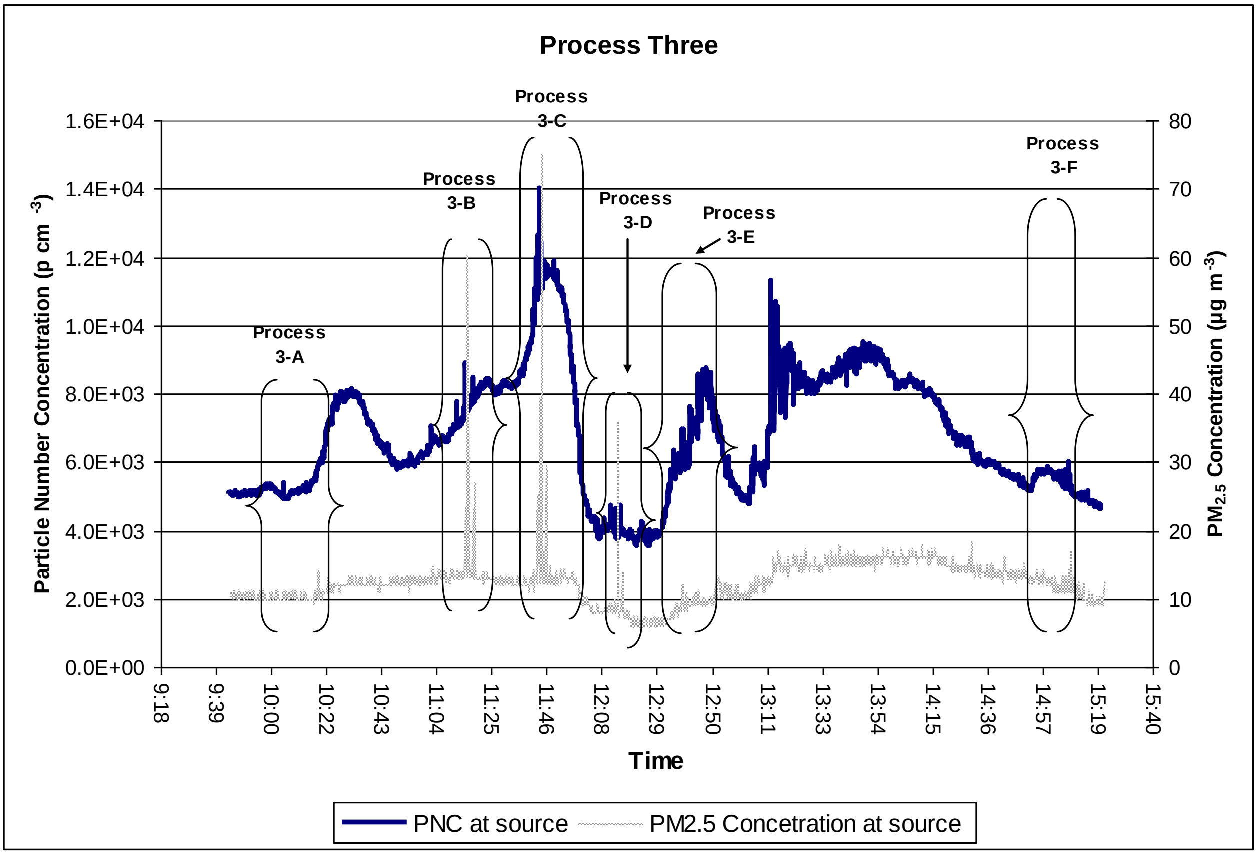
D.2.1 Time series of particle number and mass concentration, count median diameter, and alveolar deposited surface area

333. Shown below are time-series plots of PNC, $PM_{2.5}$ concentration, count median diameter, and alveolar deposited surface area for Process 3. The plotted measurement values reflect both the laboratory *local background particle concentration* and process particle metrics.

334. Figure 21 compares the particle number and mass concentration during process operation and the *local background particle concentration* as repeated six times, labelled Process 3-A to 3-F.

Figure 21. Particle number concentration (PNC) and particle mass (PM) concentration during six episodes of Process 3.

Each process involved weighing out the TiO2 powder, using a mortar and pestle to grind the powder, and pasting the powder onto a slide. The letters A-F signify six discrete occurrences of this process. The grinding during processes 3-A, -C, -E were a "wet" process that involved the addition of an acid solution, whilst processes 3-B, -D, -F were "dry" process with no solution added during grinding.



335. Over the course of the day the *local background particle concentration* fluctuated between 4.0 x 10^3 p cm^{-3} and 1.1 x 10^4 p cm^{-3}. Despite the influence of relatively high background PNC, it is clear that when compared to the background particle number and mass concentration immediately before and after

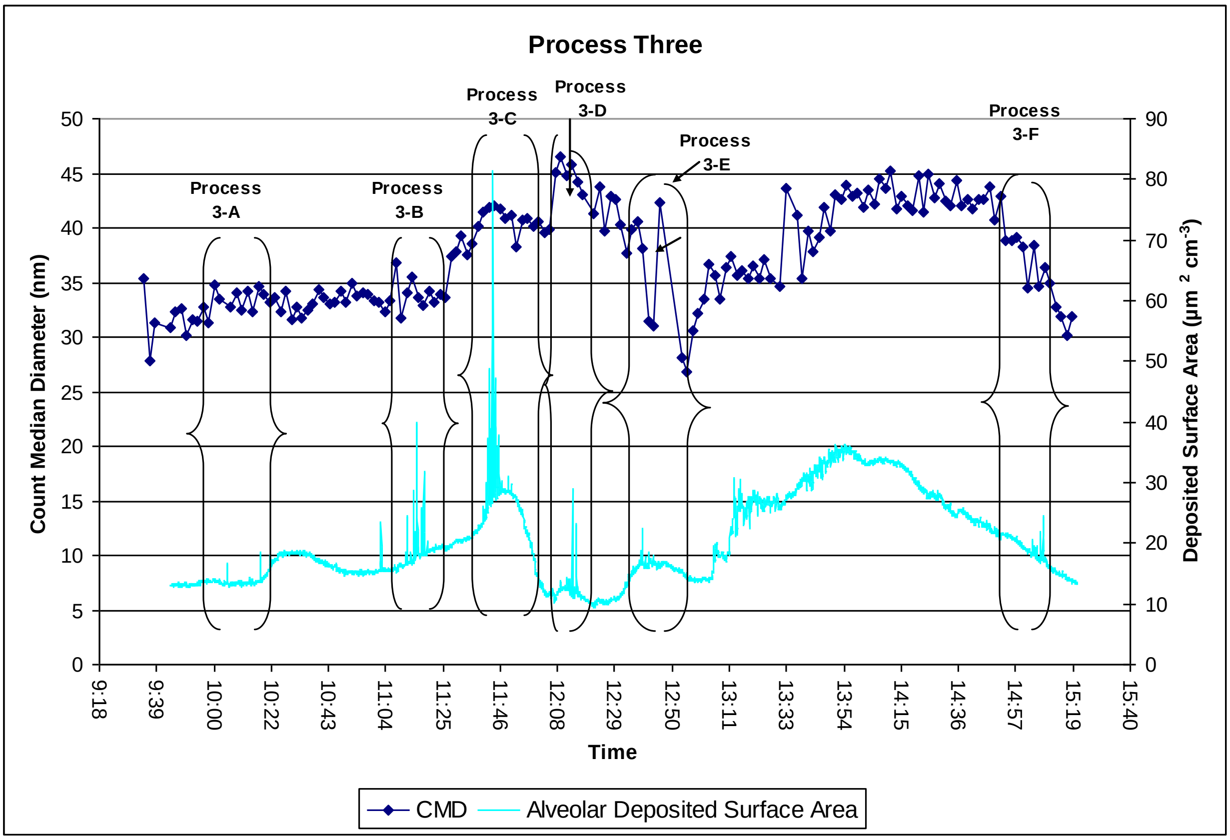
each process, peaks in both particle number and mass concentration of varying intensity are associated with the discrete time periods of the processes. Although the peaks in PNC during Process 3C and 3E are greater than the manufacturer stated accuracy for the instrument, the peaks are not greater than normal variation in background PNC.

336. However, the peaks in $PM_{2.5}$ concentration above background are significant in terms of process emission because they are greater than the normal background fluctuations and also greater than the manufacturer stated accuracy of the instrument (in this case, the greater value of 0.01% or 1 µg m^{-3}). This also indicates the use of the DustTrak is valid and sensitive for characterising relatively low particle emission from this process.

337. The CMD and the alveolar deposited surface area of the particles as measured at the emission point of Process 3 are plotted in Figure 22. There is no clear variation in CMD associated with each process. However there are clear peaks of varying intensity in the alveolar deposited surface area for processes 3-B to 3-E, which are significant when the accuracy of the instruments is accounted for.

Figure 22. Count median diameter and alveolar deposited surface area during six episodes of Process 3.

Each process involved weighing out the TiO2 powder, using a mortar and pestle to grind the powder, and pasting the powder onto a slide. The letters A-F signify six discrete occurrences of this process. The grinding during processes 3-A, -C, -E were a “wet” process that involved the addition of an acid solution, whilst processes 3-B, -D, -F were” dry” process with no solution added during grinding.



338. To further analyse the influence of individual steps of the process on the particle background, peak particle number and mass concentration, particle diameter and alveolar surface area associated with

each of the three steps of process 3A to 3F were compared against the respective mean values for the process as a whole. These results are shown in Table 12.

Table 12. Peak values associated with each discrete step for each batch of Process 3 compared to the mean values of the process as a whole

Process	**Step**	CPC's		SMPS	NSAM	DustTrak
		3781 at particle source [p cm^{-3}]	P-Trak at particle source [p cm^{-3}]	at particle source [CMD - nm]	at particle source [alveolar deposited surface area - μm^2 cm^{-3}]	at particle source [$PM_{2.5}$ μg m^{-3}]
3 A	1	5.3×10^3	3.5×10^3	32	13	10
	2	5.8×10^3	4.1×10^3	35	18	14
	3	5.3×10^3	3.8×10^3	32	13	10
	Mean of this batch	5.1×10^3	3.4×10^3	33	13	10
3 B	1	7.7×10^3	6.3×10^3	31	19	10
	2	8.8×10^3	8.0×10^3	35	39	60
	3	8.2×10^3	4.8×10^3	31	20	10
	Mean of this batch	7.4×10^3	4.7×10^3	34	19	10
3 C	1	9.4×10^3	5.9×10^3	40	24	10
	2	1.4×10^4	1.1×10^4	41	80	70
	3	1.1×10^4	7.5×10^3	40	15	10
	Mean of this batch	1.1×10^4	7.2×10^3	41	31	10
3 D	1	3.8×10^3	2.3×10^3	41	11	10
	2	4.7×10^3	3.5×10^3	45	28	30
	3	3.8×10^3	2.3×10^3	41	10	10
	Mean of this batch	4.0×10^3	2.5×10^3	44	12	10
3 E	1	5.8×10^3	3.1×10^3	39	16	10
	2	7.5×10^3	5.0×10^3	31	23	12
	3	5.8×10^3	3.2×10^3	36	16	10
	Mean of this batch	6.4×10^3	3.4×10^3	35	16	10
3 F	1	5.5×10^3	3.3×10^3	34	19	10
	2	6.0×10^3	4.5×10^3	36	24	17
	3	5.5×10^3	3.2×10^3	34	20	10
	Mean of this batch	6.6×10^3	3.1×10^3	36	18	10
Step 1 = weighing out the TiO_2 powder Step 2 = grinding TiO_2 using mortar and pestle Step 3 = pasting powder onto slides						

339. It can be seen from Table 12 that Step 2, the grinding of the TiO_2 powder, is consistently associated with peaks in PNC, $PM_{2.5}$ concentration, and alveolar deposited surface area and these are greater than the overall mean for the discrete time period of the entire process, confirming this step as the dominant source of both ultrafine and supermicrometre particles. Significant fluctuations in CMD were not evident for the process.

D.3 Discussion

340. The time-series plots from Figures 21 and 22 are reflective of the process operation and the *local background particle exposure*, and have been used in Table 13 to examine the peak PNC, mass concentration, CMD, and alveolar deposited surface area associated with Process 3.

Table 13. Summary of peak particle metrics at emission source during Process 3 operation compared to the peak associated with LBPC

Process PNC [p cm^{-3}] 20 to 1000nm **CPC P-Trak**		PNC 300 to 3000nm [p cm^{-3}] **OPC**		PNC >3000 to 10000nm [p cm^{-3}] **OPC**		PM$_{2.5}$ [µg m^{-3}] **DustTrak** [µg m^{-3}]		CMD [nm] **SMPS**		alveolar surface area [µm^2 cm^{-3}] **NSAM**	
Peak during	Peak of LBPC	Peak during	Peak of LBPC	Peak during	Peak of LBPC	Peak during	Peak of LBPC	Peak during	Peak of LBPC	Peak during	Peak of LBPC
1.1 x 10^4	3.2 x 10^3	#	#	#	#	70	10	46	37	81	35
# not measured local background particle concentration (LBPC)											

341. The data from Table 13 show that Process 3 is a peak emitter of particles within the size range of approximately 20 to 1000 nm. The peak in PM$_{2.5}$ concentration suggests a supermicrometre particle contribution. The significant peaks in alveolar deposited surface area confirm the process is a significant source of submicrometre particles. However, as described in Table 1, because of the likely concentration of supermicrometre particles associated with Process 3, the NSAM data cannot be used with confidence regarding actual alveolar deposited surface area.

342. It is clear from these results that the NSAM, DustTrak, and P-Trak are able to characterise relatively small changes in particle metrics.

APPENDIX E. PROCESS FOUR – JET MILLING OF MODIFIED CLAY PARTICLES

E.1 Experimental Design and Conditions

343. Particle measurements were conducted during the operation and post operation cleaning, of a Jet Milling Machine model Micron-Master Jet Pulveriser. This machine was used to reduce the size of modified (Process 4-A) and unmodified (Process 4-B) clay platelets. The clay platelets are then typically used in Process 2 as described above. Figure 23 shows a photograph of the Jet Milling Machine.

Figure 23. Picture of the Jet Milling Machine

344. A P-Trak, OPC, and DustTrak identified sources of particle leakage from the milling machine, including from the point where an “o” ring connects the dust collection bag to the venturi outlet, and from the funnel leading to the venturi chamber.

345. For subsequent longer duration temporal and spatial measurements, a P-Trak, OPC, and DustTrak were positioned side by side on a tray so as the instruments’ aerosol inlets could be moved in unison to the desired measurement locations. These instruments were utilised to characterise the particle number and mass concentration in the laboratory during operation of the processes and the *local background particle exposure* at measurement locations that included the point where the “o” ring connected the dust collection bag to the venturi outlet, at the funnel leading to the venturi chamber, at points several metres from the machine, and in the breathing zone of the process operator.

E.2 Results

E.2.1 Time series of particle number and mass concentration

346. Shown below are two time-series plots of the particle number and mass concentration measured during the jet milling and equipment cleaning for Process 4-A. These graphs provide data on the PNC in the size range of 20 to 10000 nm as measured using both a P-Trak and OPC, plus $PM_{2.5}$ concentration as measured with a DustTrak.

347. The simultaneous use of both the P-Trak and OPC allowed the PNC to be approximated within the following particle size bins – 20 to 1000nm, >1000 to 3000 nm; 3000 to 5000 nm; and 5000 to 10000 nm.

348. The measurements were repeated for two episodes of the jet-milling process – Processes 4A and 4B. As the instruments were used to measure temporal and spatial characteristics, different measurement locations are notated on the time series plots. In the time series plots for Process 4-A, the PNC in all the bin sizes > 1000 nm has been omitted because the particle count was effectively zero (all less than 1 particle cm^{-3}). Time-series data relating to Process 4-B showed very similar particle emission patterns to that of Process 4-A.

349. Figures 24 and 25 provide the time-series plots of particle number and mass concentration obtained during simultaneous measurement during the first run of Process 4, coded as Process 4-A.

Figure 24. Particle number concentration (PNC) at different locations during the jet milling of a modified clay product during the first jet milling event.

A P-Trak CPC was used in portable mode with the different measurement locations identified by the letters A to D. A = background concentration located 3 m from jet milling machine; B = source concentration located approximately 0.2m from the point where an "o" ring connects the dust collection bag to the venturi outlet and at 90º to the right of the machine operator position; C = breathing zone of the jet milling machine operator approximately 0.5m from Jet Milling Machine; D = source concentration approximately 0.2m from where the vibrating inlet sleeve feeds the material into a venturi chamber.

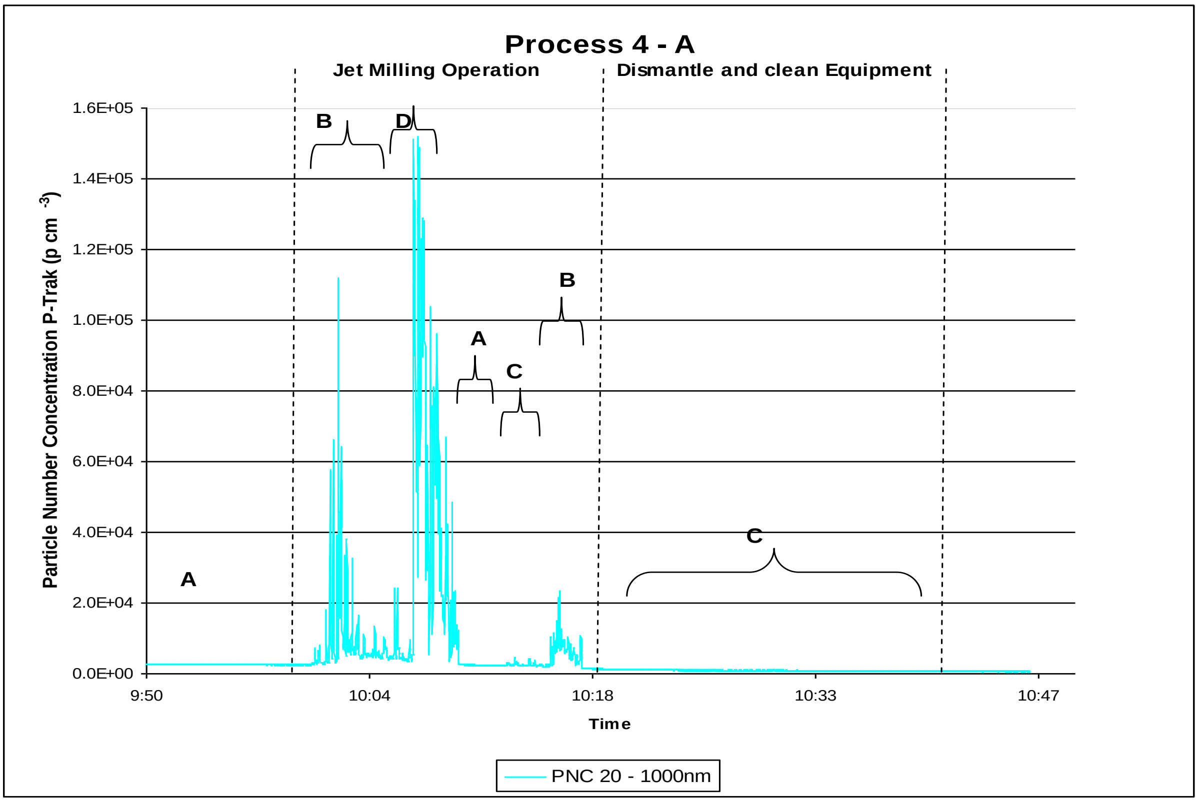
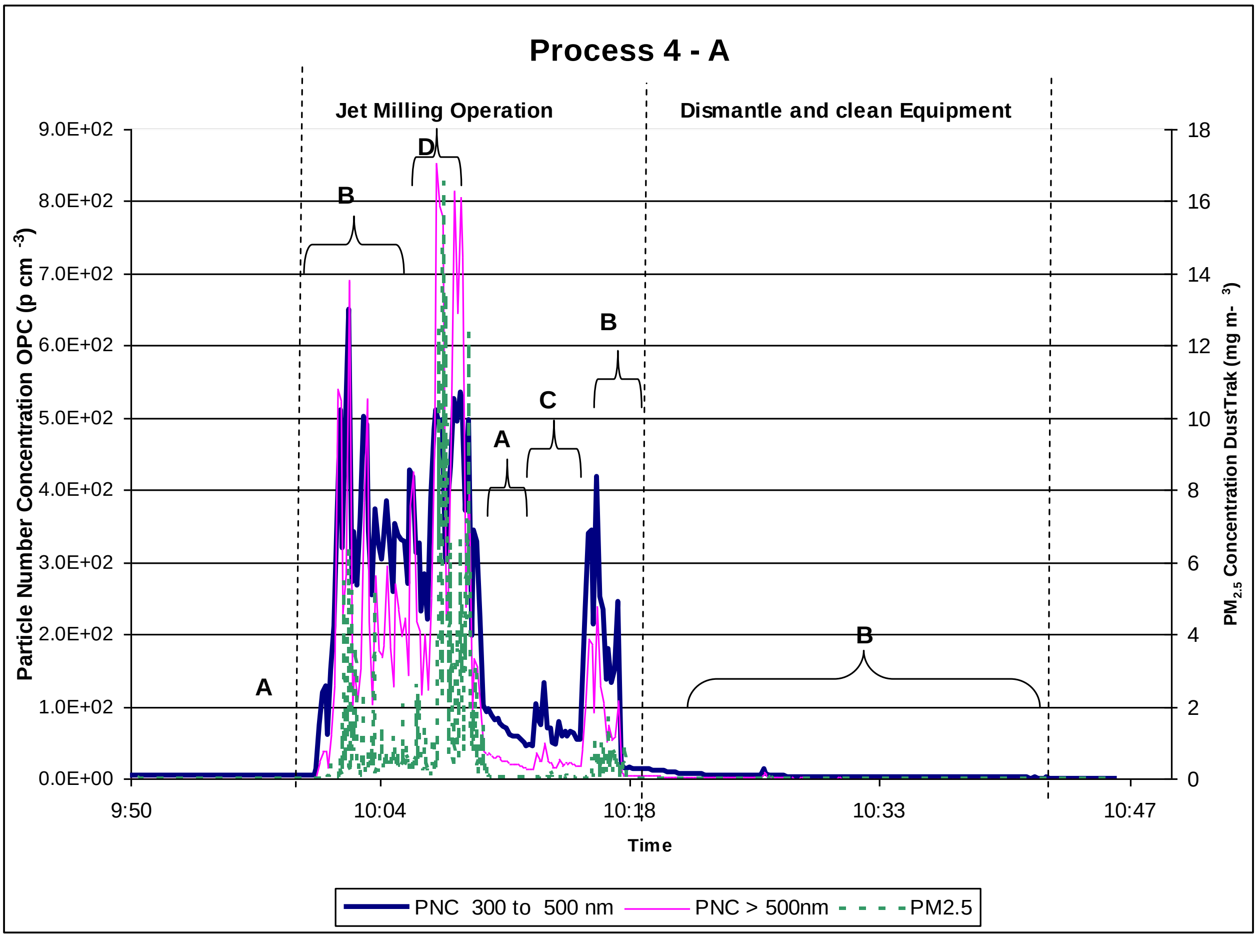


Figure 25. Particle number concentration (PNC) > 300nm and particle mass (PM2.5) concentration at different locations during the jet milling of a modified clay product during the first jet milling event.

An OPC and DustTrak were used in portable mode with the different measurement locations identified by the letters A to D. A = background concentration located 3 m from jet milling machine; B = source concentration located approximately 0.2m from the point where an "o" ring connects the dust collection bag to the venturi outlet and at 90º to the right of the machine operator position; C = breathing zone of the jet milling machine operator approximately 0.5m from Jet Milling Machine; D = source concentration approximately 0.2m from where the vibrating inlet sleeve feeds the material into a venturi chamber. PNC > 1000 nm was < zero p cm-3.



350. It can clearly be seen from Figures 24 and 25 that the jet milling process is a strong source of particles when compared to the *local background particle concentration*. In contrast, dismantling and cleaning the jet milling equipment was not a strong source of particles. Note that the PNC in the size range 20 to 1000 nm (P-Trak values in Figure 24) is three orders of magnitude greater than that of the PNC in the size range of > 300 nm (OPC values in Figure 25) indicating the predominant size range of the particles emitted from the jet milling process is submicrometre and likely to be < 300 nm. In addition, there is a similar trend for the PNC > 300 to 1000 nm and the $PM_{2.5}$ mass concentration as would be expected because of the overlap in the measurement size range of the OPC and DustTrak.

E.2.2 Influence of local mechanical dilution ventilation upon the particle concentration within the work area

351. The influence of the mechanical dilution ventilation upon particle number and mass concentration in the breathing zone of the jet milling machine operator can be seen in Figures 24 and 25. Comparison of the PNC at locations B and D (both within 0.2m of particle emission points of the jet milling machine) to location C (the breathing zone) of the machine operator, shows a spatial reduction in PNC exposure of up to two orders of magnitude for sub-300 nm particles, and approximately an eight-fold reduction in super-300 nm particle exposure. The spatial reduction in PNC between the particle source and the operator breathing zone reflects the configuration of the mechanical dilution ventilation to the work area. Two air inlet ducts from the HVAC system were located directly above and behind the breathing zone of the operator and directed an air flow, that could easily be felt when standing at the operator location, toward the particle source and away from the breathing zone of the operator.

352. The release of artificial smoke at the position of the breathing zone of the operator revealed a strong influence on air movement caused by the air conditioning inlet vents such that the smoke moved in a direction from the breathing zone toward the jet milling machine.

353. The laboratory in which the jet milling machine was located measured 7 x 7 metres with a ceiling height of 3 metres. The room was serviced by a heating, ventilation and air-conditioning (HVAC) system with nine air inlet vents and two outlet vents distributed across the ceiling surface. Each inlet vent measured 0.53 x 0.53 metres and the range of air velocities across the nine vents was between 0.5 and 1.3 m s^{-1}. The jet milling machine was positioned against one wall with an air inlet vent located on the ceiling and on either side of the machine operator. A distance of approximately two metres separated the position of each vent and the breathing zone of the machine operator. The air velocity at the face of each of the two vents was 1.2 m s^{-1} and 1.3 m s^{-1} respectively. The effect of this was the generation of an air velocity of approximately 0.2 m s^{-1}, as measured with an anemometer, at the breathing zone of the machine operator.

354. Therefore the combination of 1) the positioning of the jet milling machine relative to the two nearest air inlet vents, and the 2) the air velocity generated by these two vents resulted in the PNC in the breathing zone of the operator being maintained at well below the source PNC, but still slightly above the background PNC.

E.3 Discussion

355. The time-series plots from Figures 24 and 25 are reflective of the process operation and the *local background particle exposure*, and have been used in Table 14 to examine the peak PNC, mass concentration, CMD, and alveolar deposited surface area associated with Process 4.

Table 14. Summary of peak particle metrics at emission source during Process 4 operation compared to the peak associated with LBPC

PNC [p cm^{-3}] 20 to 1000nm **CPC P-Trak**		PNC 300 to 3000nm [p cm^{-3}] **OPC**		PNC >3000 to 10000nm [p cm^{-3}] **OPC**		PM$_{2.5}$ [µg m^{-3}] **DustTrak** [µg m^{-3}]		CMD [nm] **SMPS**		alveolar surface area [µm^2 cm^{-3}] **NSAM**	
Peak during	Peak of LBPC	Peak during	Peak of LBPC	Peak during	Peak of LBPC	Peak during	Peak of LBPC	Peak during	Peak of LBPC	Peak during	Peak of LBPC
1.5×10^5	5.5×10^2	8.0×10^2	< 1	2.0	<1	1.6×10^3	1	#	#	#	#

not measured
local background particle concentration (LBPC)

356. The data from Table 14 shows that Process 4 is a peak emitter of both sub- and supermicrometre particles, with the differences in values during and between process operation being greater than the manufacturer stated inaccuracy of the P-Trak, OPC, and DustTrak, and the normal variation in the background.

357. Comparison of the mean of the particle number and mass concentration during and the background, as shown in Table 4, reveals the particle emission is strong enough to maintain the particle number and mass concentration significantly above the background values for the duration of the process in the vicinity of the point of emission. Submicrometre particles dominate the particle signature. However, spatial PNC values, as shown in Figures 24 and 25, indicate the particle source is not strong enough to influence the *local background particle concentration* away from the source, nor the concentration in the breathing zone of the process operator, as measured at varying distances from the point of emission. The reason for this is related to the influence of mechanical dilution ventilation as explained in Appendix E.2.2.

358. It is clear the simultaneous use of the P-Trak, OPC, and DustTrak were able to reliable characterise both temporal and spatial particle characteristics, and a clear relationship existed between the PM$_{2.5}$ and OPC$_{300\text{-}1000nm}$ range. The three instruments were able to reliably characterise the particle source, breathing zone particle exposure, and effectiveness of ventilation controls. In addition, the simultaneous use of the P-Trak, OPC, and DustTrak was able to provide particle data across both the sub and supermicrometre size range.

APPENDIX F. PROCESS FIVE – DECANTING OF SINGLE AND MULTI-WALLED CARBON NANOTUBES

359. Decanting of solid state carbon nanotubes is a task often performed within laboratory workplaces as part of nanotechnology research.

F.1 Experimental Design and Conditions

360. This experiment involved creating contained, high concentration single walled and multi walled carbon nanotube aerosols so as to assess the use of:

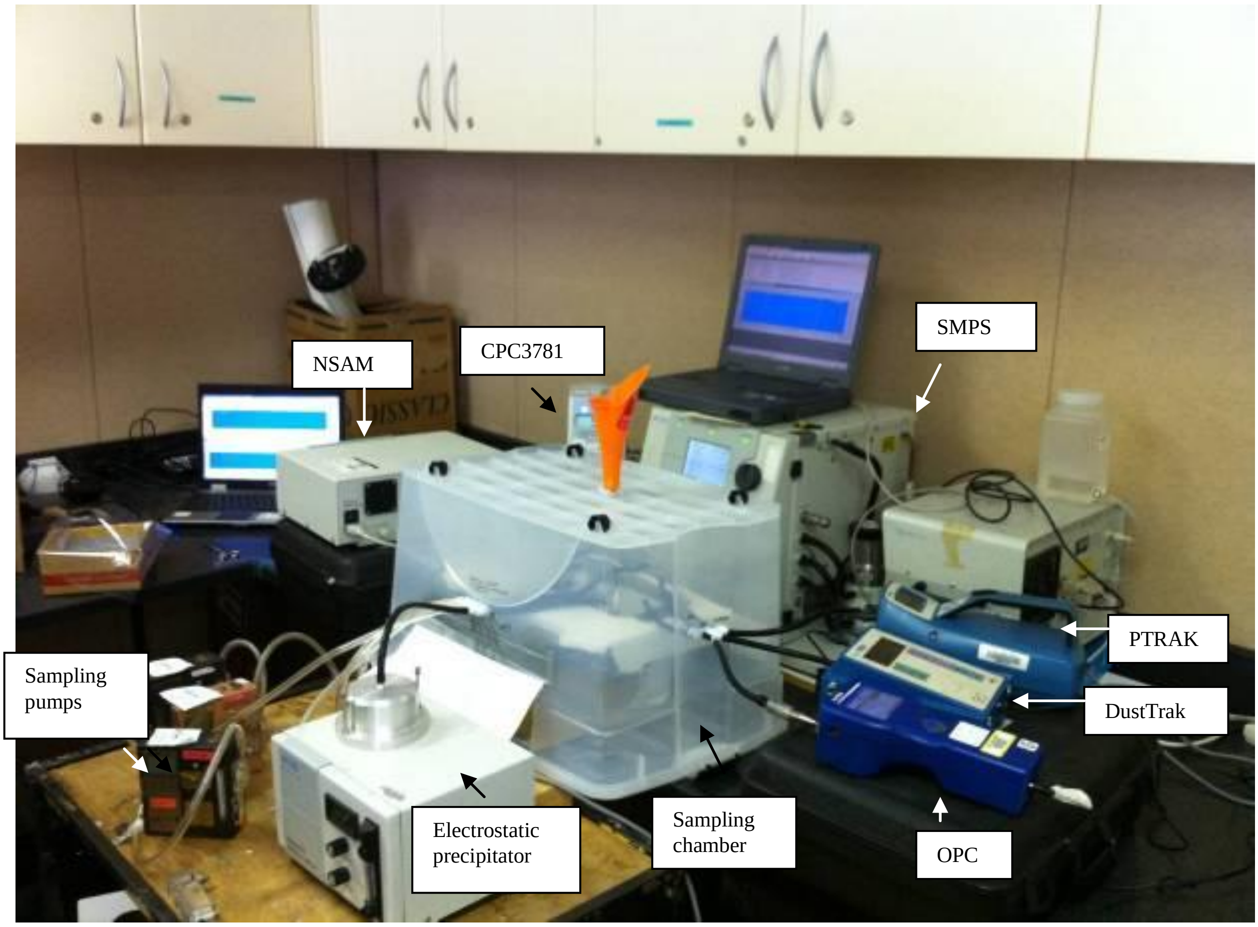
1. real-time instrumentation in characterising aerosolised carbon nanotube particle number and mass concentration, alveolar deposited surface area, and count median diameter; and
2. sampling and off-line analytical methods for characterising aerosolised carbon nanotube morphology and chemical composition.

361. A sampling chamber was constructed from a polyethylene storage container with a volume of approximately $0.07m^3$. The aerosol inlets of the following instrumentation sampled the inside of the chamber using black conductive rubber tubing connected separately to each instrument: CPC 3781, P-Trak, OPC, DustTrak, SMPS, NSAM, electrostatic precipitator containing a TEM grid, and three open face sampling cassettes containing a quartz, mixed cellulose ester, and PTFE filter respectively, all connected to SKC Aircheck Sampling pumps. Figure 26 presents a picture of this sampling chamber and instrument setup.

362. A funnel was used to introduce the carbon nanotubes (CNT), that were in a solid state powder form, to the top of the sampling chamber. The end of the funnel was positioned at a height of approximately 100mm above the sampling ends of each tube. The sampling tubes were positioned in a circle configuration at equal distances of approximately 60mm horizontally from the bottom end of the overhead funnel. The result of this configuration was a circle of sampling tubes with a circle diameter of approximately 120mm through which the CNT aerosol was propelled under the force of gravity.

363. It is noted that measured concentrations were affected by two factors; (a) the sample is divided into three tubes and (b) possible losses in the tubes, however the sampling tubing was kept as short as possible to minimise this loss. However, airborne particles were able be detected with this method.

Figure 26. Sampling chamber and instrument configuration



364. The following solid-state CNT, as described by the manufacturer specification information, were purchased for this experiment:

1. One gram of single-walled carbon nanotubes (SWCNT) – carbon >90%, ≥77% carbon as SWCNT, 0.7-0.9 nm diameter x 700 nm length (by florescence), density 1.7-1.9 g/cm^3 at 25 ºC, and produced by CoMoCAT® Catalytic Chemical Vapor Deposition (CVD) method.
2. Ten grams of multi-walled carbon nanotubes (MWCNT) – carbon >90%, >75% carbon as MWCNT, approximately 5-20 graphitic layers with MWCNT core surrounded by a fused carbon shell with the remainder being multi-layered polygonal carbon nanomaterials and amorphous and graphitic carbon nanomaterials, 7-15 nm diameter x 0.5-10 µm length, and produced by Electric Arc Discharge Method.

365. Ten aliquots of the SWCNT were introduced to the chamber via the funnel every 180 seconds on average over a period of 30 minutes. 15 aliquots of MWCNT were introduced to the chamber every 90 seconds on average over a period of 23 minutes. After each aliquot the CNTs collected in a container at the base of the sampling chamber and were then reintroduced via the funnel as the next aliquot.

366. Both types of CNT were visually observed to settle within seconds from the chamber atmosphere into the collection dish, with the MWCNTs visually settling the quickest. The first aliquot of each CNT

type consisted of the full quantity purchased. An estimated 10% of the CNTs were not retrieved over the course of the experiments with the lost CNTs being deposited upon surfaces inside the chamber. Between the introduction of the SWCNT and MWCNT, the inside surfaces of the chamber were cleaned by a wet wiping process using distilled water.

367. Because the safety data sheets for the CNTs indicated the potential for harm from inhalation, the experiment was carried out in the sealed chamber and the researchers wore P2 respirators.

368. The response of the instrumentation used in this experiment partly informed the selection of instrumentation and methodology utilised in the CNT measurements described for Process 6.

F.2 Results

369. Unlike the data presented for Processes 1 to 4, and for Process 6, the data for Process 5 does not reflect potential worker particle exposure as this data was generated within a sampling chamber in order to evaluate the response of the instrumentation and sampling methods to CNT aerosols.

F.2.1 Time series of particle number and mass concentration, count median diameter, and alveolar deposited surface area

370. Shown below are time series plots of PNC, $PM_{2.5}$, CMD, and alveolar deposited surface area for both SWCNT [Process 5-A] and MWCNT [Process 5-B]. These plots provide information on the selected particle metrics when solid CNT is aerosolised, and how the measurement and sampling methods and instrumentation respond to this type of aerosol.

371. Figures 27 and 28 compare the PNC across five particle size bands for SWCNT and MWCNT respectively. Because the PNC in the particle bin sizes of > 5000 nm were less than 1 p cm^{-3}, these PNC values have been added to the >3000nm to 5000 nm particle bin and the cumulative PNC is reported as > 3000nm to 10000nm. This process also added clarity to the data plots by reducing congestion caused by the plotting of an extra two particle bin sizes. Because the OPC particle band sizes of 300-500 nm and >500 to 1000nm overlap with the P-Trak particle band size of 20 to 1000 nm a comparison of the relative PNC strengths of each allows an estimation of the whether the aerosol is dominated by particles greater or less than 300nm. Because the operating principles of the OPC and P-Trak are very different these values have not been subtracted from one another.

372. SEM examination (discussed later in F.2.2) found that the particles measured in the aerosol could be either; (a) carbon nanotubes or (b) other particles of carbon, probably amorphous carbon arising from the nanotube synthesis.

Figure 27. Particle number concentration in submicrometre and supermicrometre size range for decanting of single-walled carbon nanotubes

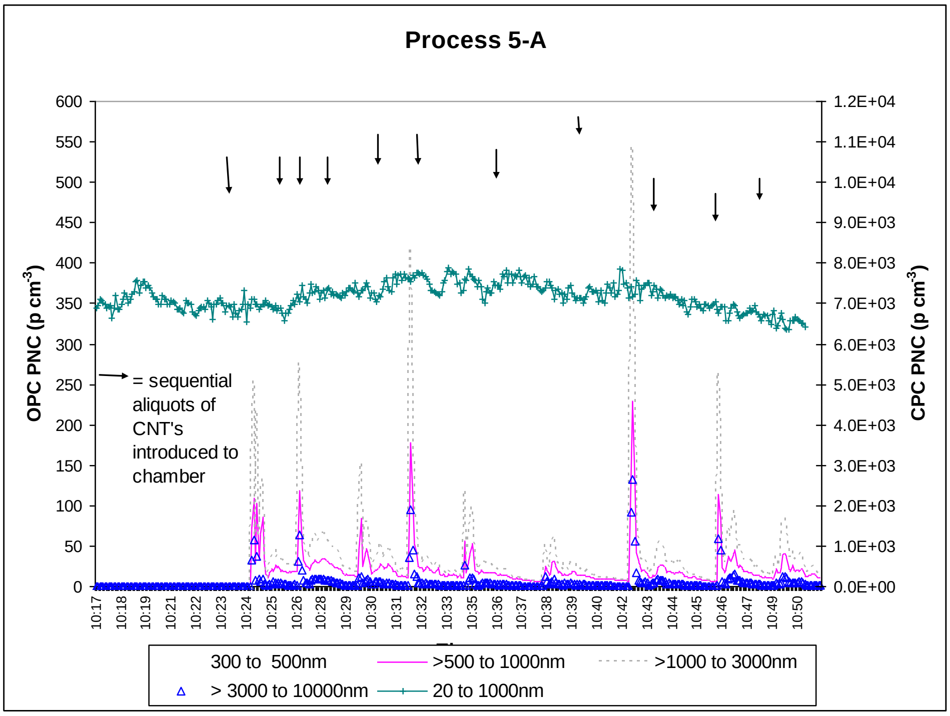
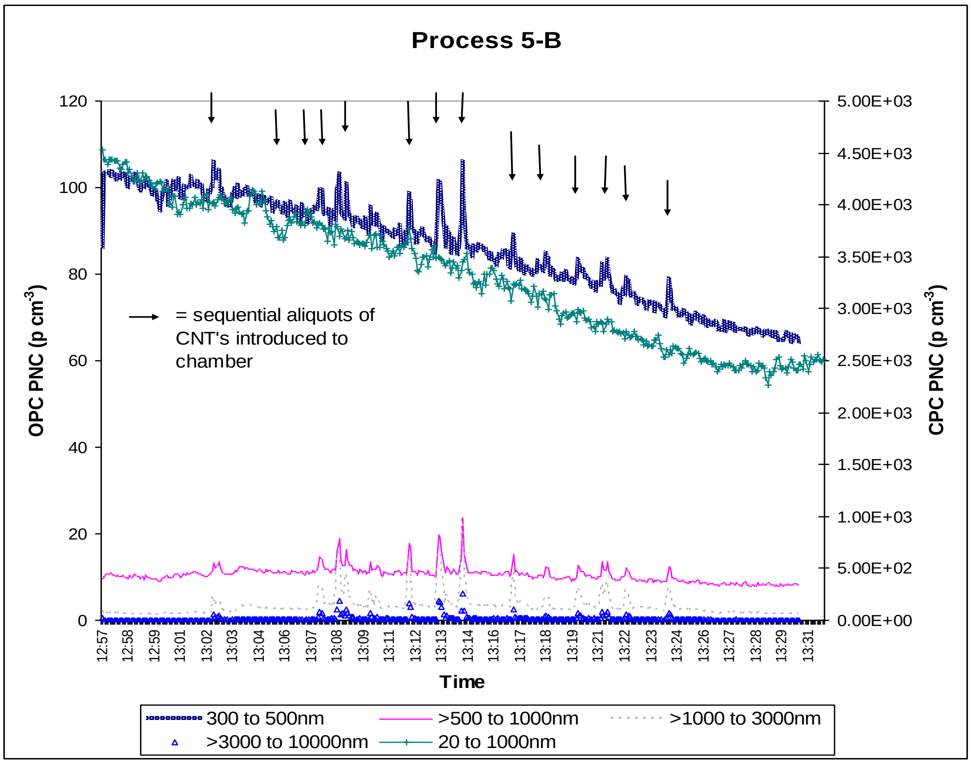


Figure 28. Particle number concentration in submicrometre and supermicrometre size range for decanting of multi-walled carbon nanotubes



373. From Figures 27 and 28 it can be seen that there is a similar trend between the introduction of each aliquot of nanotubes to the chamber and the peaks in PNC in size range > 300nm. Peaks in PNC are strongest in the size range of 300 to 3000nm for both SWCNT and MWCNT, with a stronger peak for the SWCNT compared to the MWCNT. These peaks of between 50 and 500 p cm^{-3} for the SWCNT, and 10 to 20 p cm^{-3} for the MWCNT are clearly associated with each aliquot of nanotube introduced to the chamber and these concentration values are greater than the manufacturer stated inaccuracy of the OPC. Peaks in PNC in the 20 to 1000nm size range are insignificant when the accuracy of the instrument is considered, i.e. the peaks of approximately 500 p cm^{-3} and 200 p cm^{-3} for SWCNT and MWCNT respectively are < 20% of the background (see Table 3 for data on instrument accuracy) and likely reflect normal fluctuations in background PNC.

374. Note also the bi-modal shape of the curves for many of the peaks associated with an aliquot of CNT. For the SWCNT the PNC is elevated for up to 90 seconds post aliquot, whilst for the MWCNT the PNC is elevated for up to 25 seconds post aliquot. This difference in aerosol duration is likely related to the greater density of the MWCNT's and confirms visual observation of the MWCNT's having less residency time as an aerosol than the SWCNT.

375. Figures 29 and 30 provide a comparison of particle number and mass concentration for both SWCNT and MWCNT respectively. In Figure 29, the particle mass clearly increases in line with increases in PNC (> 300nm) associated with the introduction of each aliquot of nanotubes to the chamber. Peaks in $PM_{2.5}$ concentration, also corresponding to the introduction of each aliquot of nanotubes, of up to approximately 300 µg m^{-3} were strongest for the SWCNT compared to peaks of up to 130 µg m^{-3} for MWCNT. Because these peaks correlate with the introduction of the carbon nanotubes to the chamber and because the values are greater than the manufacturer stated accuracy of the instrument they are

considered to be of significance. Peaks in PNC in size band 1000 to 3000nm correspond well to peaks in the $PM_{2.5}$ concentration which would be expected due to the similarity in particle size measurement bands of both instruments.

376. Note the particle mass series show a similar bi-modal peak shape as the > 500 nm PNC curves. In addition, the $PM_{2.5}$ concentration for the SWCNT aerosols remains elevated for longer than that of the MWCNT aerosols, a pattern similar to that observed for the supermicrometre PNC data.

Figure 29. Particle number and mass concentration in submicrometre and supermicrometre size range for decanting of single-walled carbon nanotubes

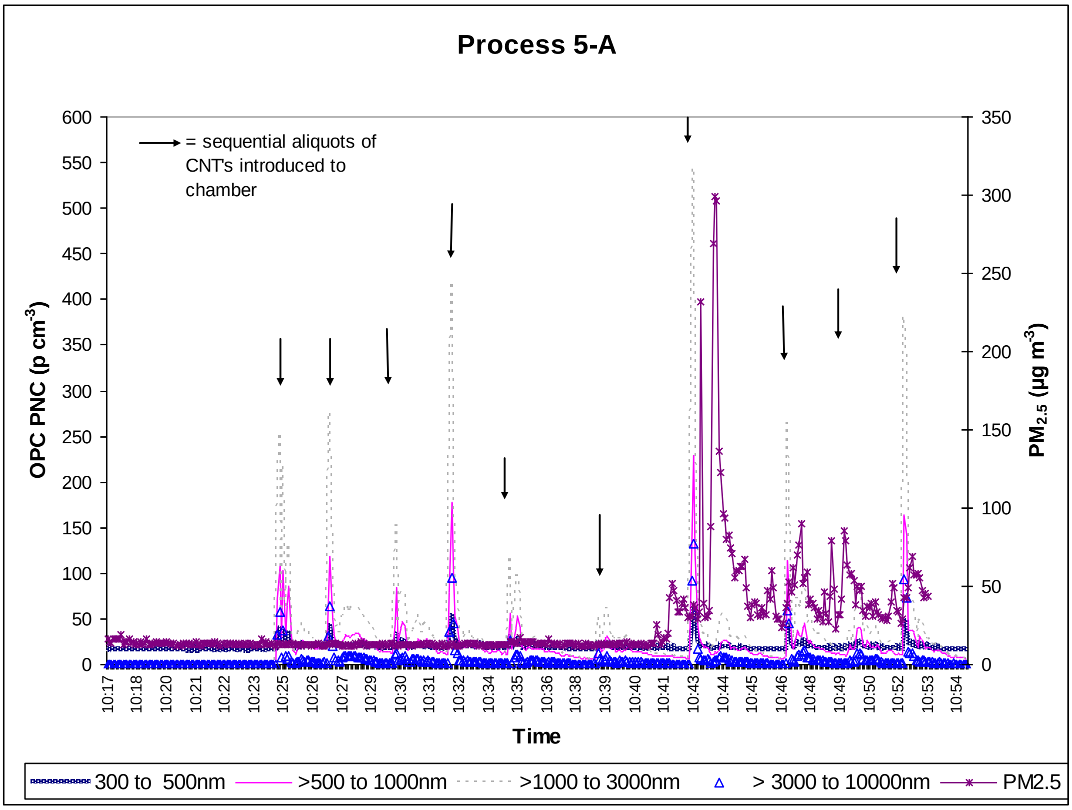
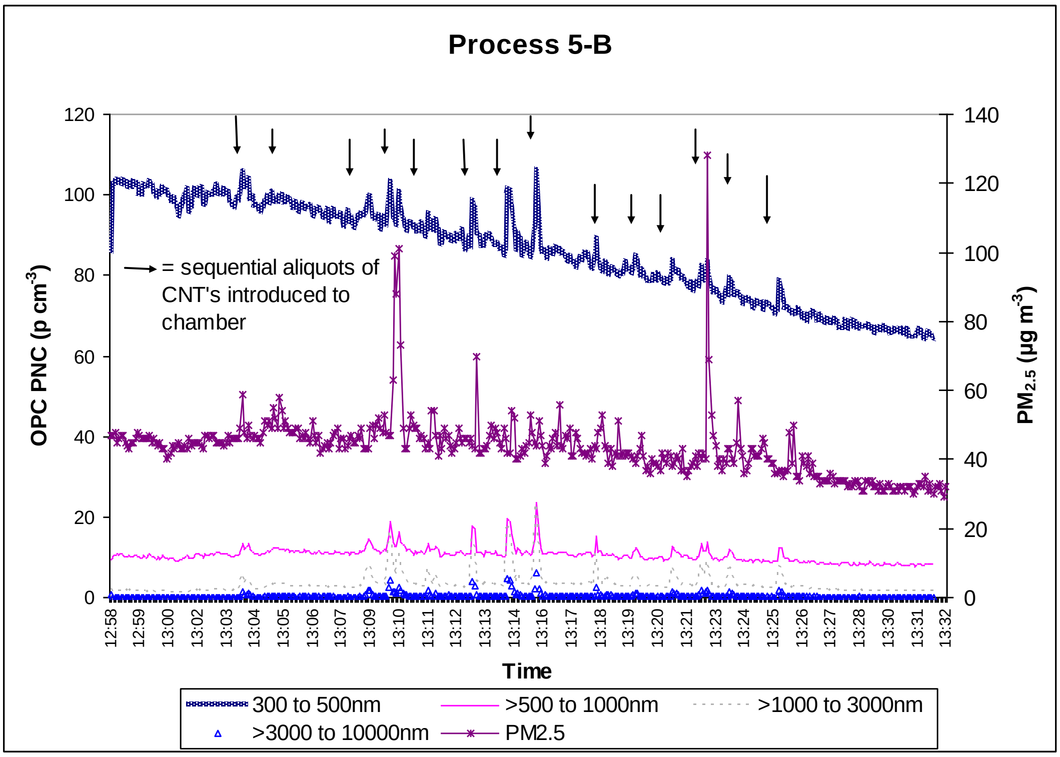


Figure 30. Particle number and mass concentration in submicrometre and supermicrometre size range for decanting of multi-walled carbon nanotubes



377. Figures 31 and 32 compare the alveolar deposited surface area and PNC > 300 nm for the SWCNT and MWCNT aerosols respectively.

Figure 31. Particle number concentration in submicrometre and supermicrometre size range and alveolar deposited surface area for decanting of single-walled carbon nanotubes

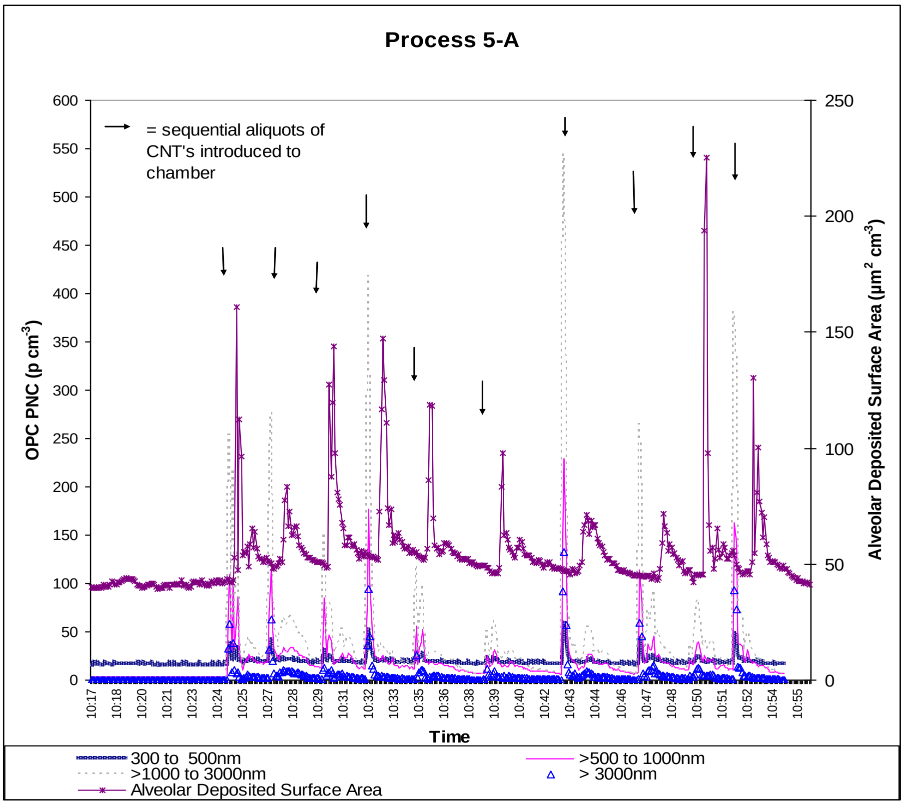
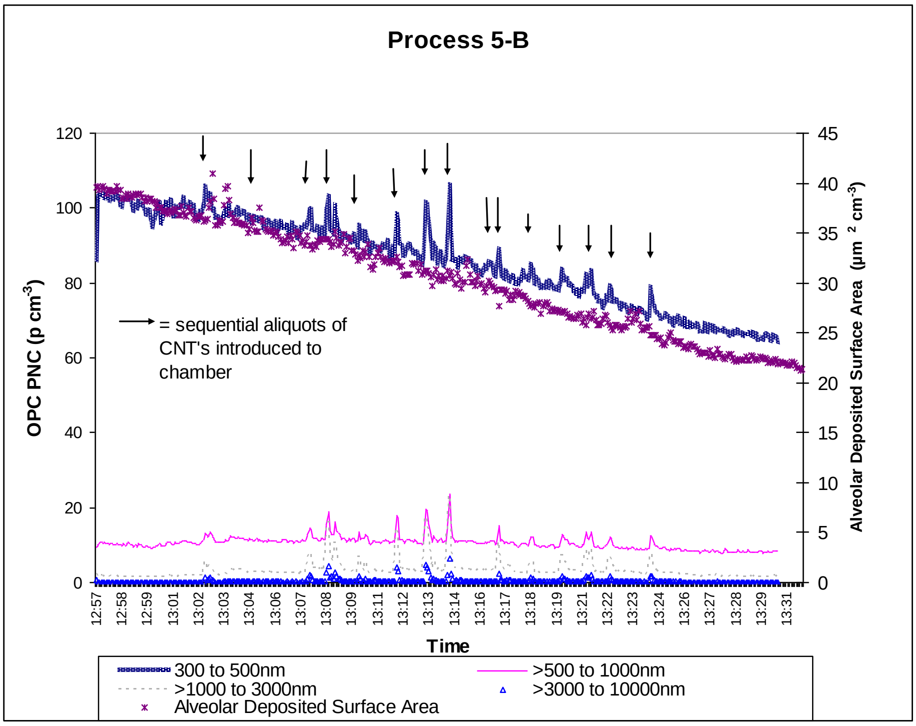


Figure 32. **Particle number concentration in submicrometer and supermicrometre size range and alveolar deposited surface area for decanting of multi-walled carbon nanotubes**



378. It can be seen the NSAM was able to detect an increase in the alveolar deposited surface area of the aerosol corresponding to the introduction of each aliquot of carbon nanotubes. The increase in alveolar deposited surface area over the background was much stronger and consistent for the SWCNT than the MWCNT, up to 200 µm^2 cm^{-3} versus 10 µm^2 cm^{-3}, respectively. This increase in alveolar deposited surface area for the SWCNT's can be considered significant when compared to background because it is greater than the manufacturer stated inaccuracy of the NSAM and the normal fluctuation in background. In contrast, the change in deposited surface area for the MWCNT's was within the manufacturer stated accuracy of the NSAM and therefore cannot be concluded to be significant. The delay in NSAM response following the peaks in PNC is likely associated with the averaging time of the NSAM instrument.

379. The significant peaks in alveolar deposited surface area confirm the process is a significant source of submicrometre particles. However, as described in Table 1, because of the likely concentration of supermicrometre particles associated with Process 5, the NSAM data cannot be used with confidence regarding actual alveolar deposited surface area.

380. The count median diameter (CMD) of the single- and multi-walled carbon nanotube aerosols are presented in Figures 33 and 34 respectively.

Figure 33. Count median diameter size range of 4 to 160nm for decanting of single-walled carbon nanotubes

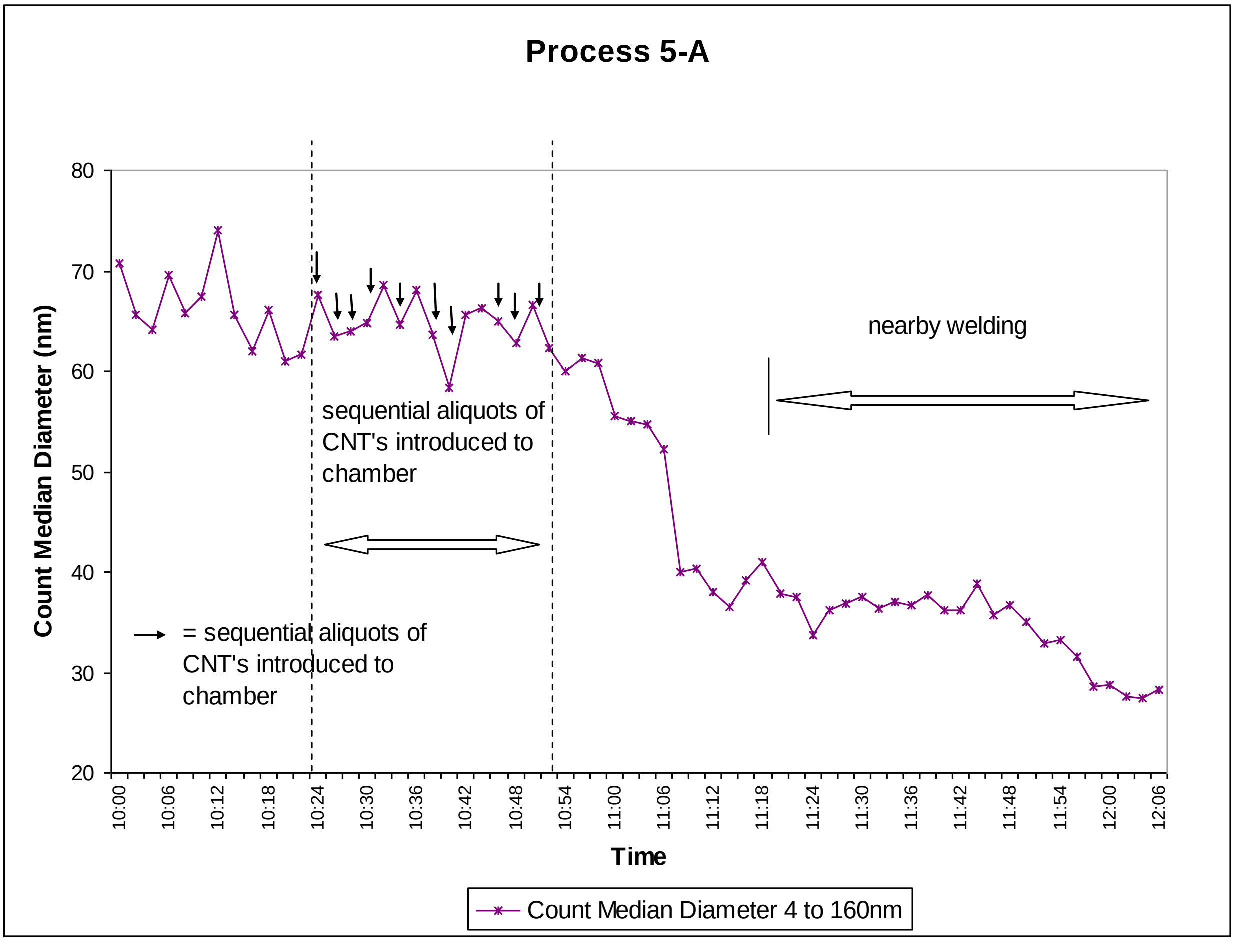
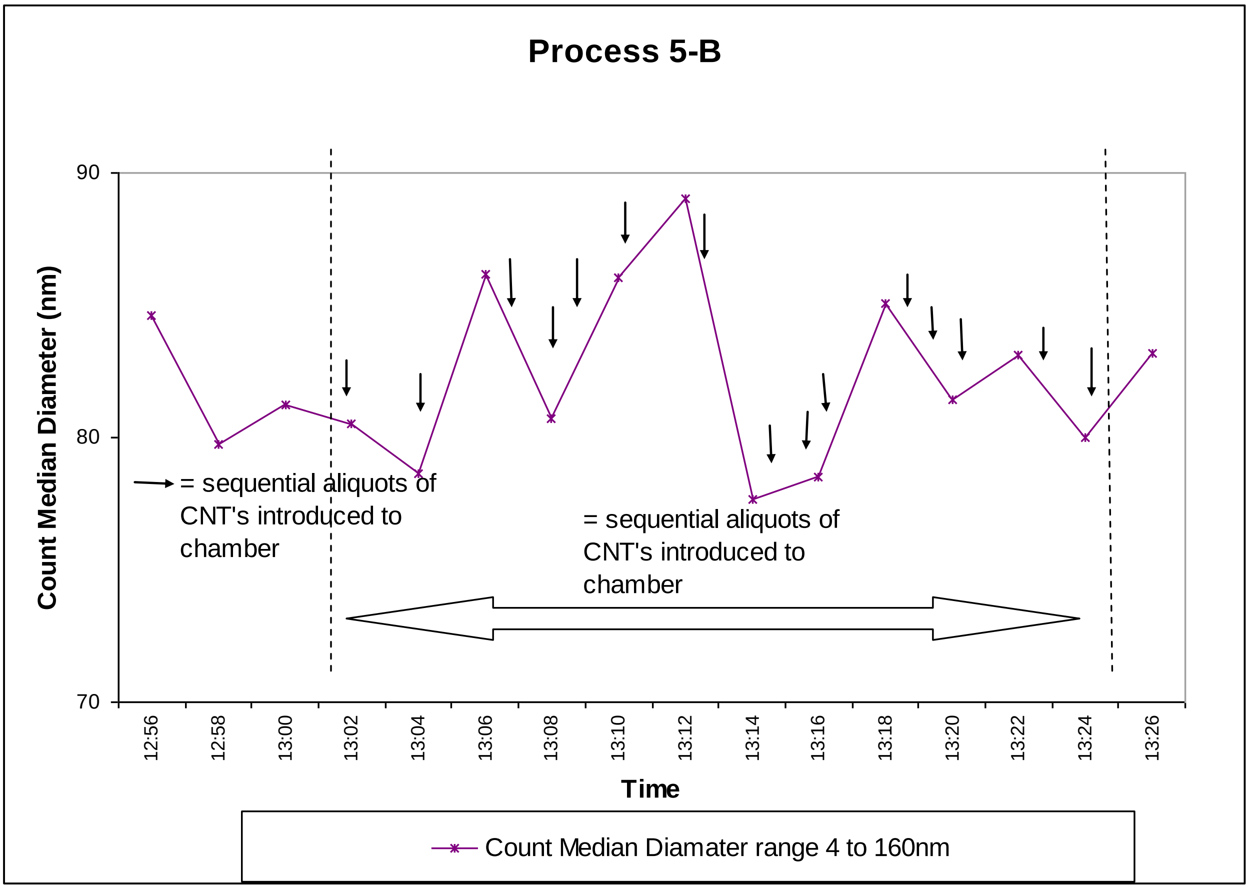


Figure 34. Count median diameter size range of 4 to 160nm for decanting of multi-walled carbon nanotubes



381. Note that the fluctuation in CMD for both the SWCNT and MWCNT is similar before, during, and after the experiment. In addition, there is no pattern of change in CMD associated with the introduction of the aliquots of carbon nanotubes. Therefore the fluctuation in CMD observed during the introduction of both the SWCNT and MWCNT is likely due to normal changes to the background. This finding is expected due to the measurement range of the SMPS being 4 to160nm and the particle number and mass concentration data presented in Figures 29 and 30 clearly showed the nanotube aerosol to be dominated by particles greater than 300nm in size, i.e. greater than the upper measurement range of the SMPS. This finding supports the conclusion that the dominant particle size of both the single and multi-walled carbon nanotubes was greater than 300nm and likely within the supermicrometre range.

F.2.2 Electron microscopy analysis of particles

Methodology

382. Following introduction of the SWCNT and MWCNT aliquots into the sampling chamber, the carbon nanotubes were collected onto open-face sampling cassettes containing mixed cellulose ester (MCE) and PTFE filter membranes, which were connected to sampling pumps. In addition, an electrostatic precipitator was used to collect SWCNT's onto a TEM grid coated with a thin polymer film. The amounts and characteristics of the nanotube samples on the filters were assessed by SEM and the grid was examined

by TEM. Segments, approximately 6 x 6mm, were cut from the filters and glued onto SEM mounts using carbon paint. The filter samples were then coated with a thin conductive layer of evaporated carbon in a high vacuum evaporator prior to examination in the SEM. Uncoated filter samples were also prepared so as to assess if the coating process changed the samples. Segments of filter not exposed to nanotubes were prepared in the same manner and were used as controls.

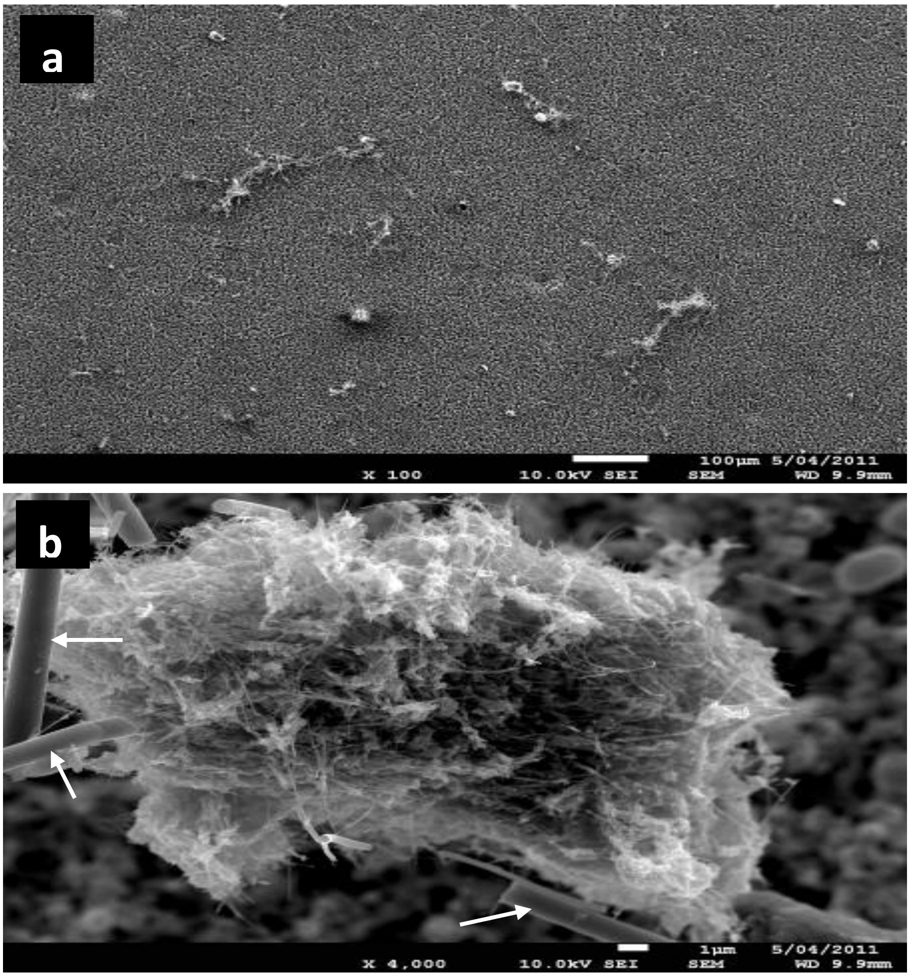
383. The filter samples were examined in a JEOL 7001F field-emission SEM. The TEM grid was examined using a Philips CM200 TEM and a JEOL 2100 TEM. The TEM's were operated at 200kV. A JEOL energy-dispersive X-ray (EDX) microanalysis system fitted to the JEOL2100 was used to check the composition of the collected nanotube samples for potential extraneous material such as catalyst particles.

Results

384. SEM examination of the MCE and PTFE control filters showed no nanotubes, and only a few small clumps of graphitic carbon originating from the evaporative coating process.

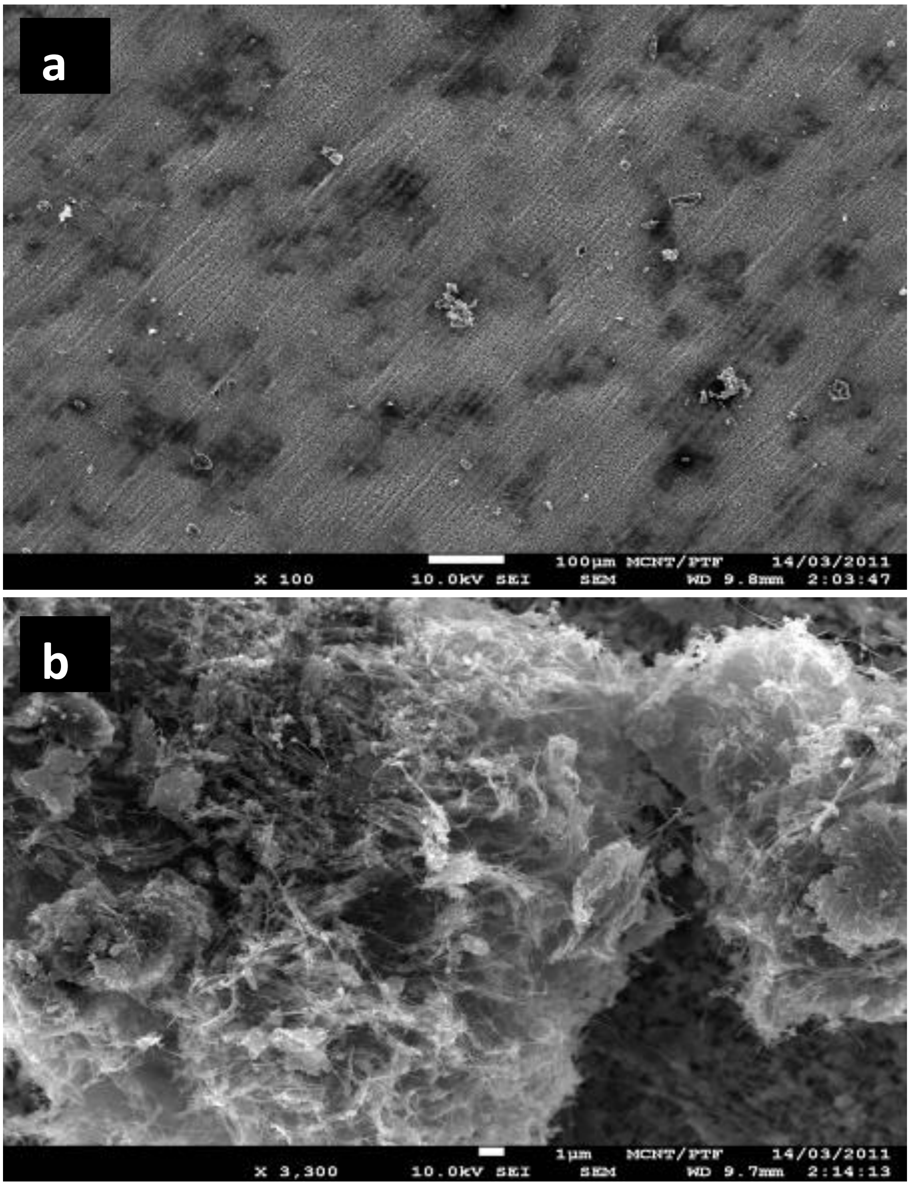
385. The MCE filter used for the MWCNT aerosol showed scattered clusters consisting of both particles and MWCNTs (Figure 35 a, b). The particulate material was found to be also carbon, probably amorphous carbon arising from the nanotube synthesis. Many of the clusters contained fibreglass fibres (identified by EDX) mixed with the nanotubes (Figure 35b).

Figure 35. MWCNT sample on MCE filter; (a) scattered clusters of nanotubes and amorphous material, (b) a cluster of amorphous carbon and nanotubes, together with some fibreglass fibres (arrows).



The PTFE filter used for the MWCNT aerosol was similar to the MCE filter in that it also contained scattered clusters of carbon particles and nanotubes, with some fine fibreglass fibres interspersed in the clusters (Figure 36 a, b).

Figure 36. MWCNT sample on PTFE filter; (a) scattered clusters of nanotubes and amorphous material on the filter; (b) a large cluster of amorphous carbon material and nanotubes.



386. The clusters observed in both MWCNT samples varied in size but many were well in excess of 10µm in length. Some smaller clusters in the range 0.5 – 2µm were observed in the MWCNT sample on the PTFE filter but these clusters contained particles only and no nanotubes which is consistent with the response of the real-time instruments in the particle bin sizes of 500 to 3000 p cm^{-3}. The likely reason for the 10 µm length particles not be characterised in real time by the OPC is: 1) the OPC has an upper measurement range of 10 µm, and 2) the OPC was calibrated for spherical particles. Therefore, the characterisation of PM$_{2.5}$ is advantageous as these larger particles are likely to have a mass able to be estimated by a photometer, and this was evident in the time series plot in Figure 30.

387. The SWCNT samples collected on the MCE and PTFE filters (Figures 37 and 38) showed a greater concentration of clusters than was observed with the MWCNT samples. The clusters comprised mainly carbon particles with aggregates of nanotubes within the clusters. The cluster sizes varied extensively from below 1µm to above 10µm, again consistent with the real-time instrument results. The images suggested that the SWCNT samples contained a large fraction of amorphous or possibly graphitic carbon content. Some octahedral Mo crystals (identified by EDX, and possibly a Mo oxide) were present in the SWCNT samples, and these probably represent a catalyst used in the synthesis of the SWCNT material.

Figure 37. SWCNT sample on MCE filter; (a) clusters observed on the filter; (b) a large cluster of mainly amorphous carbon with some nanotubes.

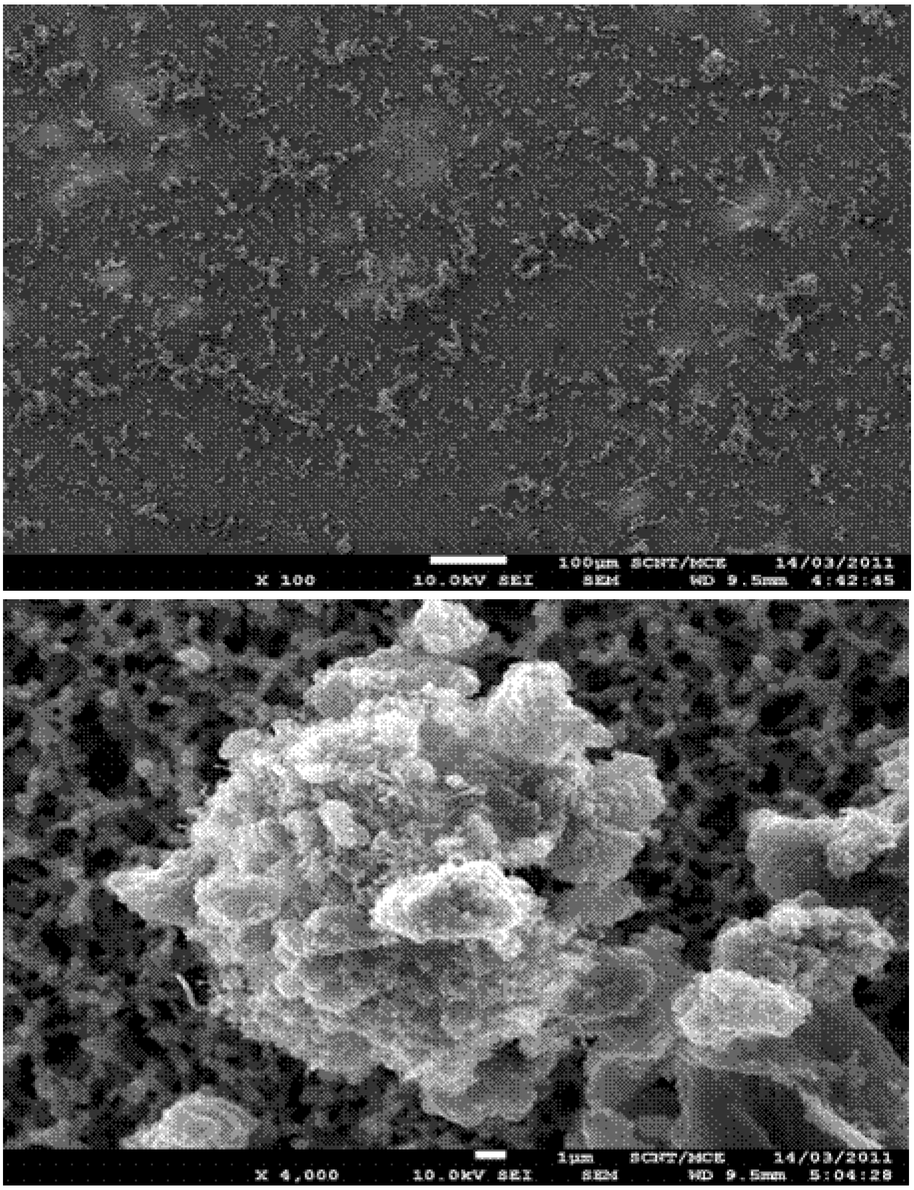
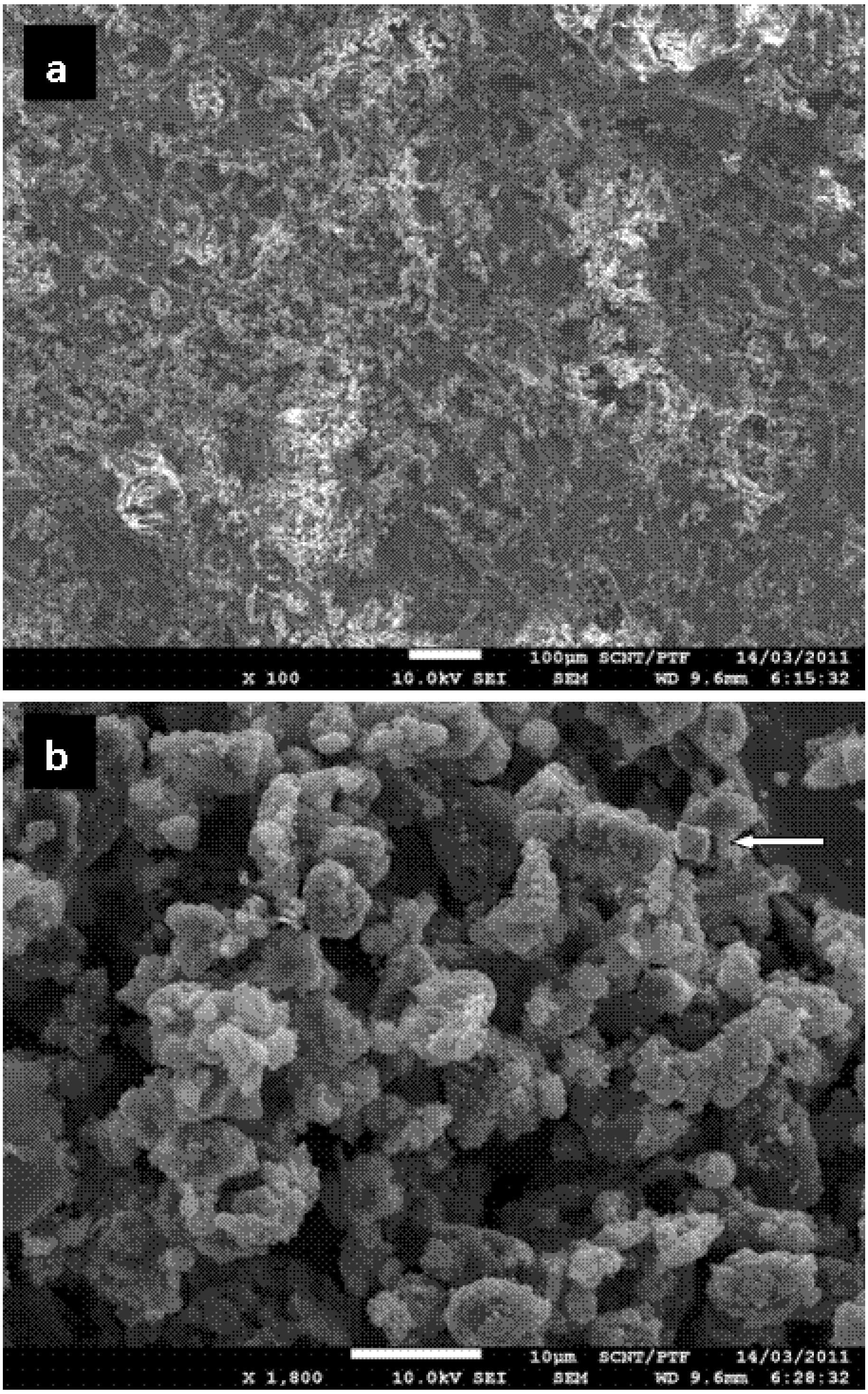


Figure 38. SWCNT sample on PTFE; (a) dense coating of clusters on the filter; (b) details of a large cluster showing smaller aggregates; the arrow indicates a Mo crystal.



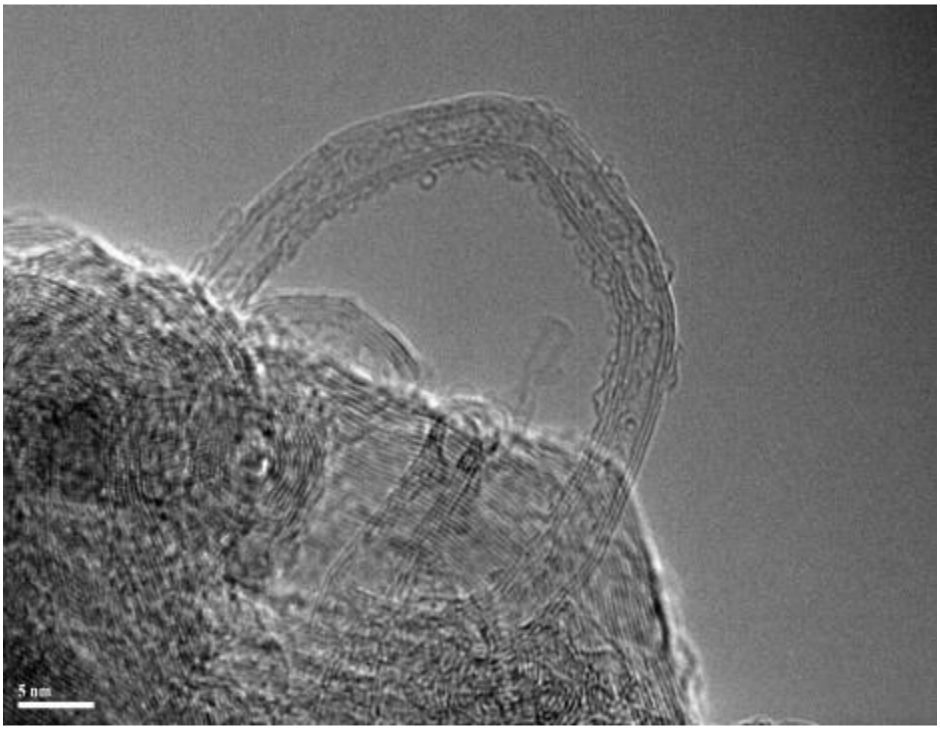
388. These SEM results showed that nanotubes were able to be successfully collected onto the MCE and PTFE filters, but that they were aggregated and mixed with substantial amounts of apparently

amorphous carbon. These clusters were also observed in the TEM examination of the grid. The cluster sizes were of the order of microns and of low aspect ratio. These results support the real-time instrumentation results of PNC in bin sizes of 1000 to 3000nm.

389. The amorphous content qualitatively appeared greater than would be expected from the manufacturer's specifications. Since the carbon coating process in SEM preparation involves a high temperature carbon arc, we checked whether the coating process might have degraded the nanotube samples. Several nanotube samples on the filters were examined uncoated using a low vacuum mode on the SEM to minimise sample charging. These images showed that considerable amorphous content was also present in the uncoated samples, and therefore we conclude that the coating process did not significantly change the samples.

390. A TEM examination of the SWCNT sample (Figure 39) showed that although SWCNTs were present much of the extraneous carbon material appeared to be graphitic, as evidenced by the lattice fringes. The clusters observed on the TEM grid were of the order of 0.2 – 2µm.

Figure 39. A high resolution TEM image of the SWCNT sample on a TEM grid.



391. Though all the collected samples contained carbon nanotubes, there was a considerable amount of non-nanotube carbon material in the samples, and this probably reflects the composition of the supplied nanotube material. When nanotubes are synthesised, much of the carbon goes into amorphous, graphitic or other fullerene carbon forms. Also, when SWCNTs are prepared it is likely that there will be a component of MWCNTs also formed.

392. Almost universally the carbon nanotubes were in the form of aggregates. Single nanotubes were almost never observed in these samples. The presence of mostly supermicrometre sized clusters in the collected nanotube samples suggest that when this CNT powder is suspended in air, it is likely that these

larger clusters would be respired rather than single nanotubes. Therefore, the potential particle exposure and health effects are a function of the morphology/form of the material.

F.2.3 Estimating mass concentration of carbon nanotube aerosols - elemental carbon analysis and real time mass concentration measurements

393. In the 2010 draft Current Intelligence Bulletin *Occupational Exposure to Carbon Nanotubes and Nanofibers*, the US NIOSH proposed a REL of 7 µg/m^3 elemental carbon (EC) 8-hr TWA for carbon nanotubes and nanofibres, which was set at the upper limit of quantitation (LOQ) for NIOSH Method 5040 [79]. In view of quantified health risks at 7 µg/m^3 and ongoing improvements in sampling and analytical methodologies, NIOSH is now proposing a REL of 1 µg/m^3 EC as an 8-hr TWA respirable mass concentration using NIOSH Method 5040 [111], noting that efforts should be made to reduce airborne concentrations to carbon nanotubes and nanofibres as low as possible.

394. The NIOSH recommendation represents a divergence from the dominant paradigm of particle number or size for exposure assessment within the scientific literature regarding nanomaterials [14, 17, 38, 41, 42].

395. Therefore an additional experiment for Processes 5A and 5B was designed to:

1. evaluate both the DustTrak and elemental carbon sampling and analysis method to provide mass concentration data, and
2. compare and contrast these results from single walled and multi walled carbon nanotube aerosols.

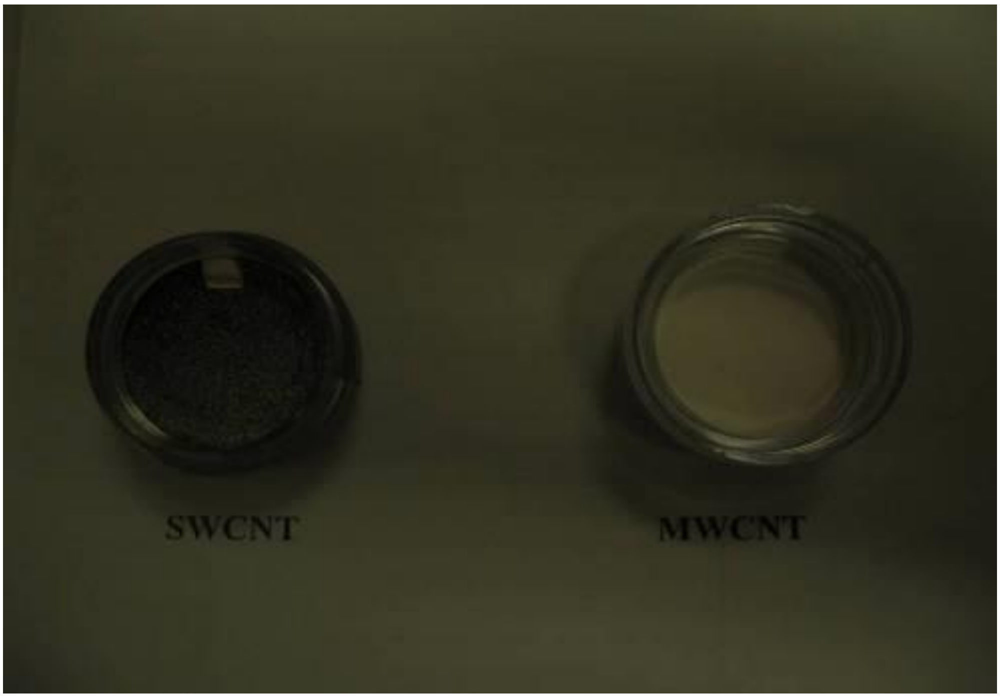
396. In this experiment, two aerosols, one containing SWCNT and the other MWCNT, were sampled using a pump to draw the aerosol through quartz filters and then the concentration of elemental carbon on the quartz filter was calculated using Evolved Gas Analysis by a thermal-optical analyser in accordance with the NIOSH Method 5040. A DustTrak simultaneously sampled the same aerosols. Note that this experiment was carried out in a sampling chamber under the conditions described in section 7.6.1 and as such, the measurement results, which can be found in Table 4, do not represent particle concentrations likely to be encountered within a workplace environment.

397. From Table 4, the elemental carbon (EC) mass concentration obtained using NIOSH Method 5040 was 1474 µg m^{-3} for Process 5A (SWCNT), and < 2 µg m^{-3} for Process 5B (MWCNT). Background elemental carbon mass concentration between the process operation was not collected, however Chan et al, [88] reported the EC component of the ambient PM_{10} in Brisbane, Australia, to be 2.367 µg m^{-3} (mean value of 47 samples). The mean of the $PM_{2.5}$ concentration from simultaneous measurements using a DustTrak were 56 µg m^{-3} for Process 5A (14 µg m^{-3} between the process), and 35 µg m^{-3} for Process 5B (25 µg m^{-3} between the process), and thus both these concentrations are significantly higher than background values. For Process 5A, peak measurements were 300 µg m^{-3} during the process and 14 µg m^{-3} between the process, and for Process 5B, peak measurements were 130 µg m^{-3} during the process and 38 µg m^{-3} between the process (Table 15).

398. The mass concentration of the SWCNT aerosol was clearly higher than that of the MWCNT aerosol and the filter from the SWCNT aerosol was overloaded with uneven particle distribution. These findings support the earlier conclusion that the MWCNT settle from the aerosol at a much quicker rate than that of the SWCNT. Although the flow rate of the pumps, filter location and orientation relative to the point of introduction of the nanotubes to the chamber, and sampling time were virtually the same, the filter used for the SWCNTs was covered with a heavy black carbon deposit, and that used for the MWCNTs had minimal particle deposition. This can be seen in Figure 40. This difference in particle deposition is also

reflected in the elemental carbon analysis conducted on these filters, with that of the SWCNTs three orders of magnitude higher than the MWCNTs.

Figure 40. Photograph of the open face cassettes containing the filters used to capture nanotubes. The SWCNT filter on the left shows significantly more particle deposition than the MWCNT filter on the right.



399. The data from this experiment, albeit from only two samples, indicates that both the NIOSH Method 5040 and the DustTrak can be used for identifying an aerosol arising from a CNT process. It also indicates that although there is a positive relationship between the results of the two methods there is not direct correlation of results. This is not surprising considering the NIOSH method is based upon thermal desorption analysis, whilst the DustTrak utilises a light scattering method and converts this to mass concentration. Results indicate that for carbon nanotubes, the DustTrak is best utilised to indicate relative changes rather than absolute concentrations.

F.3 Discussion

400. The data from Figures 27 and 34 has been used in Table 15 to examine the peak PNC, mass concentration, CMD, and alveolar deposited surface area, both during and between operation of Processes 5A and 5B.

Table 15. : Summary of peak particle metrics at the point of emission during and between operation of Processes 5A and 5B

	PNC [p cm^{-3}] 20 to 1000nm **CPC P-Trak**		PNC 300 to 3000nm [p cm^{-3}] **OPC**		PNC >3000 to 10000nm [p cm^{-3}] **OPC**		PM$_{2.5}$ [µg m^{-3}] **DustTrak** [µg m^{-3}]		CMD [nm] **SMPS**		alveolar surface area [µm^{2} cm^{-3}] **NSAM**	
	Peak during	Peak between	Peak during	Peak between	Peak during	Peak between	Peak during	Peak between	Peak during	Peak between	Peak during	Peak between
5A	7.5 x 10^{3}	7.0 x 10^{3}	550	1	130	< 1	300	14	65	74	230	50
5B	4.3 x 10^{3}	4.4 x 10^{3}	110	80	4	< 1	130	38	88	84	40	39

401. The data in Table 15 shows the peaks in supermicrometre particle number and mass concentration measured during operation of both processes 5A and 5B, and in alveolar deposited surface area for 5A, are significant when compared to the peaks between operation of the processes and the manufacturer stated inaccuracy of the instruments. The peaks associated with SWCNT aerosol were stronger than that for the MWCNT.

402. Comparison of the mean of the particle number and mass concentration during and between operation of Process 5A, as shown in Table 4, reveals the strength of the particle emission is strong enough to maintain the particle number and mass concentration significantly above the background values in the vicinity of the point of emission. In contrast, the weaker particle emissions for Process 5B had an insignificant contribution to the mean of the background particle metrics. These findings are relevant as they suggest the SWCNT may have a greater likelihood of influencing the work environment and worker exposure.

403. Under the experimental conditions generated in the chamber, the CNT particles (predominantly agglomerates of carbon nanotubes in the size range 300-3000nm, see later) did not remain in aerosol phase for prolonged periods as evidenced by the particle number and mass concentrations, and by alveolar deposited particle fractions returning to background levels within seconds of the introduction of each aliquot of CNTs.

404. The data from the P-Trak was inconclusive. The P-Trak, measurement range of 20 to 1000nm, recorded increases in PNC on average of 500 and 200 p cm^{-3} at each aliquot of SWCNT and MWCNT, respectively. Such increases, which were consistent with normal fluctuation in background and the manufacturer stated inaccuracy of the instrument (in this case < ±20% of the background) could be concluded to be insignificant. However when assessed in conjunction with the data from the OPC, NSAM, and SMPS it is possible the increases in P-Trak values reflect relatively weak increases in sub-micrometre PNC. This is an important observation in that the ability of real-time CPC to detect emissions from weak nanomaterial sources is limited when concentrations are not significantly different to background levels.

405. The particle number and mass concentration, and alveolar deposited surface area was greater for the SWCNT than the MWCNT. The likely reason is the higher mass of the larger aggregated MWCNT resulted in the nanotubes depositing on surfaces of the chamber at a greater rate.

Conclusions

406. When all the above data is considered the following general conclusions can be made regarding the CNT aerosols.

407. The CNT particles do not remain in aerosol phase for prolonged periods as evidenced by the particle number and mass concentrations, and alveolar deposited particle fractions returning to background levels within seconds of the introduction of each aliquot of CNTs.

408. The dominant particle size of both the SWCNT and MWCNT aerosols was in the range of between 300 and 3000 nm. This conclusion was deduced from analysis and comparison of the following particle data:

- The OPC particle bin sizes of between 300 and 3000nm registered a significant increase in PNC during the introduction of the CNTs to the chamber;
- The DustTrak, measurement range of 100 to 2500nm, registered a corresponding increase in mass concentration;
- The NSAM, measurement range of 10 to 1000nm, registered a corresponding increase in alveolar deposited surface area;
- The P-Trak, measurement range of 20 to 1000nm, and the SMPS, measurement range 4 to 160nm, did not register a corresponding change in PNC and CMD respectively.

409. The order of magnitude greater PNC of the SWCNT compared to the MWCNT likely reflects the difference in mass between the nanotubes with the heavier MWCNT spending less time in the aerosol phase.

410. The particle number and mass concentration, and alveolar deposited surface area were significantly higher for the SWCNT compared to the MWCNT. The likely reason the higher mass of the larger aggregated MWCNT resulted in the nanotubes depositing on surfaces of the chamber at a rate faster so that the real-time instrumentation could not fully characterise the particles. Evidence for this conclusion comes 1) from visual observations by the researchers; and 2) the degree of carbon deposition upon particle filters used to capture the nanotubes.

411. The aggregate of data provided by the PTrak, OPC, and DustTrak was useful in that it allowed cross validation of individual instrument responses. For example, the DustTrak results validated the OPC results. The SEM and TEM results confirmed the response of the real-time instruments were to CNT particles rather than background particles. The NSAM results confirmed the instrument can be used to characterise peak emission of particles, but unless the particles within the aerosol are known to be smaller in size than 400nm, the results cannot be used in regard to actual lung deposited surface area dose.

APPENDIX G. PROCESS 6 – SYNTHESIS OF CARBON NANOTUBES USING CHEMICAL VAPOUR DEPOSITION

G.1 Experimental Design and Conditions

412. This experiment involved characterising the particle number and mass concentration arising from the operation of two Chemical Vapour Deposition (CVD) processes for the production of carbon nanotubes (CNTs), and assessment of the ability of the process chambers and fume cabinets to prevent particle leakage into the laboratory atmosphere.

413. CNTs are synthesized on glass substrates coated with thin layers (10 nm) of nickel as catalyst. The CVD process is realized by decomposition of a hydrocarbon gas at high temperature (600°C-1000°C). The thermal dissociation of the gas produces carbon atoms that are free to react and diffuse into the Ni catalyst particles, giving rise to the nucleation and growth of CNTs.

414. The first process, Process 6-A, utilised a sealed furnace chamber consisting of an insulated ceramic tube, which can be heated up to 1000°C through a resistive metal spiral wrapped around it. The sample was placed downstream into the chamber and the process temperature was set. Acetylene gas was introduced into the furnace at 650°C, triggering the CVD synthesis. The gas was then passively exhausted from the chamber via a tube into a fume hood.

415. The second process, Process 6-B, utilised a SabreTube^{TM} Bench Top Thermal Processing System. It incorporated a transparent quartz tube into which a conductive sample holder made of Si can be resistively heated by direct current flow. The substrate was placed on top of the sample holder and a feedback controller set the current flow required to keep the holder at the process temperature, 750°C in this case. The temperature was constantly measured via a high-precision infrared sensor. Acetylene was allowed to flow into the tube in order to initiate the CVD synthesis. The gas was passively exhausted through a tube towards a fume hood.

416. A P-Trak, OPC, and DustTrak were positioned side by side on a tray so as the instruments aerosol inlets could be moved in unison to the desired measurement locations. These instruments were utilised to characterise the particle number and mass concentration in the laboratory during and after operation of the CVD processes (laboratory background), during operation of the processes at measurement locations that included the outside perimeters of both process chambers, and at the end of the exhaust tube within the fume cabinet. This allowed assessment of the 1) the ability of both chambers to contain particle leakage into the laboratory, 2) the particle number and mass concentration resulting from the CVD within the chambers, 3) the response of the instruments to particles arising from CVD of CNT’s, and 4) capacity of the fume cabinet to contain the particles exhausted from the CVD processes.

G.2 Results

G.2.1 Time series of particle number and mass concentration

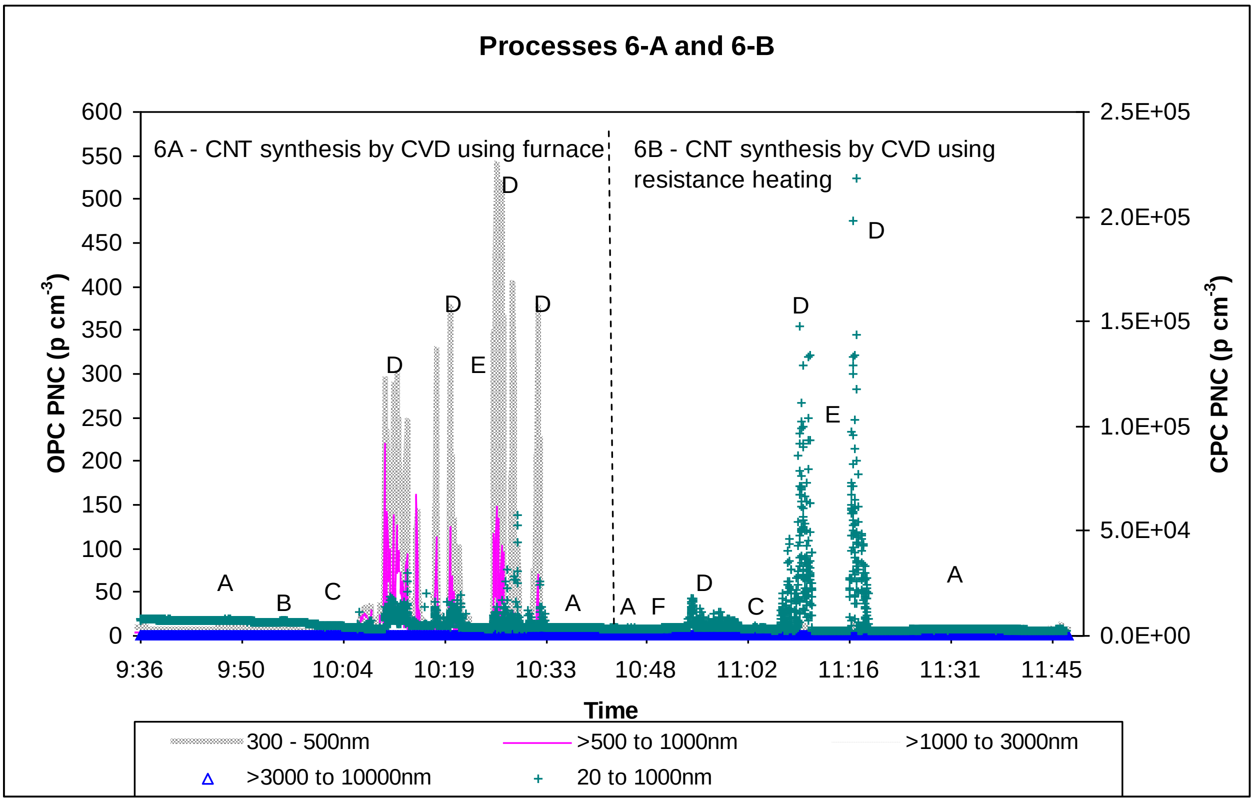
417. Shown below are time series-plots of PNC and particle mass concentration ($PM_{2.5}$), for both process 6-A and 6-B, including temporal and spatial measurement data.

418. Figure 41 provides PNC data in the range of 20nm to 10,000nm. It can be seen that the particle emission is different between both processes with the PNC for Process 6-B concentrated in the size range 20 to 1000nm whilst for Process 6-A the PNC response is significant in the 300 to 1000 nm size range. It

can also be seen that: 1) airborne particles are produced as part of the CVD process; (2) the P-Trak and OPC are capable of characterising such particles; 3) the CVD furnace enclosures contain particle leakage to the laboratory atmosphere; 4) the fume cabinet is capable of containing the particles exhausted from the processes.

Figure 41. Particle number concentration (PNC) measured at various locations during two different condensation vapour deposition CNT synthesis processes. .

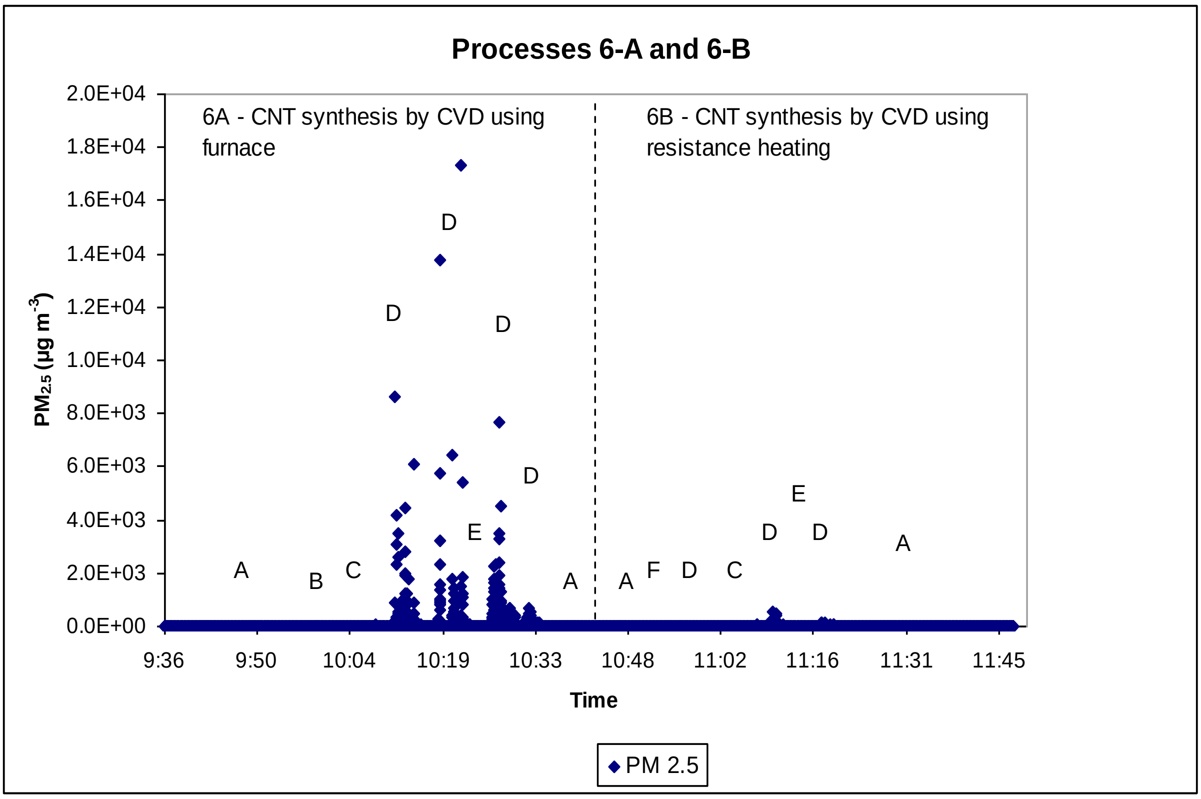
Measurement locations, marked A to F in the figure, were as follows: A = Background ambient PNC at various locations around the room; B = commencement of first CNT synthesis; C = entire outer surface of furnace; D = end of furnace extraction tube inside fume cabinet; E = outside and along sash opening to fume cabinet; F = commencement of second CNT synthesis



419. Figure 42 provides $PM_{2.5}$ concentration data measured simultaneously with that of the PNC and confirms that the particle signature for Process 6-A is within the supermicrometre size range, whilst that for Process 6-B is within the submicrometre size range. These peaks in the $PM_{2.5}$ concentration correspond well with the peaks in PNC in size band 300 to 1000nm for Process 6-A as shown in Figure 41.

Figure 42. Particle mass concentration (PM2.5) measured at various locations during two different condensation vapour deposition CNT synthesis processes. .

Measurement locations, marked A to F in the figure, were as follows: A = Background ambient PNC at various locations around the room; B = commencement of first CNT synthesis; C = entire outer surface of furnace; D = end of furnace extraction tube inside fume cabinet; E = outside and along sash opening to fume cabinet; F = commencement of second CNT synthesis



420. Therefore, although the absolute particle concentration values from the P-Trak, OPC, and DustTrak cannot be directly compared because of the different operating principles of the instruments, it is clear there is a positive relationship in the relative values recorded by the instruments.

G.2.2 Influence of process enclosure and fume cabinet upon the particle concentration within the work area

421. The time-series plots from Figures 41 and 42 are reflective of the process operation and the *local background particle exposure*, and have been used in Table 16 to examine the peak particle number and mass concentration, associated with Process 6. The point of measurement is outside the CVD chambers and inside the fume cabinet at the end of the tube to which waste aerosol was extracted from the enclosed CVD processes. Therefore these measurement values reflect particle concentrations inside the chambers in which the CVD was conducted.

Table 16. Summary of peak particle metrics at emission source during Process 6 operation compared to the peak associated with LBPC)

	PNC [p cm^{-3}] 20 to 1000nm **CPC P-Trak**		PNC 300 to 3000nm [p cm^{-3}] **OPC**		PNC >3000 to 10000nm [p cm^{-3}] **OPC**		PM$_{2.5}$ [μg m^{-3}] **DustTrak** [μg m^{-3}]		CMD [nm] **SMPS**		alveolar surface area [μm^{2} cm^{-3}] **NSAM**	
	Peak during	Peak of LBPC	Peak during	Peak of LBPC	Peak during	Peak of LBPC	Peak during	Peak of LBPC	Peak during	Peak of LBPC	Peak during	Peak of LBPC
6A	5.7×10^{4}	2.9×10^{3}	550	8	< 1	<1	18000	8	#	#	#	#
6B	2.1×10^{5}	2.9×10^{3}	4	4	1	< 1	550	8	#	#	#	#

not performed

local background particle concentration (LBPC

422. From Table 16 it is apparent that the CVD process is a strong source of both sub and supermicrometre particles.

423. Measurement of particle concentration and mass along the outside perimeters of the chambers enclosing both CVD processes established that the chambers were effective at containing particles. This is clearly shown in Figures 41 and 42 where at measurement point C (along the outer perimeter of the CVD enclosures) the particle metrics are similar to the background measured between the CVD operation (measurement points A), whilst contemporaneous measurements at the extraction point of the CVD processes clearly show particle number and mass concentrations to be significantly higher.

424. Measurement of particle concentration and mass along the outer edge of the sash opening of the fume cabinet into which the CVD exhaust aerosol was extracted established the fume cabinet operating with an average face velocity over the open sash area of 0.5 m/s was effective at containing and removing particles from the laboratory work area. This is clearly shown in Figures 41 and 42 where at measurement point E (along the edge of the fume cabinet sash opening) the particle metrics are similar to the *local background particle concentration* (measurement points A), whilst contemporaneous measurements at the extraction point of the CVD processes clearly show particle number and mass concentrations to be significantly higher.

G.3 Discussion

425. A marked difference in particle size and concentration was evident between the two processes. The literature regarding CNT synthesis by CVD provides a possible explanation for the differences in particle size. Temperature is manipulated during CVD production of CNT to control the relative ratio of single walled versus multi walled CNT, with temperatures > 700°C used to promote SWCNT formation, and < 700°C to promote MWCNT formation [89, 90]. Process 6-B was operated at a temperature of 750°C so as to generate a predominance of SWCNT, in contrast to Process 6-A operated at 650°C which aimed to generate a predominance of MWCNT. SWCNT are a smaller particles than MWCNT [89]. Therefore the characterisation of particles < 300nm for Process 6-B is likely to reflect a predominance of un-agglomerated and/or less agglomerated SWCNT within the chamber aerosol, whilst the particle size characterised from Process 6-A likely reflects the larger MWCNT.

426. Further support for the above conclusion comes from electron microscope analysis of particles generated from Processes 6-A and 6-B on a different day to that of the particle concentration and mass measurements. These micrographs are included in Figures 43 and 44.

Figure 43. SEM micrographs of CNTs generated with CVD condition]

Similar to Process 6-A (left) and Process 6-B (right), respectively [91

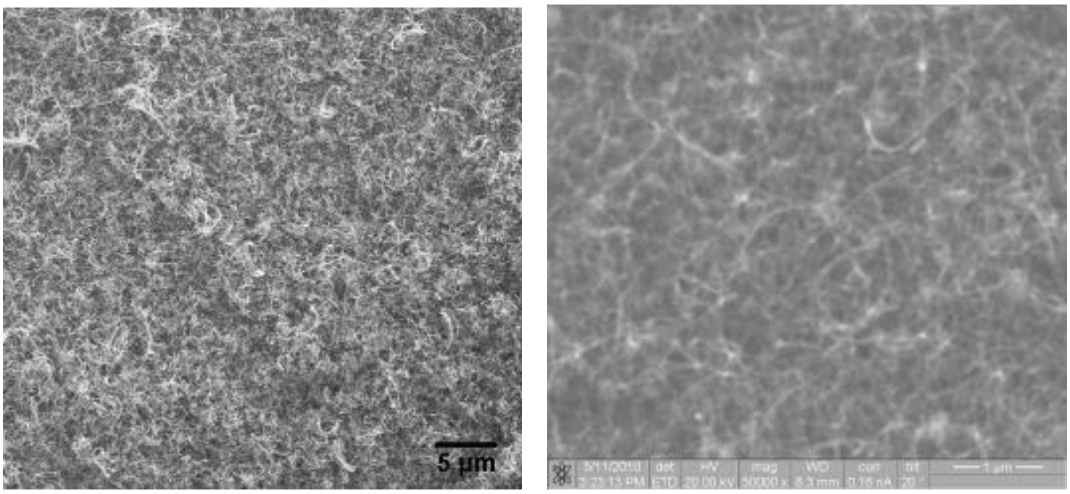
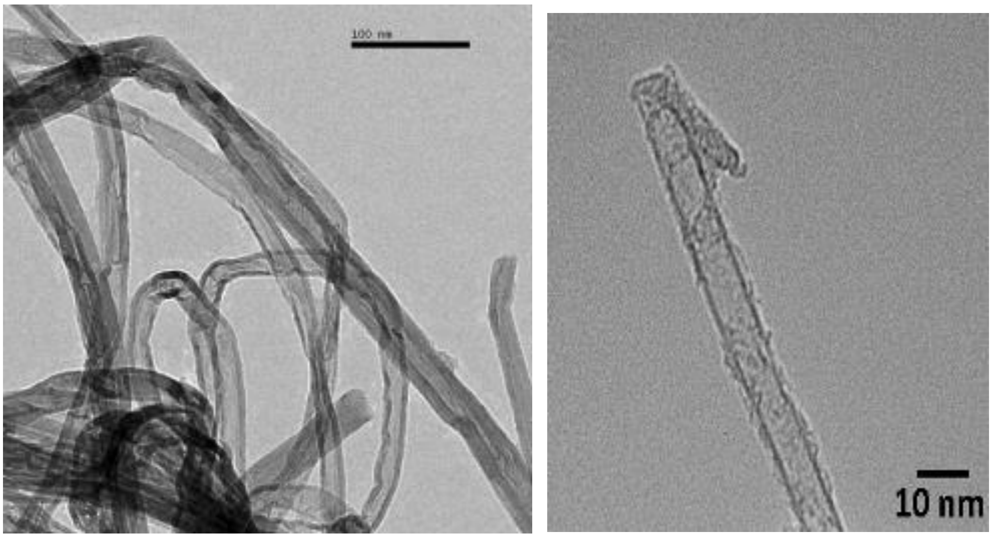


Figure 44. TEM images of CNTs collected from samples generated with CVD conditions].

Similar to Process 6-A (left) and Process 6-B (right), respectively [91



427. These electron microscope images show the average diameter of the CNT deposited upon the substrate for Process 6-A to be in the size range of 15-70 nm, whilst that for 6-B to be 0.5-10 nm.

428. In addition, the difference in particle size between the processes might be explained by the difference in heating mechanisms for both processes. Process 6-A utilised an insulated ceramic tube that

was heated through a resistive metal spiral wrapped around it resulting in the entire gas within the chamber being heated. In contrast Process 6-B utilised resistive heating whereby the conductive sample holder only was heated. It is possible the heating of the entire gas within the chamber for Process 6-A produced more incidental particles than that of Process 6-B.

429. It is clearly evident that the P-Trak, OPC, and DustTrak are capable of:

1. characterising particle emission from CNT CVD processes, and
2. evaluating the effectiveness of enclosure and extraction ventilation in containing particle emission.

430. It is also clear that the CVD furnace enclosures and the fume cabinet extraction ventilation are effective in containing particle leakage to the laboratory atmosphere.

APPENDIX H. PEARSON'S CORRELATION RESULTS

431. In relation to these results, traditionally occupational hygienists have used Pearson correlation coefficient or paired t-test to assess agreement. The former measures the degree of association (precision), while the latter measures the average difference (bias). A combination is needed to fully assess the desired agreement characteristics [98].

432. Real-time instrumentation used to monitor workplaces for nanomaterial aerosol concentrations have averaging times ranging from 1 second to 3 minutes. They generate a sequence of measurements over time, i.e. time-series data that are shown to have high autocorrelation. Standard statistics for summarizing data or regression modeling techniques which do not account for the autocorrelation structure of the data can lead to erroneous conclusions as variances are not appropriately computed. A time series analysis method such as the auto-regressive integrated moving average (ARIMA) procedure in SAS or R can be used for this purpose [98].

433. The relationships between instruments shown in Table 17 to 23 are specific for the processes examined in this work. For other processes, the relationships observed may be different due to; (a) different size distribution of manufactured nanomaterials emitted by the process and/or (b) if the process equipment produces significant quantities of incidental nanoparticles e.g. combustion products.

H.1 Grinding of titanium dioxide powder

434. Table 17 provides the Pearson's Correlation r-values for selected instruments used to characterise airborne particles during the grinding of titanium dioxide powder.

Table 17. Inter-instrument Pearson's Correlation matrix for Process 1A: grinding of titanium dioxide

	CPC 3871 (7m from particle source)	**CPC3781 (source)**	**P-Trak (source)**	**SMPS (source)**	**NSAM (source)**	**DustTrak (source)**
CPC 3871 (7m from particle source)	1					
3781 (source)	0.21	1				
P-Trak (source)	0.31	0.49	1			
SMPS (source)	0.24	0.61	0.57	1		
NSAM (source)	0.24	0.66	0.51	0.72	1	
DustTrak (source)	0.09	-0.17	0.10	0.25	-0.10	1

435. From Table 17 it can be seen that there is a poor correlation between each instrument at the source to the CPC located 7m from the source. A positive linear correlation exists for the SMPS and each

of the CPC's located at the particle source, and between the NSAM and each of the CPC's and SMPS located at the particle source. The DustTrak exhibits a poor linear correlation with the other instruments.

H.2 Extrusion of titanium dioxide and polyethylene materials

436. Table 18 provides the Pearson's Correlation r-values for selected instruments used to characterise airborne particles during the extrusion of titanium dioxide and polyethylene materials.

Table 18. Inter-instrument Pearson's Correlation matrix for Process 1-B - extrusion of titanium dioxide and polyethylene materials

	CPC3871 (7m from particle source)	CPC 3781 (source)	SMPS (source)	NSAM (source)
CPC 3871 (7m from source)	1			
CPC 3781 (source)	0.38	1		
SMPS (source)	0.36	0.10	1	
NSAM (source)	0.23	0.88	0.19	1

437. From Table 18 it can be seen that there is a poor correlation between the instrument responses for this aerosol, except for the NSAM and CPC 3781 located at the particle source.

H.3 Extrusion of clay platelets and polyurethane materials

438. Table 19 provides the Pearson's Correlation r-values for selected instruments used to characterise airborne particles during the extrusion of clay platelets and polyurethane materials.

Table 19. Inter-instrument Pearson's Correlation matrix for Process 2 - extrusion of clay platelets

	CPC3781 (7m from particle source)	CPC3022 (source)	CPC3781 (source)	P-Trak (source)	SMPS (source)	NSAM (source)	DustTrak (source)
CPC 3781 (7m from source)	1						
CPC 3022 (source)	0.79	1					
CPC 3781 (source)	0.79	0.86	1				
P-Trak (source)	0.85	0.85	0.86	1			
SMPS (source)	0.19	0.57	0.65	0.59	1		
NSAM (source)	0.69	0.67	0.68	0.83	0.19	1	
DustTrak (source)	0.21	0.19	0.15	0.29	0.43	0.16	1

439. From Table 19 it can be seen that there is a strong correlation between the all four CPC responses to this aerosol, and also a weakly positive to strong positive linear correlation between the NSAM and the four CPC's. A weakly positive relationship exists between each of the CPC's located at the particle source and the SMPS, with the CPC located 7m from the source showing a poor but slightly positive correlation. The DustTrak exhibits a poor linear correlation with the other instruments.

H.4 Grinding of titanium dioxide powder

440. Table 20 provides the Pearson's Correlation r-values for selected instruments used to characterise airborne particles during the grinding of titanium dioxide powder.

Table 20. Inter-instrument Pearson's Correlation matrix for Process 3 – grinding of titanium dioxide

	CPC 3781 (source)	**P-Trak (source)**	**SMPS (source)**	**NSAM (source)**	**DustTrak (source)**
CPC 3781 (source)	1				
P-Trak (source)	0.62	1			
SMPS (source)	0.54	0.52	1		
NSAM (source)	0.63	0.74	0.77	1	
DustTrak (source)	0.21	0.23	0.36	0.15	1

441. From Table 20 it can be seen that there is a weakly positive linear relationship between the two CPC's, the SMPS, and the NSAM. The DustTrak exhibits a poor linear correlation with the other instruments.

H.5 Jet milling of clay platelets

442. Table 21 provides the Pearson's Correlation r-values for selected instruments used to characterise airborne particles during the jet milling of clay platelets.

Table 21. Inter-instrument Pearson's Correlation matrix for Process 4 – jet milling of clay platelets

	OPC 300-500nm (source)	**OPC >500 to 1000nm (source)**	**OPC >1000 to 3000nm (source)**	**OPC >3000 to 10000nm (source)**	**P-Trak (source)**	**DustTrak (source)**
P-Trak (source)	0.71	0.72	- 0.15	- 0.17	1	
DustTrak (source)	0.48	0.47	0.2	0.09	0.43	1

443. From Table 21 it can be seen that for the portable hand-held instruments there is a weakly positive linear relationship between the P-Trak and the OPC in particle bin range 300 to 1000nm. The relationship between the P-Trak and the OPC > 1000nm is poor and this would be expected because of the

upper particle size range of 1000nm for the P-Trak. The DustTrak exhibits a weakly positive linear correlation with the P-Trak and the OPC bin sizes 300 to 1000nm.

H.6 Decanting of single-walled carbon nanotube powder

444. Table 22 provides the Pearson’s Correlation r-values for selected instruments used to characterise airborne particles during the decanting of SWCNT powder. The data used to examine correlations was taken from the period when there was no nearby welding.

Table 22. Inter-instrument Pearson’s Correlation matrix for Process 5A – SWCNT in chamber

	OPC 300 to 500nm (source)	**OPC 500 to 1000nm (source)**	**OPC >1000 to 3000nm (source)**	**OPC >3000 to 10000nm (source)**	**P-Trak (source)**	**SMPS (source)**	**NSAM (source)**	**DustTrak (source)**
P-Trak (source)	0.83	0.73	-0.19	-0.15	1			
SMPS (source)	-0.07	-0.05	0.07	0.05	-0.09	1		
NSAM (source)	0.38	0.30	-0.07	-0.05	0.61	-0.13	1	
DustTrak (source)	0.45	0.35	-0.12	-0.09	0.66	-0.25	0.84	1

445. From Table 22, a weakly positive to strong positive linear relationship exists between the P-Trak and the OPC size range 300 to 1000nm. This relationship becomes poor at the > 1000nm size range of the OPC reflecting the upper size range of 1000nm for the P-Trak. The P-Trak exhibits a weakly positive relationship with the DustTrak. The SMPS exhibits a poor linear relationship with the other instrumentation. The NSAM exhibits a weakly positive linear relationship with the P-Trak, a strong correlation with the DustTrak and a poor linear relationship with the other instrumentation.

H.7 Decanting of multi-walled carbon nanotube powder

446. Table 23 provides the Pearson’s Correlation r-values for selected instruments used to characterise airborne particles during the decanting of MWCNT powder.

Table 23. Inter-instrument Pearson’s Correlation matrix for Process 5B - MWCNT in chamber

	OPC 300 to 500nm (source)	**OPC 500 to 1000nm (source)**	**OPC >1000 to 3000nm (source)**	**OPC >3000 to 10000nm (source)**	**P-Trak (source)**	**SMPS (source)**	**NSAM (source)**	**DustTrak (source)**
P-Trak (source)	0.97	0.46	0.02	0.03	1			
SMPS (source)	-0.08	-0.21	-0.23	-0.22	-0.02	1		
NSAM (source)	0.47	0.45	0.003	0.007	0.99	0.02	1	
DustTrak (source)	0.53	0.53	0.33	0.31	0.50	-0.05	0.51	1

447. From Table 23, a strong linear relationship exists between the P-Trak and the OPC (300 to 500nm) but the relationship is weakly positive between the P-Trak and OPC (500 to 100nm). The SMPS exhibits a poor linear relationship with all instruments. The DustTrak and NSAM exhibit a weakly positive relationship with the OPC (300 to 1000nm). The NSAM exhibits a strong relationship with the P-Trak.

APPENDIX I. PARTICLE NUMBER CONCENTRATION

Table 24. Particle number concentration necessary in order for a mass concentration of 0.1 mg m-3 to be reached at a given dimension of particles (20, 50, 100, 200 nm) [83]

Name	**Density in kg/m³**	**N in cm^{-3} at 20 nm**	**N in cm^{-3} at 50 nm**	**N in cm^{-3} at 100 nm**	**N in cm^{-3} at 200 nm**
CNT, commercial product	110	217 029 468	13 889 886	1 736 236	217 029
Polystyrene	1 050	22 736 420	1 455 131	181 891	22 736
CNT	1 350	17 683 883	1 131 768	141 471	17 684
Fullerene (C60)	1 650	14 468 631	925 992	115 749	14469
Typical respirable dust	2 500	9 549 297	611 155	76 394	9 549
Titanium dioxide	4 240	5 630 481	360 351	45 044	5 630
Zinc oxide	5 610	4 255 480	272 351	34 044	4 255
Cerium oxide	7 300	3 270 307	209 300	26 162	3 270
Iron	7 874	3 031 908	194 042	24 255	3 032
Silver	10 490	2 275 809	145 652	18 206	2 276
Gold	19 320	1 235 400	79 083	9 885	1 236
N = particle number concentration required for attainment of a mass concentration of 0.1 mg m^{-3} with particles of the stated size					

REFERENCES

1. International Standards Organisation, ISO/TS 27687 *Nanotechnologies — Terminology and definitions for nano-objects —Nanoparticle, nanofibre and nanoplate*. 2008.
2. Dinardi, S.R., *Calculation Methods for Industrial Hygiene*. 1995, Melbourne: Van Nostrand Reinhold.
3. Morawska, L.; Thomas, N.; Bofinger, D.; Wainwright, D.; Neale, D.; Comprehensive characterisation of aerosols in a subtropical urban atmosphere: particle size distribution and correlation with gaseous pollutants. *Atmospheric Environment*, **1998**. *32*(14/15); 2467-2478.
4. Pope C; Burnett R; Thurston G; Thun M; Calle E; Krewksi D; Godleski J; Cardiovascular Mortality and Long-Term Exposure to Particulate Air Pollution. *Circulation*, **2004**. *109*; 71-77.
5. about.com. *Extruder*. about.com: composites/plastics 2010 [cited 2010; Available from: http://composite.about.com/od/glossaries/l/bldef_e2102.htm.
6. World Health Organisation, *WHO Air quality guidelines for particulate matter, ozone, nitrogen dioxide and sulfur dioxide Global update 2005: Summary of risk assessment* 2006.
7. Knol, A.; de Hartog, J.; Boogaard, H.; Slottje, P.; van der Sluijs, J.; Lebret, E.; Cassee, F.; Wardekker, A.; Ayres, J.; Borm, P.; Brunekreef, B.; Donaldson, K.; Forastiere, F.; Holgate, S.; Kreyling, W.; Nemery, B.; Pekkanen, J.; Stone, V.; Wichmann, H.E.; Hoek, G.; Expert elicitation on ultrafine particles: likelihood of health effects and causal pathways. *Particle and Fibre Toxicology*, **2009**. *6*(19).
8. Weichenthal S; Dufresne A; Infante-Rivard C; Indoor ultrafine particles and childhood asthma: exploring a potential public health concern. *Indoor Air*, **2007**. *17*; 81-91.
9. Delfino R; Sioutas C; Malik S; Potential Role of Ultrafine Particles in Association between Airborne Particle Mass and Cardiovascular Health. *Environmental Health Perspectives*, **2005**. *113*(8); 934-946.
10. The Royal Society, *Nanoscience and nonotechnologies: opportunities and uncertainties*. 2004, The Royal Society: London.
11. Aitken, R.; Creely, K.; Tran, C., *Nanoparticles: An Occupational hygiene review*. 2004, Health and Safety Executive.
12. Australian Safety and Compensation Council, *A Review of the Potential Occupational Health and Safety Implications of Nanotechnology*, D.o.E.a.W. Relations, Editor. 2006.
13. EPA. *Impacts of Manufactured NanoParticles on Human Health and the Environment*. 2003 [cited; Available from: http://www.epa.gov/ncer/rfa/archive/grants/03/current/2003_nano.html
14. Mark, D., *Occupational Exposure to Nanoparticles and Nanotubes*, in *Nanotechnology: Consequences for Human Health and the Environment*, R. Hester and R. Harrison, Editors. 2007, RSC Publishing: Cambridge.
15. Liu C-N; Hung S-M; Chen S-C; Uang S-H; Tsai C-J; Cheng Y-S; Zhou Y; Exposure assessment of nano-sized and respirable particles at different workplaces. *Journal of Nanoparticle Research*, **2011**. *13*; 4161-4172.
16. International Commission on Radiological Protection, *Human Respiratory Tract Model for Deposition in the Lung (ICRP Publication 66)*. 1994, Ann ICRP (UK) 24 Nos. 1-3 Pergamon Press.
17. Maynard, A.; Kuempel, E.; Airborne nanostructured particles and occupational health. *Journal of Nanoparticle Research*, **2005**. *7*; 587-614.
18. 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 Toxicology and Workplace Safety. *Toxicological Sciences*, **2006**. *92*(1); 5022.
19. Asbach C; Fissan H; Stahlmecke B; Kuhlbusch T; DYH P; Conceptual Limitations and Extensions of Lung Deposited Nanoparticle Surface Area Monitor (NSAM). *Journal of Nanoparticle Research*, **2009**. *11*; 101-109.

20. Methner, M.; Birch, M.; Evans, D.; Hoover, M., *NIOSH Health Hazard Evaluation Report 2005-0291-3025*. 2006, National Institute for Occupational Safety and Health.
21. National Institute for Occupational Safety and Health. *Approaches to Safe Nanotechnology: An Information Exchange with NIOSH*. 2006 [cited; Available from: http://www.cdc.gov/niosh/nas/rdrp/appendices/chapter7/a7-2.pdf
22. Donaldson, K.; Stone, V.; Seaton, A.; MacNee, W.; Ambient particle inhalation and the cardiovascular system: Potential mechanisms. *Environmental Health Perspectives*, **2001**. *109*; 523-527.
23. Castranova, V.; Particles and the airways: Basic biological mechanisms of pulmonary pathogenicity. *Applied Occupational Environmental Hygiene*, **1998**. *13*(8); 613-618.
24. Donaldson, K.; Li, X.; MacNee, W.; Ultrafine (nanometer) particle mediated lung injury. *Journal of Aerosol Science*, **1998**. *29*(5-6); 533-560.
25. Dreher, K.; Particulate matter physicochemistry and toxicology: In search of causality - a critical perspective. *Inhalation Toxicology*, **2000**. *12*; 45-57.
26. Dick, C.; Brown, D.; Donaldson, K.; Stone, V.; The role of free radicals in the toxic and inflammatory effects of four different ultrafine particle types. *Inhalation Toxicology*, **2003**. *15*(1); 39-52.
27. Stone, V.; Brown, D.; Watt, N.; Wilson, K.; Donaldson, K.; Ritchie, H.; MacNee, W.; Ultrafine particle-mediated activation of macrophages: Intracellular calcium signaling and oxidative stress. *Inhalation Toxicology*, **2000**. *12*; 345-351.
28. MacNee, W.; Donaldson, K.; Mechanism of lung injury caused by PM10 and ultrafine particles with special reference to COPD. *European Respiratory Journal*, **2003**. *21*(47S-51S).
29. Donaldson, K.; Tran, C.; An introduction to the short-term toxicology of respirable industrial fibres. *Mutation Research*, **2004**. *553*; 5-9.
30. World Health Organisation, *Determination of Airborne Fibre Number Concentrations - A Recommended Method, by Phase Contrast Optical Microscopy (Membrane Filter Method)*. 1997: Geneva.
31. World Health Organisation. *WHO Workshop on Mechanisms of Fibre Carcinogenesis and Assessment of Chrysotile Asbestos Substitutes 8-12 November 2005, Lyon, France SUMMARY CONSENSUS REPORT* 2006 [cited.
32. Takagi, A.; Hirose, A.; Nishimura, T.; Fukumori, N.; Ogata, A.; Ohashi, N.; Kitajima, S.; Kanno, J.; Induction of mesothelioma in p53+/- mouse by intraperitoneal application of multi-wall carbon nanotube. *The Journal of Toxicological Sciences*, **2008**. *33*(1); 105-116.
33. Poland, C.A.; Duffin, R.; Kinloch, I.; Maynard, A.; Wallace, W.A.; Seaton, A.; Stone, V.; Brown, S.; MacNee, W.; Donaldson, K.; Carbon nanotubes introduced into the abdominal cavity of mice show asbestos-like pathogenicity in a pilot study. *Nature*, **2008**.
34. Muller, J.; Huaux, F.; Moreau, N.; Misson, P.; Heilier, J.; Delos, M.; Arras, M.; Fonseca, A.; Nagy, J.; Lison, D.; Respiratory toxicity of multi-wall carbon nanotubes. *Toxicology and Applied Pharmacology*, **2005**. *207*; 221-231.
35. Sayes, C.; Liang, F.; Hudson, J.; Mendez, J.; Guo, W.; Beach, J.; Moore, V.; Doyle, C.; West, J.; Billups, W.; Ausman, K.; Colvin, V.; Functionalization density dependence of single-walled carbon nanotubes cytotoxicity in vitro. *Toxicological Letters*, **2006**. *161*; 135-142.
36. Kagan, V.; Tyurina, Y.; Tyurin, V.; Konduru, N.; Potapovich, A.; Osipov, A.; Kisin, E.; Schwegler-Berry, D.; Mercer, R.; Castranova, V.; Shvedova, A.; Direct and indirect effects of single walled carbon nanotubes on RAW 264.7 macrophages: Role of iron. *Toxicological Letters*, **2006**. *165*; 88-100.
37. Lam, C.; James, J.; McCluskey, R.; Hunter, R.; Pulmonary Toxicity of Single-Wall Carbon Nanotubes in Mice 7 and 90 Days After Intratracheal Instillation. *Toxicological Sciences*, **2004**. *77*(126-134).
38. Maynard, A.; Aitken, R.; Assessing exposure to airborne nanomaterials: Current abilities and future requirements. *Nanotoxicology*, **2007**. *1*(1); 26-41.

39. Ki Ku B; Maynard A; Comparing aerosol surface-area measurements of monodisperse ultrafine silver agglomerates by mobility analysis, transmission electron microscopy and diffusion charging. *Aerosol Science* **2005**. *36*; 1108-1124.
40. National Institute for Occupational Safety and Health, *Draft NIOSH CURRENT INTELLIGENCE BULLETIN: Evaluation of Health Hazard and Recommendations for Occupational Exposure to Titanium Dioxide*. 2005.
41. Harford, A.; Edwards, J.; Priestly, B.; Wright, P., *Current OHS best practices for the Australian Nanotechnology industry: A Position Paper by the Nanosafe Australia Network*. 2007: Victoria.
42. Brouwer, D.; Gijsbers, J.; Lurvink, W.; Personal Exposures to Ultrafine Particles in the Workplace: Exploring Sampling Techniques and Strategies. *Ann Occup Hyg*, **2004**. *48*(5); 439-453.
43. Seaton, A.; Nanotechnology and the occupational physician. *Occupational Medicine*, **2006**. *56*; 312-16.
44. Kuhlbusch T; Asbach C; Fissan H; Gohler D; Stintz M; Nanoparticle exposure at nanotechnology workplaces: a review. *Particle and Fibre Toxicology*, **2011**. *8*(22); provisional version.
45. Fissan H; Neumann, S.; Trampe A; Pui DYH; Shin WG; Rationale and principle of an instrument measuring lung deposited nanoparticle surface area. *Journal of Nanoparticle Research*, **2007**. *9*; 53-59.
46. Shin WG; Pui DYH; Fissan H; Neumann S; Trampe A; Calibration and numerical simulation of Nanoparticle Surface Area Monitor (TSI Model 3550 NSAM). *Journal of Nanoparticle Research*, **2007**. *9*; 61-69.
47. Dekati, *Electrical Low Pressure Impactor*, in *On-line product description*, 2011. http://www.environmental-expert.com/products/elpi-electrical-low-pressure-impactor-172157
48. Milller A; Frey G; King G; Sunderman C; A Handheld Electrostatic Precipitator for Sampling Airborne Particles and Nanoparticles. *NIOSH on line article*.
49. Cena L; Anthony TR; Peters T; A Personal Nanoparticle Respiratory Deposition (NRD) Sampler. *Environmental Science and Technology*, **2011**. *45*; 6483-6490.
50. Asbach C; Kaminski H; Fissan H; Monz C; Dahmann D; Mulhopt S; Paur H; Kiesling HJ; Herrmann F; Voetz M; Kuhlbusch T; Comparison of four mobility particle sizers with different time resolution for stationary exposure measurements. *Journal of Nanoparticle Research*, **2009**. *11*; 1593-1609.
51. Methner M; Hodson L; Geraci C; Nanoparticle Emission Assessment Technique (NEAT) for the Identification and Measurement of Potential Inhalation Exposure to Engineered Nanoparticles - Part A. *Journal of Occupational and Environmental Hygiene*, **2010**. *7*; 127-132.
52. Methner M; Hodson L; Dames A; Geraci C; Nanoparticle Emission Assessment Technique (NEAT) for the Identification and Measurement of Potential Inhalation Exposure to Engineered Nanomaterials - Part B: Results of 12 Field Studies. *Journal of Occupational and Environmental Hygiene*, **2010**. *7*; 163-176.
53. Peters T; Elzey S; Johnson R; Park H; Grassian V; Maher T; O'Shaugnessy P; Airborne Monitoring to Distinguish Engineered Nanomaterials from Incidental Particles for Environmental Health and Safety. *Journal of Occupational and Environmental Hygiene*, **2009**. *6*; 73-81.
54. Wallace L; Ott W; Personal exposure to ultrafine particles. *Journal of Exposure Science and Environmental Epidemiology*, **2011**. *21*; 20-30.
55. Evans D; Ki Ku B; Birch M; Dunn K; Aerosol Monitoring during Carbon Nanofiber Production: Mobile Direct-Reading Sampling. *Ann Occup Hyg*, **2010**. *54*(5); 514-531.
56. Petaja T; Mordas G; Manninen H; Aalto P; Hameri K; Kulmala M; Detection Efficiency of a Water-Based TSI Condesation Particle Counter 3785. *Aerosol Science and Technology*, **2006**. *40*; 1090-1097.
57. Jankovic J; Hollenbeck S; Zontek T; Ambient Air Sampling During Quantum-Dot Spray Deposition. *International Journal of Occupational and Environmental Health*, **2010**. *16*(4); 388 - 398.

58. McGarry P; Morawska L; He C; Jayaratne R; Falk M; Tran Q; Wang H; Exposure to Particles from Laser Printers Operating within Office Workplaces. *Environmental Science and Technology*, **2011**. *45*; 6444-6452.
59. Bello D; Wardle B; Zhang J; Yamamoto N; Santeufemio C; Hallock M; Abbas Virji M; Characterisation of Exposures to Nanoscale Particles and Fibers During Solid Core Drilling of Hybrid Carbon Nanotube Advanced Composites. *International Journal of Occupational and Environmental Health*, **2010**. *16*(4); 434-450.
60. Jankovic J; Zontek T; Ogle B; Hollenbeck S; Characterising Aersolized Particulate as Part of a Nanoprocess Exposure Assessment. *International Journal of Occupational and Environmental Health*, **2010**. *16*(4); 451-457.
61. Methner M; Effectiveness of a Custom-fitted Flange and Local Exhaust Ventilation (LEV) System in Controlling the Release of Nanoscale Metal Oxide Particulates During Reactor Cleanout Operations. *International Journal of Occupational and Environmental Health*, **2010**. *16*(4); 475-487.
62. Wang Y-F; Tsai P-J; Chen C-W; Chen D-A; Hsu A; Using a Modified Electrical Aerosol Detector to Predict Nanoparticle Exposures to Different Regions on the Respiratory Tract for Workers in a Carbon Black Manufacturing Industry. *Environmental Science and Technology*, **2010**. *44*(17); 6767–6774.
63. Tsai C-J; Huang C-Y; Chen S-C; Ho C-E; Huang C-H; Chen S-W; Chang C-P; Tsai S-J; Ellenbecker MJ; Exposure assessment of nano-sized and respirable particles at different workplaces. *Journal of Nanoparticle Research*, **2011**. *13*; 4161-4172.
64. Ku, B.; Maynard, A.; Comparing aerosol surface-area measurements of monodisperse ultrafine silver agglomerates by mobility analysis, transmission electron microscopy and diffusion charging *Aerosol Science*, **2005**. *36*; 1108-1124.
65. Lee S-B; Lee J-H; Bae G-N; Size response of an SMPS-APS system to commercial multi-walled carbon nanotubes. *Journal of Nanoparticle Research*, **2010**. *12*; 501-512.
66. Marra J; Voetz M; Kiesling HJ; Monitor for detecting and assessing exposure to airborne nanoparticles. *Journal of Nanoparticle Research*, **2010**. *12*; 21-37.
67. TSI Incorporated, *Model 3089 Nanometer Aerosol Sampler - Operating Instructions*: 500 Cardigan Road St. Paul, MN 55126 USA.
68. McMurry P; Ghimire A; Ahn H-K; Sakurai H; Moore K; Stolzenburg M; Smith J; Sampling Nanoparticles for Chemical Analysis by Low Resolution Electrical Mobility Classification. *Environmental Science and Technology*, **2009**. *43*; 4653-4658.
69. Marra J; Using the Aerasense NanoTracer for simultaneously obtaining several ultrafine particle exposure metrics. *Journal of Physics: Conference Series 304:012010*, **2011**.
70. van Broekuizen P; van Brokehuizen F; Cornelissen R; Reijnders L; Use of nanomaterials in the European construction industry and some occupational health aspects thereof. *Journal of Nanoparticle Research*, **2011**. *13*; 447-462.
71. National Institute for Occupational Safety and Health; Elemental Carbon (Diesel Particulate) Method 5040. *NIOSH Manual of Analytical Methods*, (Fourth Edition).
72. Marra J; Matthias V; Kiesling HJ; Monitor for detecting and assessing exposure to airborne nanoparticles. *Journal of Nanoparticle Research*, **2010**. *12*; 21-37.
73. Sem G; Design and performance characteristics of three continuous-flow condensation particle counters: a summary. *Atmospheric Research*, **2002**. *62*; 267-294.
74. Hermann M; Wehner B; Bischof O; Han HS; Krinke T; Liu W; Zerrath A; Wiedensohler S; Particle counting efficiencies of new TSI condensation particle counters. *Aerosol Science*, **2007**. *38*; 674-682.
75. Mordas G; Manninen H; Petaja T; Aalto P; Hameri K; Kulmala M; On Operation of the Ultra-Fine Water-Based CPC TWI 3786 and Comparison with Other TSI Models (TSI 3776, TSI 3772, TSI 3025, TSI 3010, TSI 3007). *Aerosol Science and Technology*, **2008**. *42*; 152-158.

76. OECD. *Emission Assessment for the Identification of Sources and Release of Airborne Manufactured Nanomaterials in the Workplace: Compilation of Existing Guidance. ENV/JM/MONO(2009)16*. 2009
77. Air Quality and Sustainable Nanotechnology Institute of Energy and Environmental Technology e.V. (IUTA); Federal Institute for Occupational Safety and Health (BAuA); German Social Accident Insurance Institution for Raw Materials and Chemical Industry (BG RCI); German Chemical Industry Association (VCI); Institute for Occupational Safety and Health of the DGUV (IFA); Research Group Mechanical Process Engineering Institute of Process Engineering and Environmental Technology Technical University Dresden (TUD), *Tiered Approach to an Exposure Measurement and Assessment of Nanoscale Aerosols Released from Engineered Nanomaterials in Workplace Operations*, 2011.
78. Safe Work Australia. *Hazardous Substances Information System*. 2010 [cited.
79. National Institute for Occupational Safety and Health, *NIOSH Current Intelligence Bulletin - Occupational Exposure to Carbon Nanotubes and Nanofibers (draft)*. December 2010, Department of Health and Human Services - Centers for Disease Control and Prevention.
80. Japan National Institute of Advanced Industrial Science and Technology (AIST); Final Reports on Risk Assessments of Three Manufactured Nanomaterials. 2011 http://www.aist-riss.jp/main/modules/product/nano_rad.html. *(http://www.aist-riss.jp/main/modules/product/nano_rad.html?ml_lang=en)*
81. British Standards Institution, *Nanotechnologies - Part 2: Guide to safe handling and disposal of manufactured nanomaterials.* . 2007, British Standards Institution.
82. Benke G; Dennekamp M; Priestly B; Sim M; Morris H. *Engineered Nanomaterials: Feasibility of establishing exposure standards and using control banding in Australia*. 2011, Safe Work Australia
83. Institut für Arbeitsschutz der Deutschen Gesetzlichen Unfallversicherung (IFA), *Criteria for assessment of the effectiveness of protective measures http://www.dguv.de/ifa/en/fac/nanopartikel/beurteilungsmassstaebe/index.jsp*.
84. McGarry P; Morawska L; He C; Jayaratne R; Falk M; Wang L; Morris H, *Nanoparticles from Printer Emissions in Workplace Environments.* Safe Work Australia. *http://www.safeworkaustralia.gov.au/AboutSafeWorkAustralia/WhatWeDo/Publications/Documents/635/Nanoparticles_from_printer_emissions.pdf*. 2011.
85. National Occupational Health and Safety Commission, *Exposure Standards for Atmospheric Contaminants in the Occupational Environment - Guidance Note [NOHSC:3008(1995)]*, Australian Government Publishing Service: Canberra.
86. The American Conference of Governmental Industrial Hygienists, *Threshold Limit Values for Chemical Substances and Physical Agents & Biological Exposure Indices*. 2010, Signature Publications.
87. American Conference of Governmental Industrial Hygienists, *Industrial Ventilation: A Manual of Recommended Practice (24th edition)*. 2001, Cincinnati.
88. Chan Y.C.; McTainsh G.H.; Simpson R.W.; Vowles P.D.; Cohen D.D.; Bailey G.M; Contributions of Different Sources to Primary and Secondary PM10 Aerosols in Brisbane, Australia. *Clean Air*, **2002**. *36*(2); 32-37.
89. O'Connell, M., *Carbon nanotubes: properties and applications*. 2006, Boca Raton: Taylor & Francis.
90. Kumar, M.; Ando, Y.; Chemical Vapor Deposition of Carbon Nanotubes: A Review on Growth Mechanisms and Mass Production. . *Journal of Nanoscience and Nanotechnology*, **2010**. *10*(6); 3739-3758.
91. Capasso, A., *PhD Thesis: Controlled growth of carbon nanotubes for electronic and photovoltaic applications*. 2011, Queensland University of Technology.

92. Timko M; Yu Z; Kroll J; Jayne J; Worsnop D; Miake-Lye R; Onasch T; Liscinsky D; Kirchstetter T; Destaillats H; Holder A; Smith J; Wilson K; Sampling Artifacts from Conductive Silicone Tubing. *Aerosol Science and Technology*, **2009**. *43*; 855-865.
93. Jankovic J; Hall M; Zontek T; Hollenbeck S; Ogle B; Particle Loss in a Scanning Mobility Particle Analyzer Sampling Extension Tube. *International Journal of Occupational and Environmental Health*, **2010**. *16*(4); 429-433.
94. Perkins JL, *Modern Industrial Hygiene Volume 1 2nd edition*. 2008, Cincinnati: ACGIH.
95. Ramachandran G, *Chapter 13 Direct Reading Instruments for Aerosols* in *Occupational Exposure Assessment for Air Contaminants*. 2005, CRC Press.

96 van Broekhuizen P, van Veelen W, Streekstra WH, Schulte P, Reijnders L. Exposure Limits for Nanoparticles: Report of an International Workshop on Nano Reference Values. Ann. Occup. Hyg., Vol. 56, No. 5, pp. 515–524, 2012

97 Asbach, C., Kaminski, H., Fissan, H., Monz, C., Dahmann, D., Mülhopt, S., Paur, H.R., Kiesling HJ, Herrmann F, Voetz M, Kuhlbusch, T.A.J. Comparison of four mobility particle sizers with different time resolution for stationary exposure measurements. Journal of Nanoparticle Research 11 (7) , pp. 1593-1609. 2009

98. Brouwer D, Berges M, Abbas Virji M, Fransman W, Bello D, Hodson L, Gabriel S, Tielemans E.. Harmonization of Measurement Strategies for Exposure to Manufactured Nano-Objects; Report of a Workshop. Ann. Occup. Hyg., Vol. 56, No. 1, pp. 1–9, 2012.
99. Tsai C-J, Liu C-N, Hung S-M, Chen S-C, Uang S-N, Cheng Y-S, Zhou Y. Novel Active Personal Nanoparticle Sampler for the Exposure Assessment of Nanoparticles in Workplaces. Environ. Sci. Technol., 2012, 46 (8), pp 4546–4552
100. Zhu Y, Smith TJ, Davis ME, Levy JI, Herrick R, Jiang H. Comparing gravimetric and real-time sampling of PM(2.5) concentrations inside truck cabins. J Occup Environ Hyg. 2011 Nov;8(11):662-72.
101. McGarry P, Morawska L, Morris H, Knibbs L, Bostrum T, Capasso A. *Measurements of particle emissions from nanotechnology processes, with assessment of measuring techniques and workplace controls.* Safe Work Australia, 2012 http://www.safeworkaustralia.gov.au/sites/swa/about/publications/pages/measurements-particle-emissions-nanotechnology-processes-with-assessment-measuring-techniques-workplace-controls
102. Pal M, Pal U, Jimenez J, Perez-Rodriguez F. Effects of crystallization and dpant concentration on the emission behavior of TiO_2:Eu nanophsphors. Nanoscale Research Letters 2012, 7:1.
103. DFG. New Threshold Values for Fine Dust at the Workplace. 2011.
104. NANEX. Development of Exposure Scenarios for Manufactured Nanomaterials. Final Report (2010)
105. Asbach C, Kuhlbusch TAJ, Kaminski H, Stahlmecke B, Plitzko S, Götz U, Voetz M, Kiesling H-J, Dirk Dahmann D. nanoGEM. Standard Operation Procedures. For assessing exposure to nanomaterials, following a tiered approach. (2012)
106. United Nations. Globally Hamonized System of Classification and Labelling of Chemicals (GHS), Revision 4. United Nations Economic Commission for Europe, 2011.
107. Osmond M, Waddington L, McCall M, Hawkins S, Poland C, Murphy F, Donaldson K, Aitken R, Clark S, Morris H. Durability of carbon nanotubes and their potential to cause lung inflammation. 2011. Safe Work Australia.
108. Japan National Institute for Occupational Safety and Health. Three-tiered approach for measurement of nanomaterials in air (Publication pending).
109. Safe Work Australia. Guidance on the interpretation of workplace exposure standards for airborne contaminants, 2013.
110. International Standards Organisation, ISO/TS 80004-1:2010 *Nanotechnologies — Vocabulary - Part 1: Core terms.*

111. National Institute for Occupational Safety and Health, *NIOSH Current Intelligence Bulletin 65 - Occupational Exposure to Carbon Nanotubes and Nanofibers,* March 2013, Department of Health and Human Services - Centers for Disease Control and Prevention.
112. OECD, 2015, harmonized tiered approach to measure and assess the potential exposure to airborne emissions of exposure to engineered nano-objects and their agglomerates and aggregates in workplaces [ENV/JM/MONO(2015)19].
113. TSI Incorporated, Aerosol Statistics Lognormal Distributions and $dN/dlogD_p$ - Application Note PR-001, 2012: 500 Cardigan Road St. Paul, MN 55126 USA.