MEASUREMENTS OF PARTICLE EMISSIONS FROM NANOTECHNOLOGY PROCESSES WITH ASSESSMENT OF MEASURING TECHNIQUES AND WORKPLACE CONTROLS

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safe work australia

Measurements of Particle Emissions from Nanotechnology Processes, with Assessment of Measuring Techniques and Workplace Controls

Acknowledgement

Disclaimer

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Report submitted to:

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1 Executive Summary

Scope and limitations of this study

The overall aim of this project was 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.

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. It did not include the toxicological evaluation of the aerosol and therefore, no direct conclusion was made regarding the health effects of exposure to these particles.

Our 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

The main findings of this study are summarised under the following headings. *Italic font has been used for a number of key terms defined in the glossary.*

Particle exposure and emission

1. 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* arises from sources of particles ubiquitous in the general environment. Therefore, it is essential that this *local background particle exposure* 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 exposure* for the nine nanotechnology environments included in this study were particle number concentrations (PNC): $PNC_{20-1000nm}$ - 5.5×10^2 particles cm^{-3} to 1.1×10^4 particles cm^{-3}, $PNC_{300-3000nm}$ - < 1 to 37 particles cm^{-3}, and mass concentration of particles with aerodynamic diameter <2.5 μm ($PM_{2.5}$): − 1 μg m^{-3} to 25 μg m^{-3}.

2. Mean particle concentrations measured at emission points of the nine processes showed that for seven of the processes the $PNC_{20-1000nm}$, and $PM_{2.5}$ were the same

order of magnitude as that of the *local particle background exposure*, with the other two processes being one order of magnitude higher. Of the five processes for which $PNC_{300-3000nm}$ was characterised, three were of the same order of magnitude as that of the local particle background, one was an order of magnitude higher, and one was two orders of magnitude higher.

3. 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 exposure* showed the median value of the peaks exceeded the *local background particle exposure* 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.

4. Therefore, because of the constant influence of background particle concentrations, characterisation of peak concentration values, across both the sub and supermicrometre size range, relative to the background is a better indicator of when a process may require control of particle emission, in contrast to absolute concentration values.

5. 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 *local particle background exposure*. When considered together, this data indicates that particle emissions and exposures from these nanotechnology processes are unlikely to be exclusively ultrafine in nature.

Advice on particle assessment

6. 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. Our results clearly indicate that a complimentary set of instruments such as a P-Trak [i.e. a portable condensation particle counter (CPC)], optical particle counter (OPC), and DustTrak can be used to gather both temporal and spatial data.

7. Characterisation of particle mass in conjunction with number concentration is also required so as to account for measurement error caused where the 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 may be identified by a mass concentration based instrument. This was evident from the results of carbon nanotube aerosol measurement where electron microscopy indicated that the particles' with dimensions were greater than 10μm, as significant $PNC_{300-3000nm}$ and $PM_{2.5}$ response was evident, but insignificant $PNC_{>3000nm}$ was recorded. In addition our results clearly indicate the DustTrak $PM_{2.5}$ mass concentration correlates positively with the PNC in size range of 300 to 2500 nm for sources of both fibrous and non-fibrous particles. Pearson correlation values showed

a consistent positive relationship between particle number and mass concentration values.

8. In addition, if further information on particle emission and exposure is 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.

9. Utilise the following hierarchy of *Particle Control Values* when assessing the significance of particle emission and exposure, most preferred first:
   - A company or laboratory's in-house control limits – if these are lower, i.e. more stringent, than applicable regulatory limits
   - Australian Workplace Exposure Standards. The model Work Health and Safety (WHS) Regulations require that a person conducting a business or undertaking must ensure that no person at the workplace is exposed to a substance or mixture in an airborne concentration that exceeds the relevant exposure standard for the substance or mixture.
   - Overseas national exposure limits or recommended national exposure limits, e.g. Recommended Exposure Limits from the United States National Institute for Occupational Safety and Health (US NIOSH)
   - 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

   Appropriate application of this hierarchy of *particle control values* when assessing the significance of nanomaterial emissions and exposure will increase the number of *particle control values* available for use.

10. Utilise a three tiered particle assessment process as follows as outlined in points 11 to 13.

11. 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 whether a Tier Two measurement process is required.

12. Tier Two (if indicated following Tier One assessment): the Tier Two assessment process is designed to be relatively simple to implement and as such does not involve off-line particle analysis. 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 in not in operation. This is of paramount importance so as to differentiate background particles from particle of interest.
       I. Plot the time-series data.
       II. Calculate the average of the *local background particle exposure* particle number and mass concentration – this is the *local particle reference value.*

III.   Identify the presence of peak particle concentration values. Exclude particle values that are within ± of the manufacturer stated accuracy of the instrument, i.e. peak values that are within ± of *the local particle reference value*.

IV.   Calculate the *peak* particle and mass concentration values for the *local background particle exposure*

b)   Measure real-time particle number and mass concentration data at emission points, within the breathing zone of worker, 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 particle values that are within ± of the manufacturer stated accuracy of the instrument, i.e. peak values that are within ± 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

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*.

d)   Compare this ratio to the general *excursion guidance criteria* as a trigger for to review of particle controls and/or conduct a Tier Three assessment, as described below;

    I.   General *excursion guidance criteria* - a nanotechnology process could be considered to require further assessment if:

        a.   Short term emissions/exposures exceed three times the *local particle reference value* for more than a total of 30 minutes during a work day; and/or

        b.   If a single short term (*peak*) value exceeds five times the *local particle reference value*.

13. Tier Three assessment. 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 particle morphology and chemical composition. The results of the off-line particle morphology and chemical composition analysis can also be compared to real-time measurement results. A Tier Three process can include:

- Collection of aerosols onto a filter membrane connected to a sampling pump or transmission electron microscopy (TEM) grid within an electrostatic precipitator, with analysis by scanning electron microscopy and X-ray diffraction (SEM/XRD) and TEM/XRD respectively.

- Utilisation of the sampling and analytical method recommended for an Australian Workplace Exposure Standard, overseas exposure limit (e.g. Recommended Exposure Limits), proposed workplace exposure limit, or benchmark exposure level.

- Use of a scanning mobility particle sizer with the minimum particle measurement size possible. Significant differences between the count median diameter during the process compared to the *local background particle exposure* would suggest the nanotechnology process is emitting particles. These particles may be within the ultrafine size fraction but could also be of larger particle sizes due to agglomeration of particles.

14. Do not use photometers (e.g. DustTrak) as a substitute for the sampling and analytical method recommended for an exposure standard, Recommended Exposure Limit (REL), or proposed exposure limit. This is because the sampling and analytical method of operation of photometers is fundamentally different. 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.

Triggers for particle control strategies

15. Where the calculated ratio of the peak particle concentration measured during process operation to *local particle reference value* does not exceed the *excursion guidance value*, changes to particle control strategies are not generally required, but may be required in the case of nanomaterials that are potentially highly hazardous.

16. Where the results of Tier Three assessment confirm the excursion in particle concentration is associated with the nanotechnology process, particle control strategies should be 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.

17. Measurement of particle concentrations during the use of local extraction ventilation (LEV), 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. 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. Thus to control exposure, 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.

Abbreviations

AC/h	Air changes per hour
ACGIH	American Conference of Industrial Hygienists
AIST	Japan's National Institute of Advanced Industrial Science and Technology
BEL	Benchmark Exposure Limit
BSI	British Standards Institution
C_{60}	Fullerene
CMAR	Carcinogenic, mutagenic, asthmagenic, or reproductive toxins
CMD	Count median diameter
CNT	Carbon nanotube
CPC	Condensation Particle Counter
CVD	Chemical vapour deposition
DustTrak	DustTrak Aerosol Monitor
EC	Elemental carbon
EDX	Energy-dispersive X-ray spectrometry
ELPI	Electrical Low Pressure Impactor
ES	Exposure Standard
ESEM	Environmental scanning electron microscope
FMPS	Fast Mobility Particle Sizer
HVAC	Heating, ventilation and air-conditioning
ICRP	International Commission on Radiological Protection
IFA	Institute for Occupational Safety and Health of the German Social Accident Insurance
IOSH	Taiwan Institute of Occupational Safety and Health
LEV	Local exhaust ventilation
LOQ	Limit of quantitation
LPM	Litres per minute
µm	Micrometre
$m^3 h^{-1}$	Cubic metres per hour
MCE	Mixed cellulose ester
MWCNT	Multi-walled carbon nanotube
NCTU	National Chiao Tung University, Taiwan
NEAT	Nanoparticle Emission Assessment Technique (US NIOSH)
NIOSH	United States National Institute for Occupational Safety and Health
nm	Nanometre
NRD	Nanoparticle Respiratory Deposition
NSAM	Nanoparticle Surface Area Monitor
OEL	Occupational Exposure Limit
OPC	Optical Particle Counter
$p\ cm^{-3}$	Particles per cubic centimetre
PM	Particulate Matter
PNC	Particle Number Concentration
PNOS	Particles not otherwise specified
P-Trak	Model 8525 P-Trak Ultrafine Particle Counter
PTFE	Polytetrafluoroethylene
QUT	Queensland University of Technology
REL	Recommended Exposure Limit

SEM	Scanning electron microscopy
SMPS	Scanning Mobility Particle Sizer
TEM	Transmission electron microscopy
TEOM	Tapered Element Oscillating Microbalance
TLV	Threshold Limit Value
TWA	Time-Weighted Average
WEL	Workplace Exposure Limit
WES	Workplace Exposure Standard
WHO	World Health Organisation
XRD	X-Ray Diffraction

Glossary

Italic font is used in the report for a number of key terms from this glossary.

Excursion guidance criteria **–** triggers for implementation of exposure controls used in conjunction with either the *local background particle concentration* benchmark or the *particle reference value* benchmark. Exposure controls must be implemented if:

- If exposure/emission levels exceed three times the *local particle reference value* for more than a total of 30 minutes during a work day; and/or

- If exposure/emission exceeds five times the *local particle reference value.*

Local background particle exposure **(LBPE)** – local work area average particle number or mass concentration that excludes any contribution of particles from the nanotechnology process. This value is specific to each work environment and the period of measurement should be sufficient so as to characterise typical flucuations in background particle exposure. 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 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, $PM_{2.5}$ concentration values during periods when the relevant nanotechnology process was not in operation.

Local particle reference value **–** the local background particle exposure, 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 repeated evaluation of the local background particle exposure. This is not a health based occupational exposure limit (OEL) or Workplace Exposure Standard (WES), but is intended as a pragmatic guidance level.

Mean particle concentration - arithmetic average over the period of measurement.

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

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 workplace exposure standards set by regulatory authorities, recommended exposure limits, exposure limits proposed by researchers, and Local Background Particle Reference Values based upon background nanoparticle 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 assessment of the nanotechnology process. This is the highest concentration recorded by the instrument. The ability to resolve the peak concentration is influenced by the sampling average time. Therefore, the sampling time should be set to shortest period possible for that instrument. In addition, to ensure comparison of such values between instrumentation is meaningful each instrument should where possible be set to the same sampling time. In our study the sampling period for the P-Trak, OPC, DustTrak, CPC 3781, and NSAM were all set at 5 seconds because this was the shortest sampling time possible for the OPC (shorter sampling times were however possible for the other instruments. In contrast the SMPS scans take much longer and we used a scan time of 90 seconds as this allowed a reasonable trade-off between speed and performance.

PM_1 – Particle Mass concentration of particles with an aerodynamic diameter smaller than 1 μm.

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

PM_{10} – Particle Mass concentration of particles with an aerodynamic diameter smaller than 10 μm.

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.

Submicrometre particles – particles smaller than 1 micrometre in diametre.

Supermicrometre particles – particles larger than 1 micrometre in diametre.

Time-weighted average (TWA) - 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 or guidance level. Common averaging times (denominator) include 8-hours, and 15 minutes [2].

Ultrafine particle – 100 nm in diameter or less [1]. See also nanoparticle.

2 Introduction

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].

Exposure to ambient PM$_{2.5}$ particles are known to be associated with respiratory and cardiovascular disease [4]. Evidence for specific health effects relating to nanoparticles is inconclusive mainly because the research is not as substantial as that for size distributions including supermicrometre particles. With the exception of 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].

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 have been reported in the literature [7-9]. Therefore a precautionary approach[5] is prudent regarding exposure to particles associated with nanotechnology where understanding of the particle hazards is limited.

3 Overall Aim

The overall aim of this project was 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.

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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.

4 Objectives

1. Identify and review scientific literature regarding methods and methodology pertinent to the characterisation of airborne engineered nanoparticles
2. Identify and quantify particle emission sources in workplaces that manufacture or handle engineered nanoparticles, e.g. fibrous nanomaterials, nanoparticles that are carcinogenic, mutagenic, asthmagenic, or reproductive toxins (CMAR), insoluble nanomaterials, and soluble nanomaterials (subject to availability)
3. Characterise the emitted particles in terms of airborne concentration, size, and morphology at the emission point (temporal study)
4. Pilot a study of spatial particle characteristics so as to gain insight into the transport and fate of particles, and
5. Identify, quantify and propose measures for the mitigation of the potential exposure relative to the task.

5 Scientific Literature Regarding Common Methods and Instrumentation Pertinent to the Characterisation of Airborne Engineered Nanoparticles

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 engineered nanoparticles.

5.1 Properties of nanoparticles that influence measurement decisions

Evidence of the toxicity of nanoparticles comes mainly from 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.

5.1.1 Particle size

A nanometer (nm) is one billionth of a meter (10^{-9}m). Many terms are used to describe particles in this size range including ultrafine particle, ultrafine aerosol, nanoparticle, and nanoparticle aerosols, however these terms have not been rigorously defined and nor is there agreement on definition for these terms [11]. In addition, nanoparticles are structurally and chemically diverse and should not be considered as a group of similar compounds [12]. Common to the various definitions of ultrafine particles was "at least one dimension less than 100 nm" [11, 12].

The 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 engineered nanomaterials because the novel and differentiating properties [of nanoparticles] are developed at a crucial length scale of typically under 100 nm [11, 13]. This definition is not particularly useful for particle assessment because nanoparticles 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 nanoparticles in workplaces [15]. However, if agglomerates or aggregates of nanoparticles 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 nanoparticles [14].

The concepts of primary particle size, 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 nanoparticles. A cut-off size for nanoparticles 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 a minima for the tracheobronchial and alveolar regions until the size range of 300-400nm. A health based metric will need to consider an upper size limit based upon the mechanism of particle deposition within the lung.

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]. The toxicity of nanoparticles increases 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].

5.1.2   The surface area and the reactivity of that surface area

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].

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

5.1.3   Particle number

For constant size distribution, an increase in airborne particle number concentration (and associated higher mass concentration) will generally lead to an increase in exposure and thus higher health risk.

A given mass of nanomaterials will contain a significantly larger number of particles, and will therefore have a higher total surface area, than the same mass of macrosized particles. Thus, the nanoscale form of materials will generally have higher toxicity/unit mass than the macroscale form.

5.1.4   Solubility and biopersistence

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 through a process of the poorly soluble substances retained in the lungs causing oxidative stress leading to inflammation, fibrosis, or cancer.

5.1.5   Shape and fibres

The definition of a hazardous fibre varies and includes, a fibre that is thinner than 3 micrometers (µm), longer than approximately 20 µm, and biopersistent in the lungs [29], and particles with diameter < 3 µm, length > 5 µm, and aspect ratio (length to width) greater than or equal to 3 to 1 [30].   However, these size definitions appear to be arbitrary and related to the need to define regulatory fibre sizes for health assessment because for all fibres, the fibres must be respirable to pose an appreciable hazard. Respirability is mainly determined by diameter and density, thus with a given fibre diameter a higher specific density is associated with lower respirability [31].

Carbon nanotubes (CNTs) are engineered to form fibrous or rod shaped particles with high aspect ratios [32]. Chemico-physical 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].

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.

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.

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

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].

5.1.6 Primary particle size, aggregation, and agglomeration

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."

This has a direct influence on methods of nanoparticle measurement, and the selection and use of measuring equipment.

5.2 Measurement of nanoparticles

5.2.1 Metrics, methods, and instruments

There is considerable uncertainty over how exposure to nanoparticles should be measured because of the different toxicological pathways arising from the diversity of nanoparticle physico-chemical traits [38].

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 nanoparticles 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 nanoparticle exposure.

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 ultrafine (i.e. nanoscale) and fine titanium dioxide (TiO$_2$) published by the National Institute for Occupational Safety and Health are mass based, but these vary with particle size as they are based on surface area which relates to the health endpoint [40].

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

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

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 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].

There is strong agreement in the literature that mass [14, 41], or at least mass on its own, is not an appropriate measurement for nanoparticle exposure. Nanoparticle 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.

However, because surface area is not well understood and it is dependent upon the measurement method used, exposure to nanoparticles 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].

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 more comprehensive measurements [42].

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].

5.2.2 Summary of some of the currently available instruments and methods for characterising particle emission and transport

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.

In summary, of the 28 studies of nanoparticle measurement and methodology reviewed and reported by us, the following particle characterisation methodologies were 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)

Kuhlbusch et al. [44] also reviewed 25 studies and reported the following particle characterisation methods:
- Particle number concentration (all 25 studies)
- Particle size distribution down to below 100nm (21 of the studies)
- Mass concentration, using either optical particle sizer measurements, stationary and personal filtration samples, and PM_1, $PM_{2.5}$, PM_{10} samplers (slightly more than half of the studies)
- Electron microscope (12 of the studies)
- Consecutive chemical analysis (8 of the studies)

Table 1: Some currently available instruments for the characterising submicrometre particles in workplaces

Instrument/Device	Capabilities/Notes	Metric	Brief Description of Operating Principle, plus limitations	Specific literature that reported using this instrument/method
Condensation Particle Counter (CPC)	Real-time particle number concentration measurements between approximately 10 nm 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)	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	Particle number concentration and size distribution in real-time. 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™)	Real-time size-selective (aerodynamic diameter) measurement of size distribution or active surface area, and	Particle number concentration and size distribution in real-time. (Data may	The operating principle can be divided into three major parts: particle charging in a unipolar corona charger, size classification in a cascade impactor and electrical detection with sensitive electrometers. Because particles tend to	[42], [44], [55]

Instrument/Device	Capabilities/Notes	Metric	Brief Description of Operating Principle, plus limitations	Specific literature that reported using this instrument/method
	particle number concentration. Sensitive to 6-7 nm to 10 µm. Size selected samples may be further analysed off-line.	be interpreted in terms of aerosol mass concentration but only if particle shape and density are known)	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.	[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	[19], [45], [62]

Instrument/Device	Capabilities/Notes	Metric	Brief Description of Operating Principle, plus limitations	Specific literature that reported using this instrument/method
			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 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	[48], [68], [59]

Instrument/Device	Capabilities/Notes	Metric	Brief Description of Operating Principle, plus limitations	Specific literature that reported using this instrument/method
			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.	
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	Particle size accuracy can be as high as +/-10nm. The particle number concentration has an inherent zero error due to the noise level of the electrometer. The instrument specifications state this being up to as 1500 particles cm^{-3}, but our unpublished data put it at about 500 particles cm^{-3}. If particle size and particle number concentration are being recorded simultaneously, the minimum averaging time is 16 seconds. If only particle number concentration is being recorded the averaging time can be set to as low as 1 second. The longer averaging time may result in a significantly lower peak number concentration being recorded by the instrument.	[69], [66], [70]
Personal Nanoparticle Respiratory Deposition (NRD) Sampler	Full-shift personal sampler designed to collect particles with efficiency matching respiratory tract deposition of particles < 300 nm in diameter. 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.	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, 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. H2O). 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).	[49]
IOSH-NCTU Personal Nanoparticle Sampler (PNS)	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 H2O 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 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 engineered nanoparticles, in particular the agglomeration phase of the particles. Measurement accuracy is reduced where the optical	[55], [58], [59], [60]

Instrument/Device	Capabilities/Notes	Metric	Brief Description of Operating Principle, plus limitations	Specific literature that reported using this instrument/method
			properties of the aerosol differs markedly to that of the particle used to calibrate the instrument [44].	
Transmission Electron microscope	Off-line analysis of particle shape, morphology, size		Frequently used with EDX analysis to identify the chemical composition 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 to identify the chemical composition 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 presences of 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]

5.2.2.1 Personal samplers for time resolved nanoparticle measurements

Review of the literature shows minimal data on measurement of *personal* exposure to engineered 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.

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.

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.

The third is the IOSH-NCTU[6] 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.

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.   Some observations from our use of the Nanotracer are included in Table 1.

5.2.3 Response of instruments to aerosols dominated by specific particle characteristics

Real-time particle instruments are calibrated using specific aerosolised substances such as NaCl. These particles are usually 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 Nanoparticle Surface Area Monitor (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].

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[6] IOSH – Taiwan Institute of Occupational Safety & Health
NCTU – National Chiao Tung University, Taiwan

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.

The response of a water-based CPC to both n-butanol and propanol –based CPCs 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.

5.2.4 Sampling and measurement strategy issues

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 nanoparticle 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 nanoparticles 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 engineered nanoparticles at workplaces [44].

Mark [14] states that unless outdoor sources of nanoparticles (such as vehicle exhausts, other industrial actions) are excluded or minimised (using for example clean room conditions or high efficiency filters on the inlet air ducts) from the workplace environment, these ambient particles will penetrate indoors and 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. 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 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 engineered particle emission and exposure assessment, and 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[7] to 10,000 nm before, during, and after process operation. 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 the Scanning Mobility Particle Sizer (SMPS).

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.

Kuhlbusch et al. [44] examined 25 peer reviewed studies from the scientific literature and concluded that there is a lack of a harmonised approach concerning measurement strategies and techniques, metrics, size ranges, and data analysis procedures. These authors concluded that the measurement strategy used 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
- Approach based on comparative studies with and without the nanomaterial
- Size resolved chemical and/or morphological analysis.

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.

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;

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[7] 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.

- Tier 3 – employ the latest state-or-the-art measurement technology to assess workplace exposure to nanoscale aerosols.

5.2.5   Conclusions from review of literature

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 engineered nanoparticles in that the particle metrics chosen by researchers for characterisation differ, as does the methodology and instrumentation used. The literature reflects an over-emphasis on attempts to demarcate only the sub-100 µm fraction of aerosols adding complexities to measurement methods. 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.

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.

6   Research Methodology

6.1   General Information

Data characterising the emission and transport of particles associated with nanotechnology processes was collected during the operation of six processes involving engineered nanoparticles. In order to compare and evaluate the response of different instrumentation to airborne engineered 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[8] both during and between operation of the processes, so as to characterise particles arising from the nanotechnology process and

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[8] Note these results are not personal exposure measurements but rather are estimates of personal exposure as hand-held instruments were used when the worker/s were at usual process operation locations.

background particle sources. In addition, to evaluate the response of the hand-held condensation particle counter (CPC), optical particle counter (OPC), and DustTrak, these instruments were used to characterise particles arising from selected nanotechnology processes and from laser printer operation. Laser printers were also evaluated for two reasons – 1) as a known emitter of nanoparticles it allowed further evaluation of the response of the instruments, and 2) it allowed for comparison of instrument response to nanotechnology and non-nanotechnolgy generated aerosols.

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: Summary of 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[9], 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
Process 2 Modified clay platelets	Fine, functionalised clay platelets and polyurethane plastic beads were simultaneously added to an extrusion machine[10], designed to homogenise and heat the mixture so as to form a clay-polyurethane nanocomposite material.	2-A, 2-B, 2-C

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[9] 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.

[10] See footnote 2

Process and primary nanomaterial	Description of process	Measurement identification codes
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
Process 4 Modified 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 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 6 Carbon nanotubes	Chemical Vapour Deposition 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

6.2 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 5 seconds, 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 in the nanometre range was measured by a Scanning Mobility Particle Sizer (SMPS) comprising of a TSI Model 3080 Electrostatic Classifier 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), with a sampling time of 5 seconds.
- 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), and a sampling time of 5 seconds, 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, and a sampling time of 5 seconds.
- 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 was measured by a TSI Velocicheck hot-wire anemometer.

6.3 Experimental design

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.

6.4 Analyses

6.4.1 Transmission Electron Microscope, Scanning Electron Microscope and Energy-dispersive X-ray spectrometry

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.

6.4.2 Thermal optical analysis of elemental carbon

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.

6.4.3 Processing and Analysis of Data

All statistical analyses (correlation, t-test) were conducted using Microsoft Excel. A level of significance of $p = 0.05$ was used for all statistical procedures.

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.

7 Qualifying the Significance of the Results of Particle Measurement

This section discusses options for triggering a review of particle emission controls based upon particle measurement results.

7.1 Particle control values

Underpinning the application of the precautionary approach is the need for a *particle control value* that would guide the decision making in regard to controlling particles arising from nanotechnology processes.

There are a number of different types of *particle control values* that might be used for nanomaterial aerosols. These might be used in the following order of priority:

1. A company or laboratory's in-house control limits – if these are lower, i.e. more stringent, than applicable regulatory limits
2. Australian Workplace Exposure Standards
3. National exposure limits or recommended national exposure limits from another country, e.g. Recommended Exposure Limits (US NIOSH)
4. Proposed workplace exposure limits – from research results
5. Benchmark exposure levels – which have some consideration of health effects
6. Local particle reference values derived from characterising background particle levels

Appropriate application of this hierarchy of *particle control values* when assessing the significance of nanomaterial emissions and exposure will increase the number of *particle control values* available for use.

7.1.1 Australian Workplace Exposure Standards

In the model Work Health and Safety (WHS) Regulations, Regulation 49 states that: *A person conducting a business or undertaking must ensure that no person at the workplace is exposed to a substance or mixture in an airborne concentration that exceeds the relevant exposure standard for the substance or mixture.*

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}.

7.1.2 Recommended Exposure Limits

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

- for fine TiO_2 of 2.4 mg m^{-3} and
- ultrafine TiO_2 of 0.3 mg m^{-3}.

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].

7.1.3 Proposed workplace exposure limits

NIOSH has proposed a mass based REL [eight-hour time-weighted average standard] for carbon nanofibres, including carbon nanotubes of:

- 0.007 mg m^{-3}, based upon the elemental carbon mass [79] This is the upper limit of quantitation (LOQ) of NIOSH Method 5040. Risk estimates based upon animal data indicate that workers may have >10% excess risk of developing early stage pulmonary fibrosis if exposed over a full working lifetime at the upper LOQ.

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}

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

7.1.4 Benchmark Exposure Level

An alternative approach, in the absence of an exposure standard, REL 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 has also been proposed in the British Standards Institution (BSI) document – Nanotechnologies: Part 2: Guide to safe handling and disposal of manufactured nanomaterials [81] (the BSI Guide). The document proposed mass-based BELs for four types of nanomaterials [81]:

1. Fibrous nanomaterials : BEL = 0.01 fibres/ml
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 nanomaterials: BEL = 0.5 x WEL of the bulk material.

For insoluble nanomaterials, a BEL based on particle number concentration is also proposed. In the UK, current urban pollution is in the range 20 000 to 50 000 particles/ml. It is suggested that the lower end of this range 20 000 particles/ml discriminated from the ambient environmental particle concentration is an appropriate benchmark.

The document reports that these BELs are intended to be used as benchmarks to assess workplace exposures by measurement with the note that:

> "These are intended to provide reasonably cautious levels and are based in each case on the assumption that the hazard potential of the nanoparticle form is greater than the large particle form. This assumption will not be valid in all cases. Although these benchmark levels relate to current exposure limits, they have not been rigorously developed. Rather, they are intended as pragmatic guidance levels only and should not be assumed to be safe workplace exposure limits." [81]

Benke et al., [82] examined these BELs and reported that:

"While there are some issues associated with the hazard type groups suggested in the BSI Guide, they appear to be practical groupings of nanomaterials. In relation to each of the BELs proposed in the BSI Guide for each of the hazard type groups, this report finds:

- The BEL for insoluble fibrous nanomaterials should be modified to 0.1 fibre/ml, rather than the 0.01 fibre/ml recommended in the BSI Guide, as

there is no evidence that these nanomaterials are more toxic on a fibre-by-fibre basis than asbestos, and also, a higher number of fibres will be counted by electron microscopy which is needed to resolve fine fibres, e.g. carbon nanotubes. This BEL may also be applied to poorly soluble fibrous nanomaterials.

- There is currently limited scientific evidence to support a quantitative BEL for nanomaterials which are already classified in their larger form as carcinogenic, a reproductive toxin, asthmagenic or mutagenic (CMAR) of 0.1 x WEL, as proposed in the BSI Guide. This was a recommendation based on prudence and a rule of thumb, and should be supported by following a precautionary approach until knowledge is enhanced.

- In regard to insoluble nanomaterials, there is toxicological evidence to support the BSI Guide recommendation of a quantitative BEL of 0.066 x WEL for nanomaterials similar to TiO_2, but there is a lack of quantitative evidence for most insoluble nanomaterials. Combining the use of mass-based BELs and the particle number concentration BEL of 20 000 particles/ml may be the optimum approach. The particle size range over which a particle number concentration BEL should be measured needs to be defined.

- Although there is currently insufficient evidence to support the BSI recommendation of a quantitative BEL of 0.5 x WEL for soluble nanomaterials, this may be prudent due to the possibility that the size, shape and surface chemistry of soluble nanoparticles may lead to increased dose rates, or doses to parts of the body not usually exposed to such materials. However, a number of soluble nanomaterials do not have bulk forms for which exposure limits are set.

There are a number of other issues associated with these BELs. Firstly, a significant number of the bulk materials for engineered nanomaterials do not have exposure standards.

With regard to the benchmark of 20 000 particles/ml, how does this relate to mass concentrations? The relationship between number concentration and mass concentration for the BELs has been examined by the German Institute for Occupational Safety and Health of the German Social Accident Insurance (IFA) [83]. In this work, particle size and density variation were considered, and the number concentration required to give a mass concentration of 0.1mg m^{-3} was calculated for a number of manufactured nanomaterials (Appendix C, Table 23). Thus, a 20 000 particle/ml benchmark will correspond to a higher airborne mass concentration as a material's density and/or size increases, with a resultant higher mass exposure.

The benchmark of 20,000 particles/ml is based on comparison with urban pollution. However, the particle size and density will differ amongst nanomaterial aerosols from unique sources, and are also likely to differ from that of urban pollution. As will be shown later, engineered nanomaterial emissions contain a significant number of larger particles as agglomerates. Therefore in practice, a 20,000 particles/ml benchmark will correspond to a wide range of mass concentrations of airborne engineered nanomaterials.

7.1.5   Local Particle Reference Value

An alternative precautionary approach, in the absence of an Australian Workplace Exposure Standard, other national exposure limits, proposed workplace exposure limits, and BEL for a nanomaterial, could include reference to the *local background particle exposure*[11] of the workers. This is then used as the basis of a *local particle reference value*[12] to guide decision of when excursion from this value is unacceptable.

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 engineered nanoparticles is provided in Sections 8, 9, and 10 of this report.

7.2   Criteria for assessing excursion above the particle control values

Where feasible, 8 hr time-weighted average (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 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.

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 7.3.

Although these excursion criteria are applicable to *particle control values* in general, the remainder of this report explores the use of excursion criteria relative to *local particle reference values*.

7.3   Factors that should be considered when comparing and interpreting particle measurement data

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

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[11] See glossary for definition
[12] See glossary for definition

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 may be misinterpreted 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. This data for the instruments used in this study is contained in Table 3.

Table 3: Manufacturer specified instrument particle concentration accuracy data

Instrument	Particle concentration accuracy
TSI Model 3781 CPC	±10% at 5×10^5 particles cm^{-3}
TSI Model 8525 hand-held P-Trak	±20% of the reading*
TSI Model 3022 CPC	±10% at 5×10^5 particles cm^{-3}
TSI Model 3025 CPC	±10% at 5×10^5 particles cm^{-3}
TSI Model 3550 NSAM	±20% or 0.5 µm^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 5×10^5 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	

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.

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. Therefore, all instruments should be co-located and operated simultaneously to characterise an aerosol source. A correction factor for one of the instruments should be calculated as per equations 1 and 2, and the correction factor applied to the field data. This concept is illustrated below using two different CPC's as an example.

$$F_{CPC1} = \frac{TC_{CPC1}}{TC_{CPC2}}$$
Eq.1

where F_{CPC1} is the correction factor for CPC1, and TC_{CPC1} and TC_{CPC2} are the total number concentrations measured by each, respectively, during selected periods for an aerosol.

The corrected measurements for the CPC1 readings are then calculated as:

$$CTC_{CPC1} = \frac{TC_{CPC1}}{F_{CPC1}}$$

where, CTC_{CPC1} is the corrected total number concentration data for CPC1.

The discussion in this report of particle measurement results is in terms of these factors that influence accuracy.

8 Results of the Characterisation of Particle Emission, Transport, Morphology, and Chemical Composition for Six Engineered Nanoparticle Aerosols

The results of particle measurement data have been organised so as to,

- 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 over the period of measurement[13] 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, and

- 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.

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

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[13] In this situation, mean refers to the mean of the pooled measurement data, demarcated as during the process operation, and before process operation.

This data is also summarised in Table 4.

8.1 Mean particle metrics for all six nanomaterial aerosols

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 sections 8.2 to 8.7.

Differences of between 10 and 20% in the spatial PNC were 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.

Table 4: Summary of mean particle metrics reflecting the nanotechnology process in operation and the *local background particle exposure* (LBPE), measured simultaneously at the nanomaterial emission source and 7 m from source for six nanomaterial aerosols

	At nanomaterial emission source															Spatial data at 7m from emission source	
	Mean PNC [particles cm^{-3}] **CPC 3781**		Mean PNC [particles cm^{-3}] **CPC P-Trak**		Mean PNC 300 to 3000nm [particles cm^{-3}] **OPC**		Mean PNC 3000 to 10000nm [particles cm^{-3}] **OPC**		Mean PM$_{2.5}$ [µg m^{-3}] **DustTrak**		Mean CMD [nm] **SMPS**		Mean alveolar surface area [µm^2 cm^{-3}] **NSAM**		Elemental Carbon NIOSH Method 5040 [µg m^{-3}]	Mean PNC [particles cm^{-3}] **CPC 3781**	
Process	During	LBPE	During	LBPE	During	LBPE	During	LBPE	During	LBPE	During	LBPE	During	LBPE	During	During	LBPE
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$^\Delta$	#	#	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$^\square$	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	#	#	#	#	#	#	#

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 analyist noted "filter overloaded and uneven particulate distribution"

* mean *local background particle exposure* for of 2A, 2B, 2C combined values, whilst peak value reflects the highest value for 2A, 2B, 2C

^ mean *local background particle exposure* for 3A to 3E are combined values, whilst peak value reflects the highest value for 3A to 3E

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.

8.2 Process One – grinding and extrusion of modified TiO$_2$

8.2.1 Experimental Design and Conditions

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.

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 the stages of the process. Spatial PNC, including within operator breathing zone, was also measured using a P-Trak as a hand-held device 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.

8.2.2 Results

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

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 exposure* and particles being emitted from Processes 1A and 1B.

Figure 1 compares the particle number and mass concentration during process operation and the *local background particle exposure* 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.
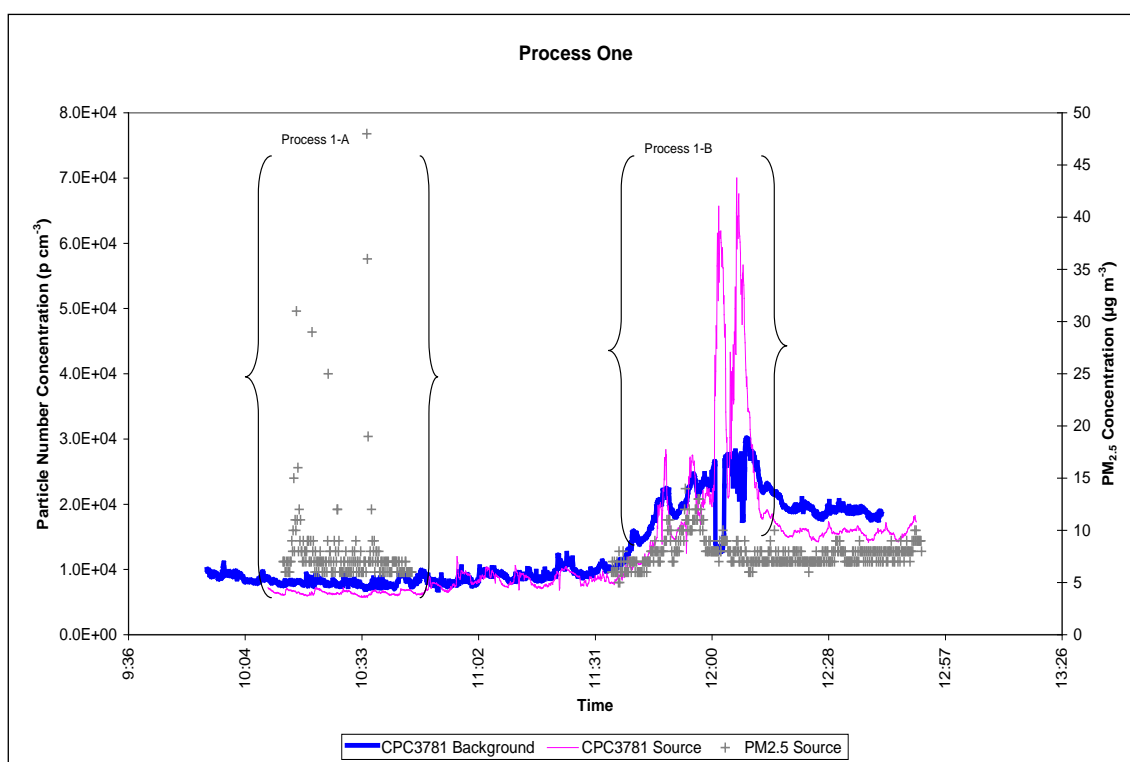
Figure 1: Comparison of PNC and PM$_{2.5}$ concentration during stages 1-A and 1-B and the local background particle exposure. The background CPC was situated approximately 7m from the process particle source and the source PM$_{2.5}$ and CPC were situated approximately 0.2m from particle emission point.

Figure 2 compares the time series of particle number and mass concentration during specific tasks that were undertaken during stage 1-A. The process was repeated three times for the purposes of measurement and labelled batches A, B, and C, with each batch task labelled Task A to F as follows - Task A = Crushing Fe Stearate; Task B = Weighing out Fe Stearate; Task C = adding oil and mixing; Task D = crushing and adding P25 TiO$_2$; Task E = Mixing the above using a spatula; and Task F = Pouring the above into another container. No extraction or mechanical dilution ventilation was in operation during any batch.

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. For example, the peak PNC of 7.0 x 10^3 particles cm^{-3} is approximately 1.0 x 10^3 particles cm^{-3} greater than the lower value of 6.0 x 10^3 particles cm^{-3}. This difference of 1.0 x 10^3 particles cm^{-3} is within the manufacturer stated inaccuracy (± 20%) of the CPC as ± 20% of 6.0 x 10^3 particles cm^{-3} = ± 1.2 x 10^3 particles cm^{-3}.
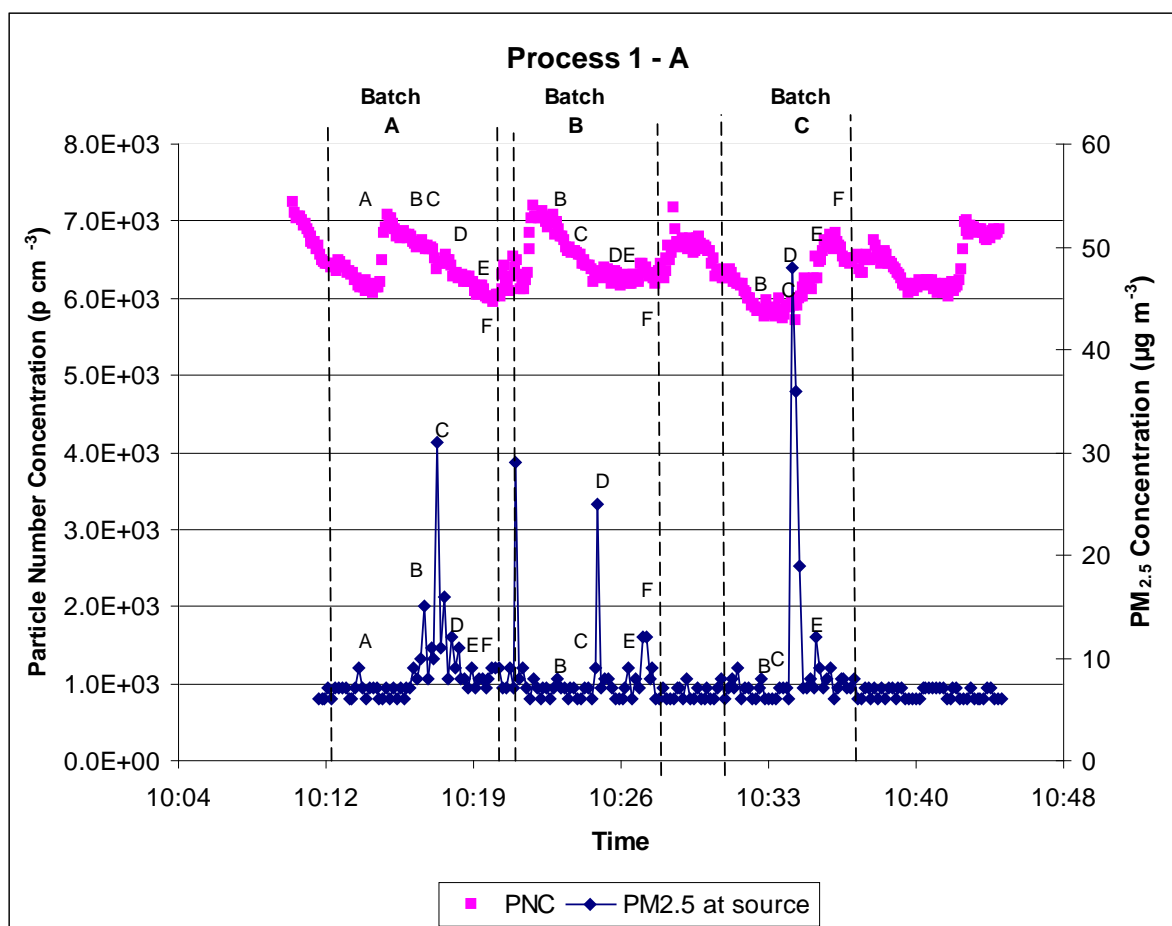
Figure 2: Process 1, stage 1-A was repeated over three batches. For each batch the main tasks are labelled A to F, with Task A = Crushing Fe Stearate; Task B = Weighing out Fe Stearate; Task C = adding oil and mixing; Task D = Adding P25 TiO$_2$; Task E = Mixing the above using spatula; Task F = Pouring the above into another container.

Peak PM$_{2.5}$ concentration associated with specific tasks is also evident in Figure 2. 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. The tasks that involved pouring of both iron stearate (Task B) and TiO$_2$ powders (Task D) and the hand mixing of these (Task E) are most frequently associated with peak PM$_{2.5}$ concentration. In absolute terms the maximum peak PM$_{2.5}$ value of 47 µg m^{-3} was only 41 µg m^{-3} above the background of 5 µg m^{-3} and therefore of very limited significance in practical terms. 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 3 provides additional PNC and PM$_{2.5}$ concentration time series for stage 1-B. Figure 3 presents the results of spatial measurements obtained with a P-Trak and DustTrak,

including within the breathing zone[14] of the process operator during the process operation. Measurement locations are signified on graph as follows: A = at extruder control panel approximately 0.5 m from the extruder machine and in the approximate breathing zone of the operator, B = 2.4 m to right of extruder machine, C = 2.4 m to the left of extruder machine, D = at receiving hopper for final product, approximately 5 metres from the extrusion machine. No extraction or mechanical dilution ventilation was in operation during this stage.   Similar to the concentrations presented in Figure 1, 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.
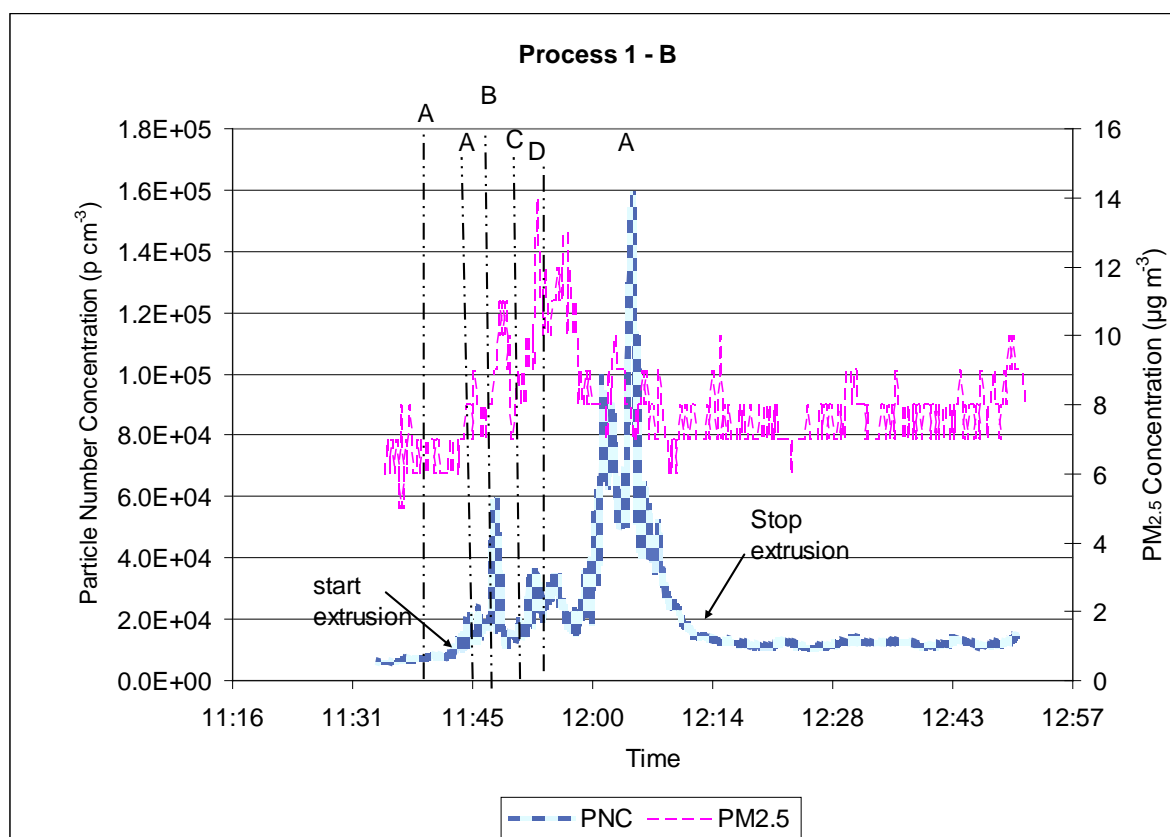
Figure 3: Difference in particle number and mass concentration at different locations during the extrusion process. PNC obtained using a P-Trak, and PM2.5 concentration using a DustTrak. Locations are signified on graph as follows: A = at extruder control panel 0.5 m from source in breathing zone of 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.

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 4. 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 each batch. However these peaks are

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[14] Note these results are not personal exposure measurements but rather are estimates of personal exposure as hand-held instruments were used when the worker/s were at usual process operation locations.

relatively small when compared to background, and the accuracy of the instruments is considered as outlined in Table 2.
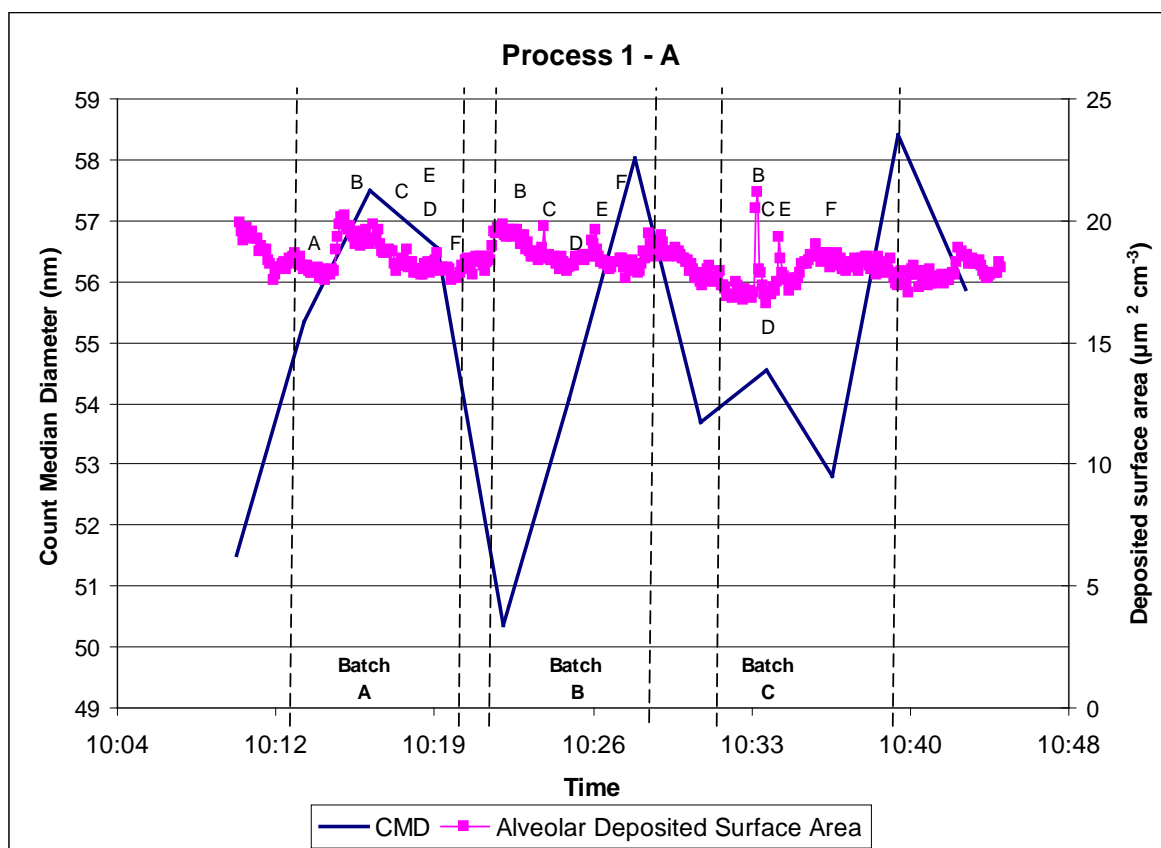
Figure 4: Count Median Diameter and alveolar deposited surface area of particles at the emissions source for stage 1-A. Common process steps are notated on the figure as follows: A = Crushing Fe Sterate; B = Weighing out Fe Sterate: C = adding oil and mixing; D = Adding P25 TiO2; E = Mixing the above using spatula; F = Pouring the above into another container.

The CMD and the alveolar deposited surface area of the particles as characterised at the emission point of stage 1-B is presented Figure 5. 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, and when the accuracy of the instruments is considered, as outlined in Table 3.
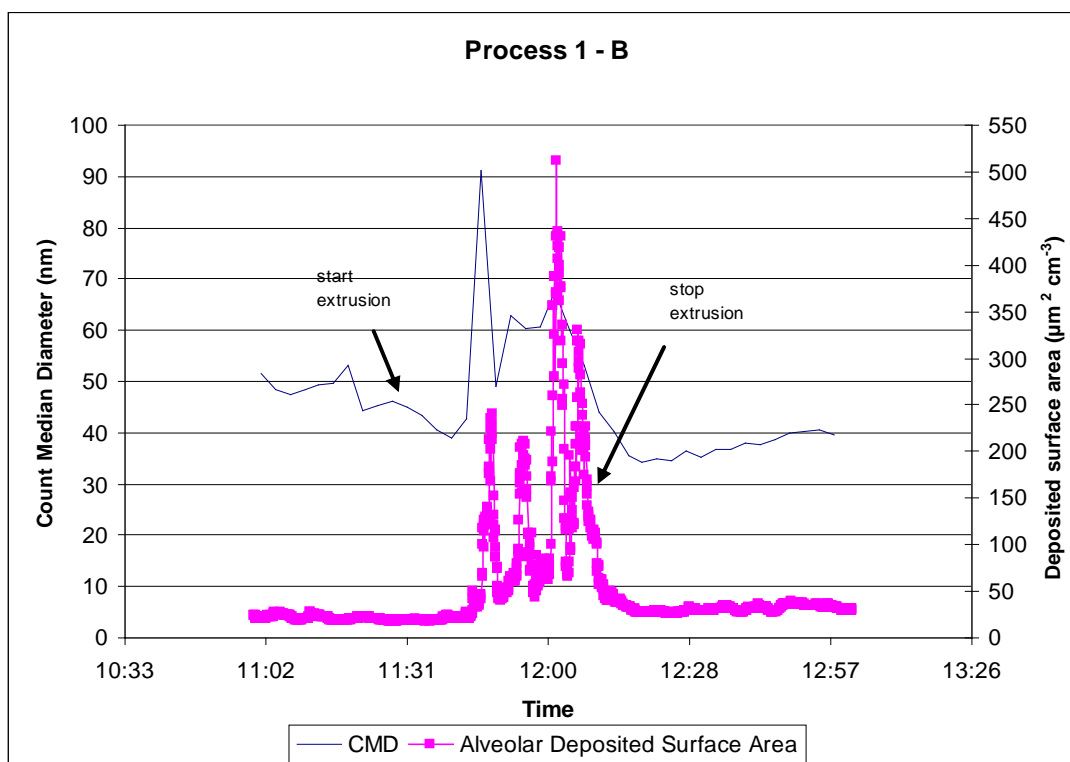
Figure 5: Count Median Diameter and alveolar deposited surface area of particles at the emission source for stage 1-B.

8.2.2.2 *Electron microscope*

Figure 6 depicts the SEM and energy dispersive X-ray spectroscopy results for aerosol particles collected using 37 mm polytetrafluoroethylene (PTFE) filter, open face cassette, and pump method during Process 1A. These filters were co-located with the real-time measurement instruments described above.
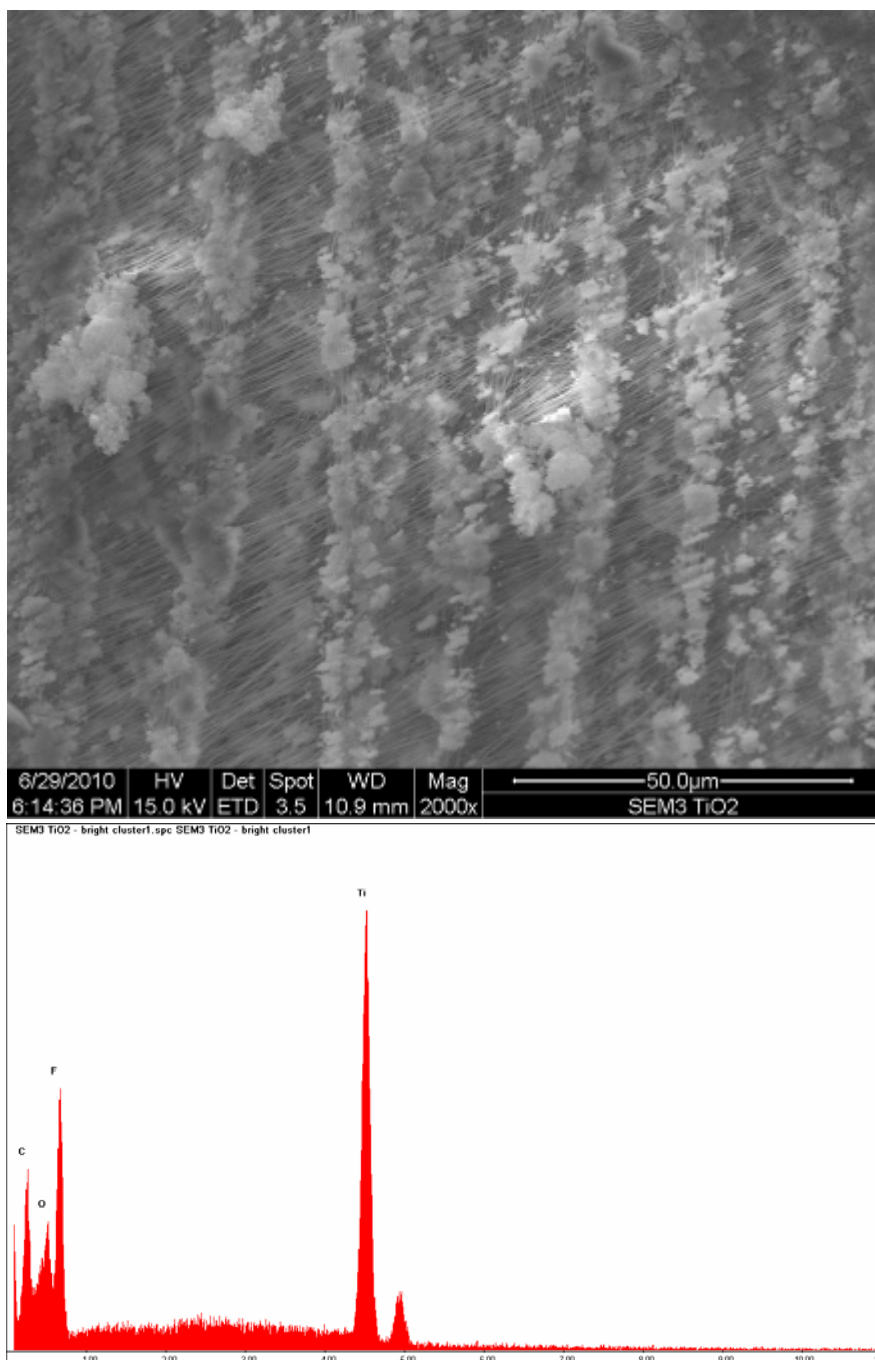
Figure 6: SEM image and energy-dispersive X-ray spectroscopy of particles sampled from Process 1-A. The open face cassette used for this sampling was located at same point as that of the real-time particle measurement instruments used for Process 1-A.

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 EDAX 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.

8.2.2.3 Discussion

The data from Figures 1 to 5 is reflective of the process operation and the *local background particle exposure*, and has been used in Table 5 to examine variability in peak PNC, mass concentration, CMD, and alveolar deposited surface area associated with Processes 1A and 1B.

Table 5: Summary of peak particle metrics at emission source during process operation compared to the peak associated with *local background particle exposure* (LBPE)

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 LBPE	Peak during process	Peak of LBPE	Peak during process	Peak of LBPE	Peak during process	Peak of LBPE	Peak during process	Peak of LBPE	Peak during process	Peak of LBPE
1A	7.0 x 10^3	5.7x 10^3	#	#	#	#	50	9	58	53	24	19
1B	1.6 x 10^5	1.3 x 10^4	#	#	#	#	1.6 x 10^1	1.0 x 10^1	90	50	500	45

\# not measured

It is evident from Table 5 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. Differences in CMD and alveolar deposited surface area, during the process and the background , are not significant. In contrast for Process 1B, there are significant differences in CMD and alveolar deposited surface area and this reflects: 1) the influence of the submicrometre particle emission, and 2) the particle size being predominantly within the submicrometre measurement range of the SMPS and NSAM respectively.

However, the insignificant difference between the mean of the particle metrics during the process and the background, as summarised in Table 4, indicates the peak particle emissions from Process 1A are weak with insignificant impact upon mean particle metrics when compared with the background. In contrast for Process 1B, the mean of the PNC, CMD, and alvelolar 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 sources of particles with the submicrometre particles dominating the particle signature. However, the spatial PNC values indicate the particle source is not strong enough to influence *local background particle exposure* as measured at 7 meters from the point of emission.

The likely reason for the insignificant difference in the means of the CMD and alveolar deposited surface area, between during process operation and the background, is that the

particle contribution from the nanotechnology process was minor relative to the *local background particle exposure*, and therefore mean particle size values would reflect the predominance of background particles. This contrasts for Process 1B where the particle emission had the strength to influence the background particle CMD and alveolar deposited surface area.

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. However, 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. 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.

In analysing the particle concentrations recorded during the operation of process 1B the probability of the extrusion machine, which was operating at a temperature of approximately 200ºC, contributing particles associated with vapour generation, must be considered as high. Therefore, as particles were not sampled for off-line analysis of composition, it is possible the source of elevation in particle concentrations during the operation of process 1B originated from vapour generation.

The results of the off-line analysis of aerosol indicates 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.

8.3   Process Two – manufacture of clay-polyurethane nanocomposite material

8.3.1   Experimental Design and Conditions

This nanotechnology process involved instilling a clay product as a composite into a polyurethane polymer 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 operator exposure, at the location of the control panel, was measured using a P-Trak, and the room *local background particle exposure* was characterised using a CPC 3781 located ~7 m away. Figure 6 illustrates the configuration of the sampling rig.

Figure 6: Configuration of measurement equipment, with sampling manifold, relative to the location of the extruder machine.

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.

8.3.2 Results

8.3.2.1 *Time series of particle number and mass concentration, count median diameter, and alveolar deposited surface area*

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 7 and 8.

Figure 7 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 at both measurement locations, (ii) when the extraction ventilation is turned on the PNC displays an obvious reduction 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 7: 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.

As expected, 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 for at least two 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 allowed a greater PNC to be characterised, and (2) particles may exhibit significant differences in solubility between water and alcohol. Therefore, when collecting spatial data the same model of CPC should be used. Despite the differences in the CPC's both were able to characterise similar patterns in particle variability associated with specific process events.

The CMD and the alveolar deposited surface area on the particles as measured at the emission point of Process 2-A are presented in Figure 8. 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 7.
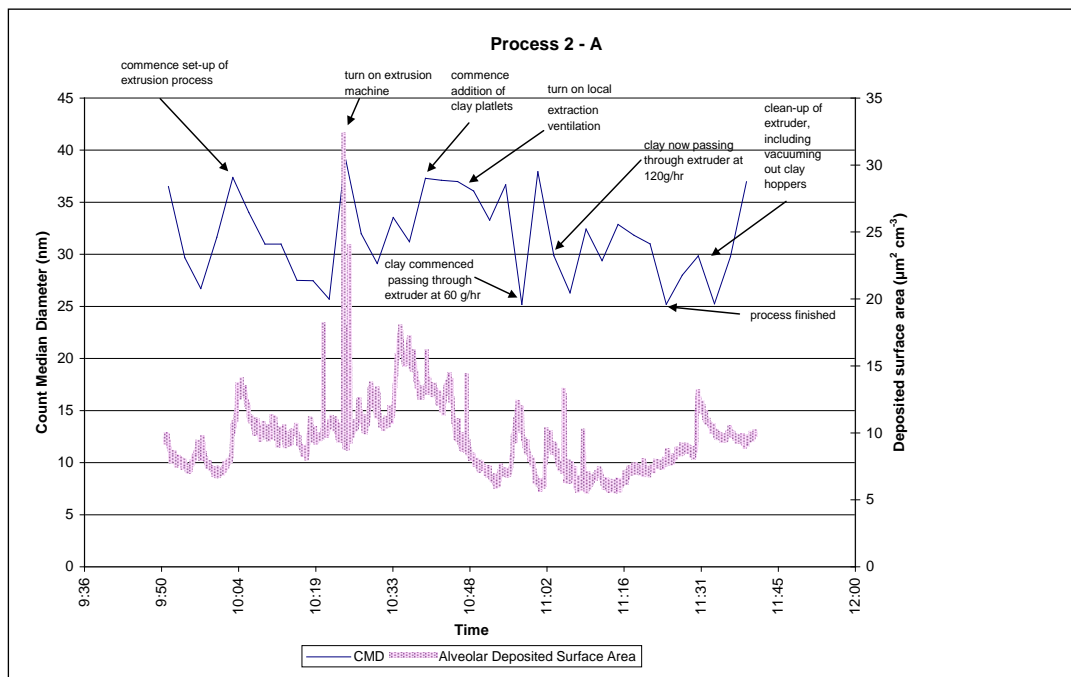
Figure 8: Count Median Diameter and alveolar deposited surface area of particles at the extruder emissions source of Process 2-A

Patterns in particle number and mass concentration, particle diameter, and alveolar deposited surface area are discernible 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 at the source, and an increase in the 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.

8.3.2.2 Influence of local extraction ventilation upon the particle concentration within the work area

Figures 9 and 10 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 and on at 12:43 hours in Figure 9, and again in Figure 10 when the LEV is switched on at 12:50 hours.
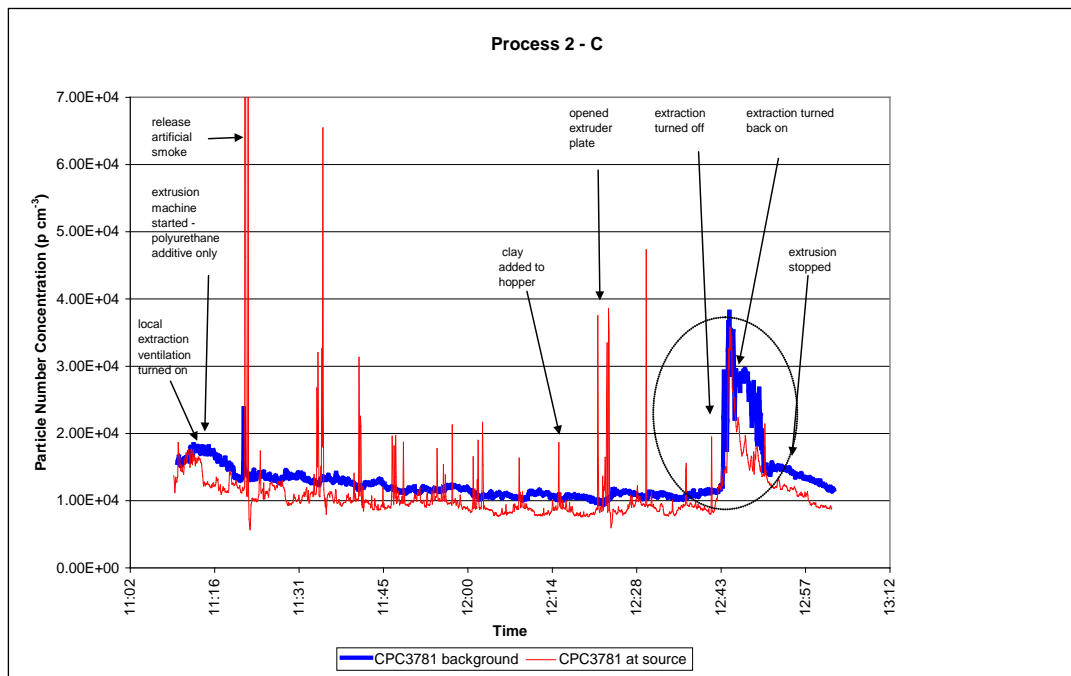
Figure 9: Comparison of PNC at extruder source and at background 7 metres away. Note effect on PNC of turning local extraction ventilation off at approximately 12:43 hours and back on at approximately 1250 hours (circled area).
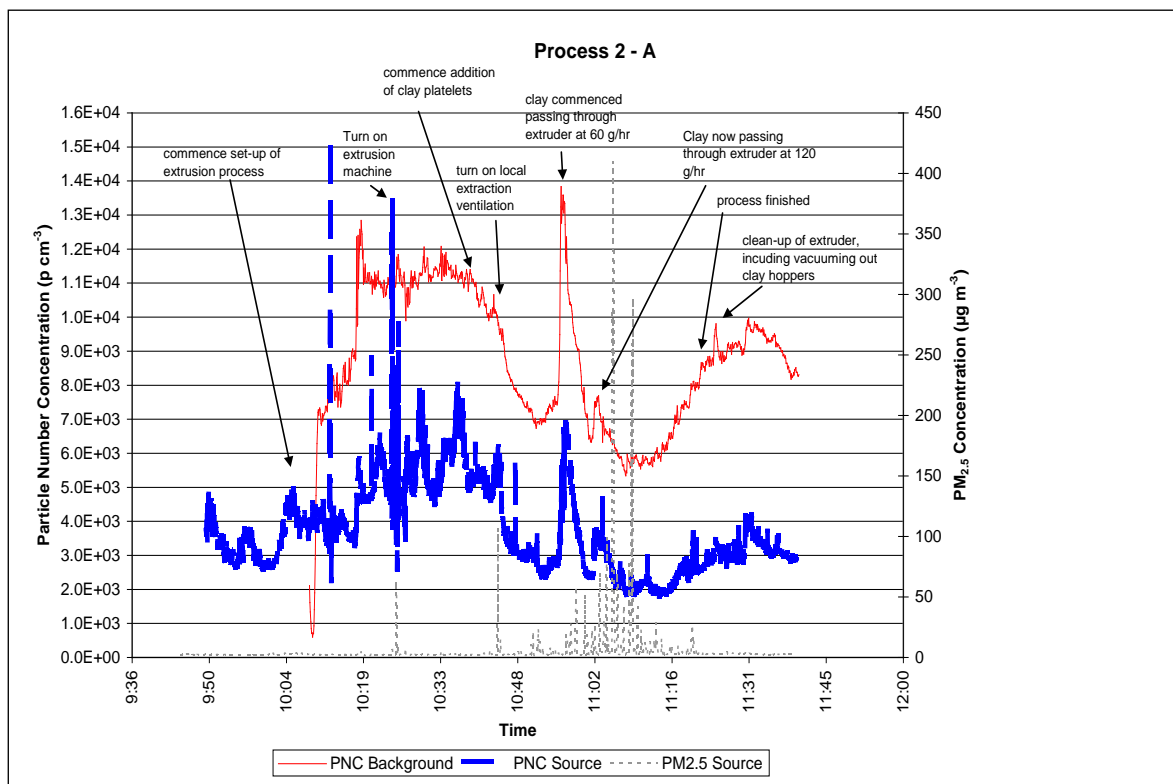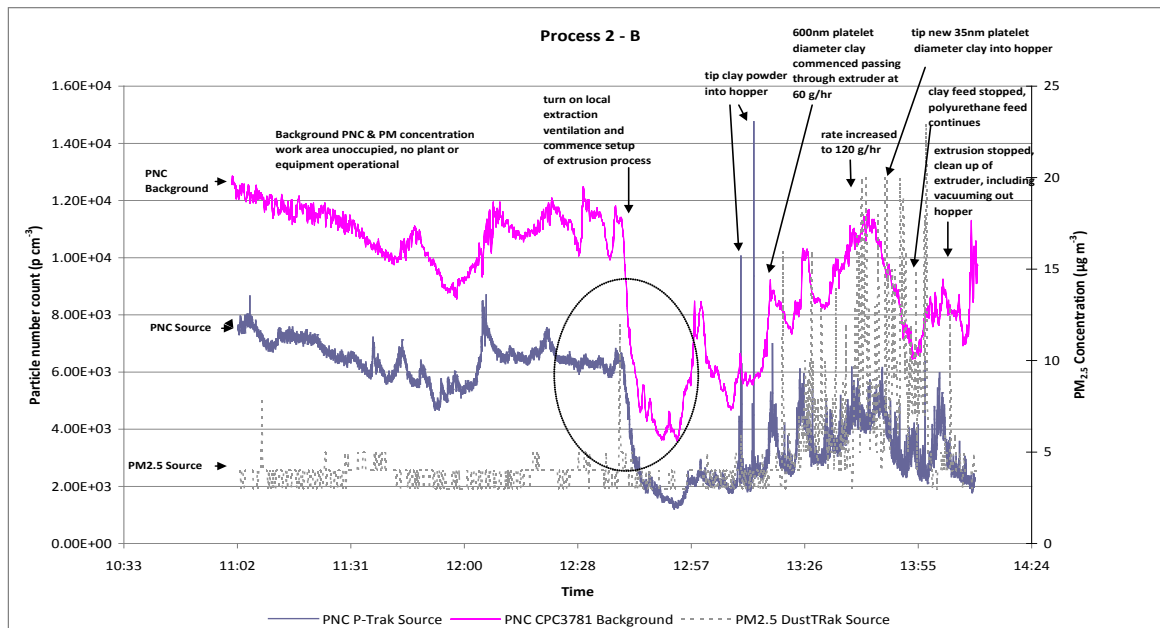
Figure 10: Comparison of PNC at extruder source (CPC P-Trak) and at background 7 metres away (CPC 3781), plus particle mass concentration (DustTrak). Note effect of switching on local extraction ventilation at approximately 12:40 hours (circled area).

Further evidence of the effect of LEV on reducing the PNC is provided by comparison of the mean PNC measured at the point of particle emission for Processes 1B and 2, as shown in Table 4. Both these processes used the same extruder process, however the difference in the mean PNC for Process 1B during operation and without LEV is one order of magnitude higher than for Process 2 which had LEV in operation.

8.3.2.2.1 Description of the local extraction ventilation servicing the extruder machine

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 insitu 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.

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 45º 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 45º to the extruder and 3 metres straight line from the centre of the extruder machine.

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}.

Using equation 1, 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.

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

Where 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.

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,

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

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}.

Although the PNC values plotted in Figure 6 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 6).

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].

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

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

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.

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.

8.3.2.3 *Electron microscopy analysis of particles*

Figures 11 and 12 show the TEM and SEM images respectively, along with energy-dispersive X-ray (EDX) spectroscopy analysis spectra for aerosols arising from process 2A, whilst Figure 13 contains the same type of data for the raw material used in Process 2A. Figure 13 shows the nominal chemical formula for the functionalised clay platelets used during Process 2A, and this differs to that used during Processes 2B and 2C.

Comparison of Figures 11, 12, 13 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.

The weight percent of the elements identified in the CM200 TEM EDX spectra of the collected nanoparticles 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 6, 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.
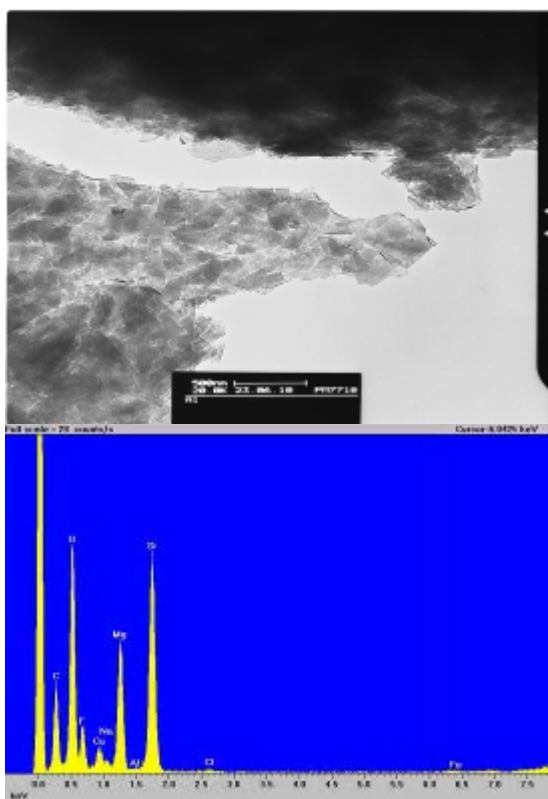
Figure 11: TEM image and energy-dispersive X-ray spectroscopy of particles sampled from Process 2-A. The aerosol sampling inlet of the electrostatic precipitator used for this sampling was located at same point as that of the real-time particle measurement instruments used for Process 2-A.
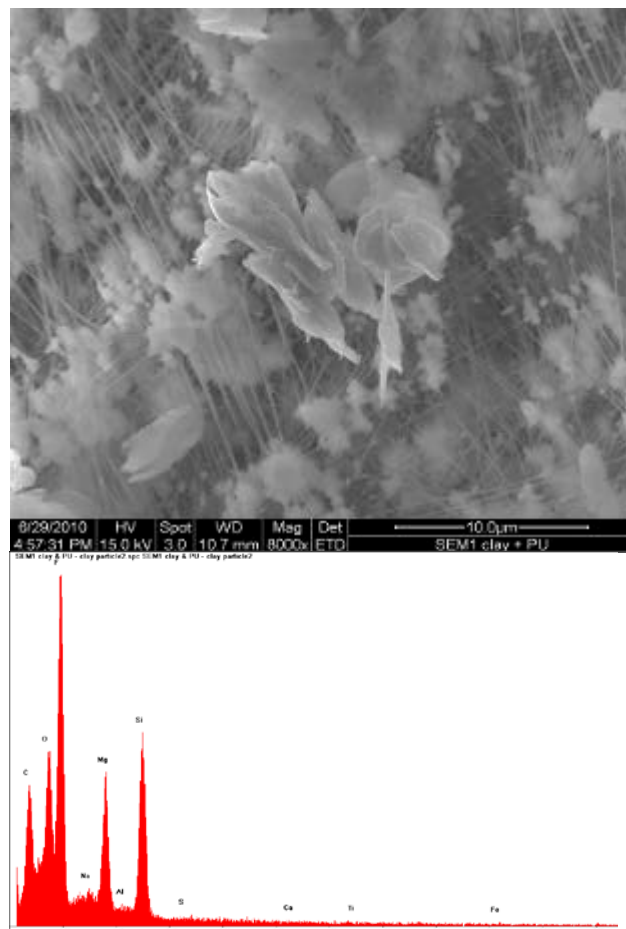
Figure 12: SEM image and energy-dispersive X-ray spectroscopy of particles sampled from Process 2-A. The open face cassette used for this sampling was located at same point as that of the real-time particle measurement instruments used for Process 2-A.
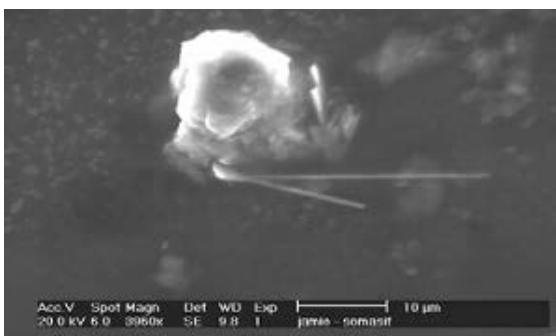
Figure 13: SEM image of particles contained in the raw material used in the nanotechnology Process 2.

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

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

Table 6: Calculated elemental weight percent composition of raw material and aerosol particles for Process 2A analysed in the TEM. (The substrate carbon peak has been omitted from these calculations.)

	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.						

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.

8.3.2.4 Discussion

The data from Figures 7 and 8 is reflective of the process operation and the *local background particle exposure*, and has been used in Table 7 to examine variability in peak PNC, mass concentration, CMD, and alveolar deposited surface area associated with Process 2.

Table 7: Summary of peak particle metrics at emission source during Process 2 operation compared to the peak associated with *local background particle exposure* (LBPE)

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 LBPE	Peak during	Peak of LBPE	Peak during	Peak of LBPE	Peak during	Peak of LBPE	Peak during	Peak of LBPE	Peak during	Peak of LBPE
6.0×10^4	1.7×10^4	#	#	#	#	4.0×10^2	1.0×10^1	50	45	90	33
# not measured											

The data in Table 7 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. The CMD of particles attributable to the emission

source is likely to be greater than 160 nm as evidenced by the insignificant difference in CMD during the process and that of the local background recorded by the SMPS (which had a measurement size range of 4 to160nm).

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 as described in section 8.3.2.2.

In analysing the particle concentrations recorded during the operation of processes 2A, 2B, and 2C, the probability of the extrusion machine, which was operating at a temperature of approximately 200ºC, contributing particles associated with vapour generation, must be considered as probable.

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.

We have shown in section 8.3.2.2 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.

8.4   Process Three – grinding of titanium dioxide powder

8.4.1   Experimental Design and Conditions

This fabrication 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).

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 14 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.
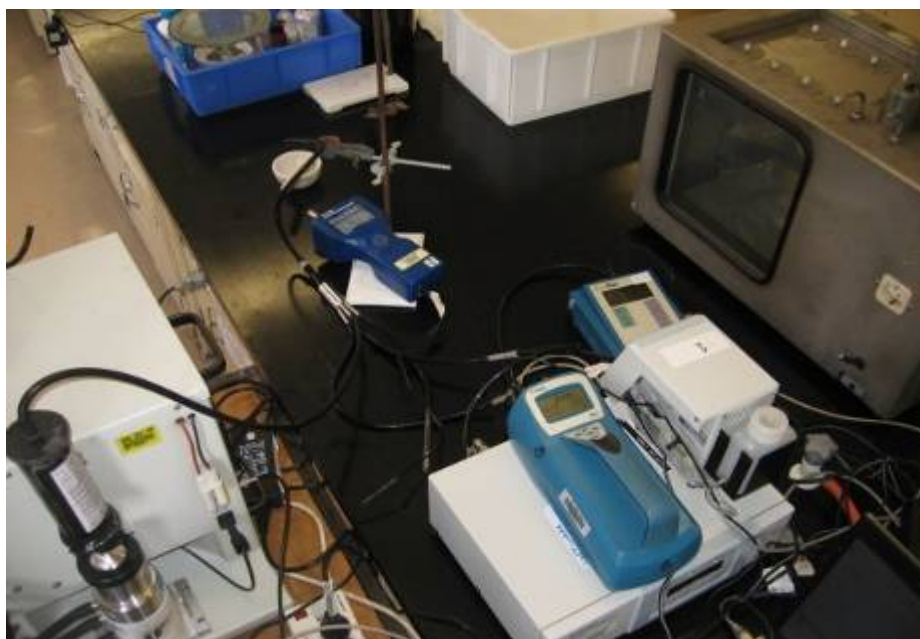
Figure 14: Photograph showing the measurement instrumentation configuration for the SMPS, Ptrak, CPC 3781, DustTrak, OPC, NSAM, plus the mortar and pestle at the particle generation source.

8.4.2   Results

8.4.2.1   *Time series of particle number and mass concentration, count median diameter, and alveolar deposited surface area*

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 exposure* and process particle metrics.

Figure 15 compares the particle number and mass concentration during process operation and the *local background particle exposure* as repeated six times, labelled Process 3-A to 3-F. The grinding step during processes 3-A, -C, -E were "wet" processes that involved the addition of an acid solution, whilst processes 3-B, -D, -F were "dry" processes with no solution added during grinding.
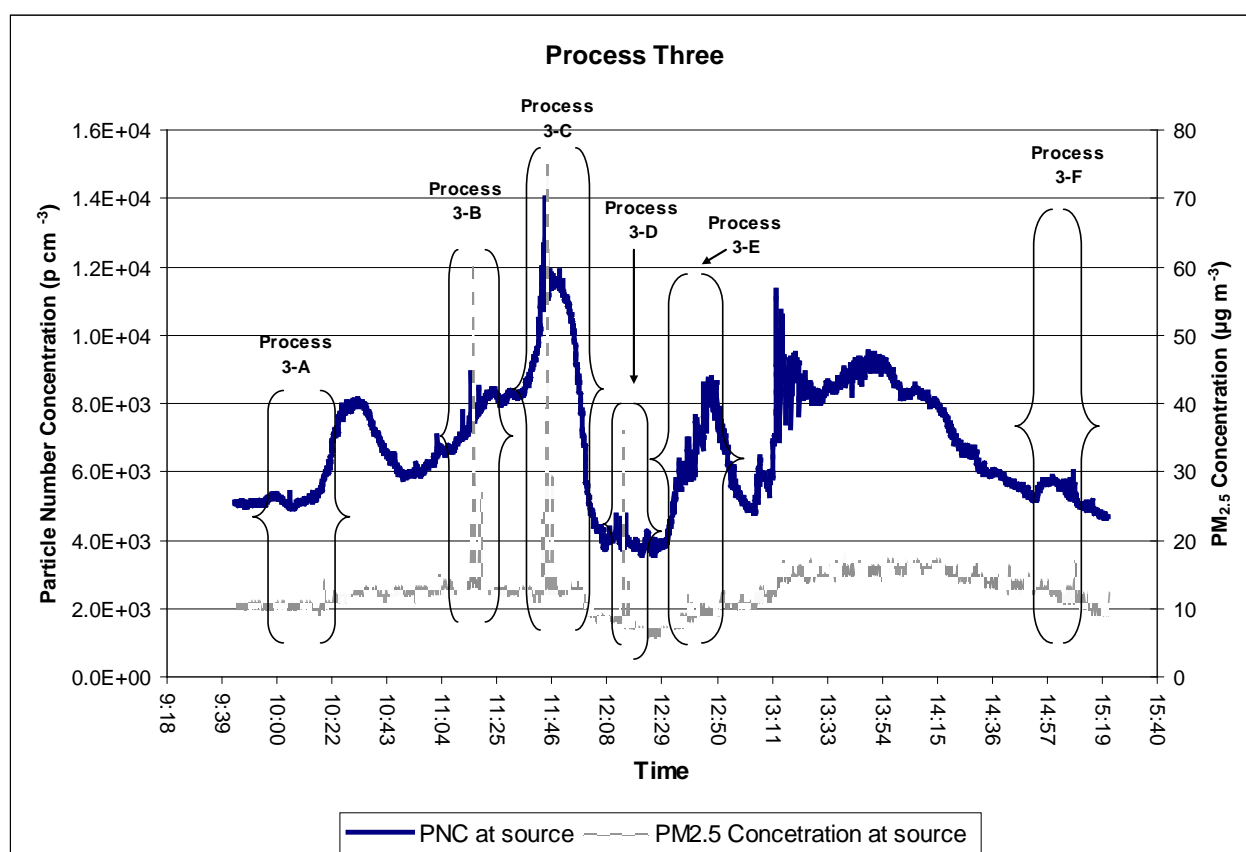
Figure 15: Particle number concentration (PNC) and particle mass (PM) concentration during six episodes of process number three. Each process involved weighing out the TiO$_2$ powder, using a mortar and pestle to grind the powder, and pasting the powder onto a slide. The letters A-F signify six discrete 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

Over the course of the day the *local background particle exposure* 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.

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.

The CMD and the alveolar deposited surface area of the particles as measured at the emission point of Process 3 are plotted in Figure 16. Note the variation in background CMD and alveolar deposited surface area over the course of the day. 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 and which are significant when the accuracy of the instruments is accounted for.
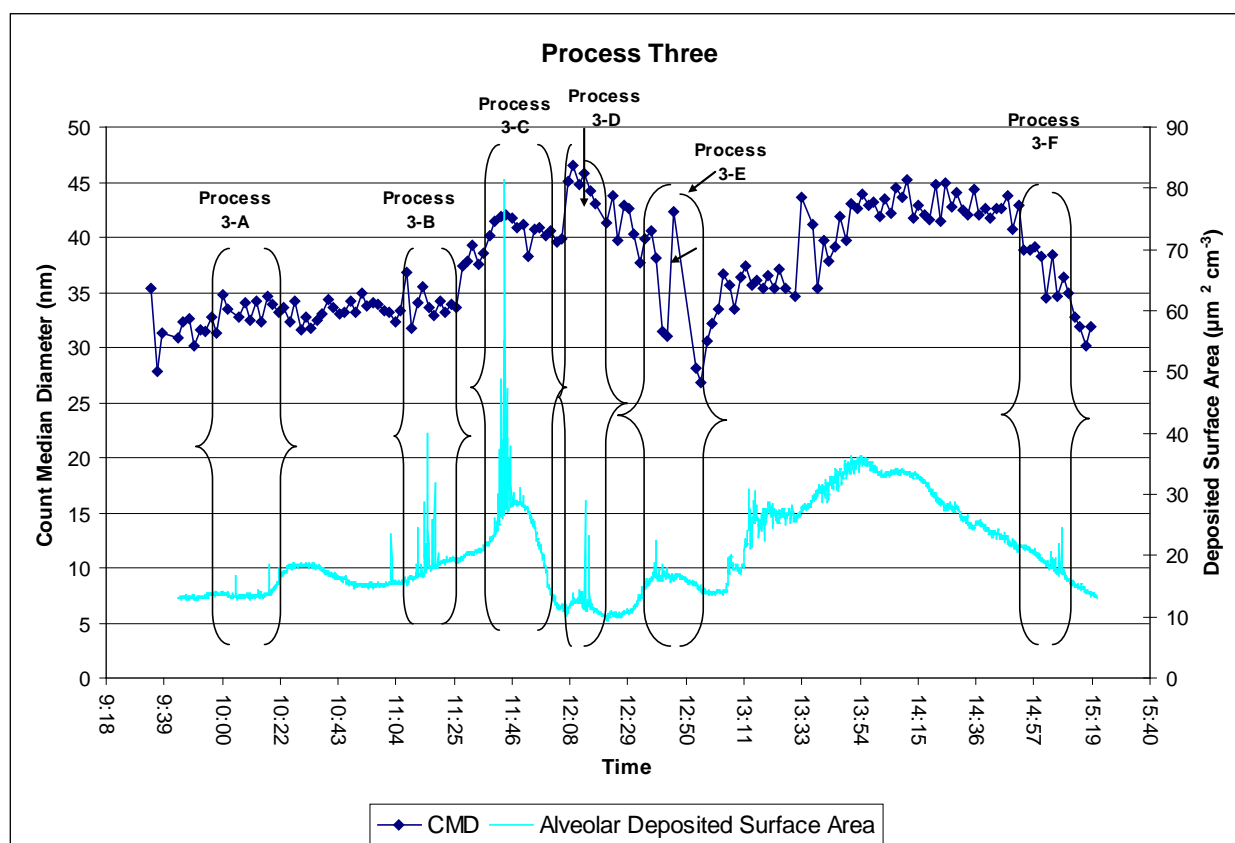
FFigure 16: Count median diameter and alveolar deposited surface area during six episodes of process number three. Each process involved weighing out the TiO₂ powder, using a mortar and pestle to grind the powder, and pasting the powder onto a slide. The letters A-F signify six discrete occurrences of 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.

To further analyse the influence of individual steps of the process upon 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 8. Step 1 = weighing out of the TiO₂ powder, Step 2 = the manual grinding of the powder using a mortar and pestle, and Step 3 = pasting the powder onto the slides.

It can be seen from Table 8 that Step 2, the grinding of the TiO₂ powder, is consistently associated with peaks in PNC, PM₂.₅ 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.

Table 8: 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						

8.4.2.2   Discussion

The time-series plots from Figures 15 and 16 are reflective of the process operation and the *local background particle exposure*, and have been used in Table 9 to examine variability in peak PNC, mass concentration, CMD, and alveolar deposited surface area associated with Process 3.

Table 9: Summary of peak particle metrics at emission source during Process 3 operation compared to the peak associated with *local background particle exposure* (LBPE)

Process PNC 20 to 1000nm [p cm^{-3}] **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**		CMD [nm] **SMPS**		alveolar surface area [µm^2 cm^{-3}] **NSAM**	
Peak during	Peak of LBPE	Peak during	Peak of LBPE	Peak during	Peak of LBPE	Peak during	Peak of LBPE	Peak during	Peak of LBPE	Peak during	Peak of LBPE
1.1×10^4	3.2×10^3	#	#	#	#	70	10	46	37	81	35
# not measured											

The data from Table 9 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, whilst the SMPS data (upper size range of 160 nm) indicates insignificant ultrafine 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.

Despite these peaks, the mean particle metrics during Process 3, as shown in Table 4, are not significantly different to the *local background particle exposure*, indicating the process peaks are of low strength compared to the background.

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

8.5   Process Four – jet milling of modified clay particles

8.5.1   Experimental Design and Conditions

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.

The operation of the Micron-Master Jet Pulveriser is described in the machine operating manual as follows. The feed injector injects the feed supplied to it by the mechanical feeder into the grinding chamber. A series of high velocity jets in the Peripheral Wall pick up and impel the feed material against a circulating mill load. Grinding occurs due to the impact of one particle against another. Centrifugal force holds the large particles in the grinding chamber. The ground product is entrained in and carried out by the spent grinding air. A built-in cyclone collector collects 90-98% of the ground product. Smaller fractions are separated out and collected in a bag type dust collector. A vibrating inlet sleeve feeds the material into a venturi chamber from where the milled

material is collected in a product receiver chamber, and larger particles are collected in a dust collection bag. Figure 17 shows a photograph of the Jet Milling Machine.

Figure 17: picture of the Jet Milling Machine

A P-Trak, OPC, and DustTrak identified sources of particle leakage from the milling machine as 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.

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.

8.5.2   Results

8.5.2.1   *Time series of particle number and mass concentration*

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.

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.

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.

Figures 18 and 19 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.
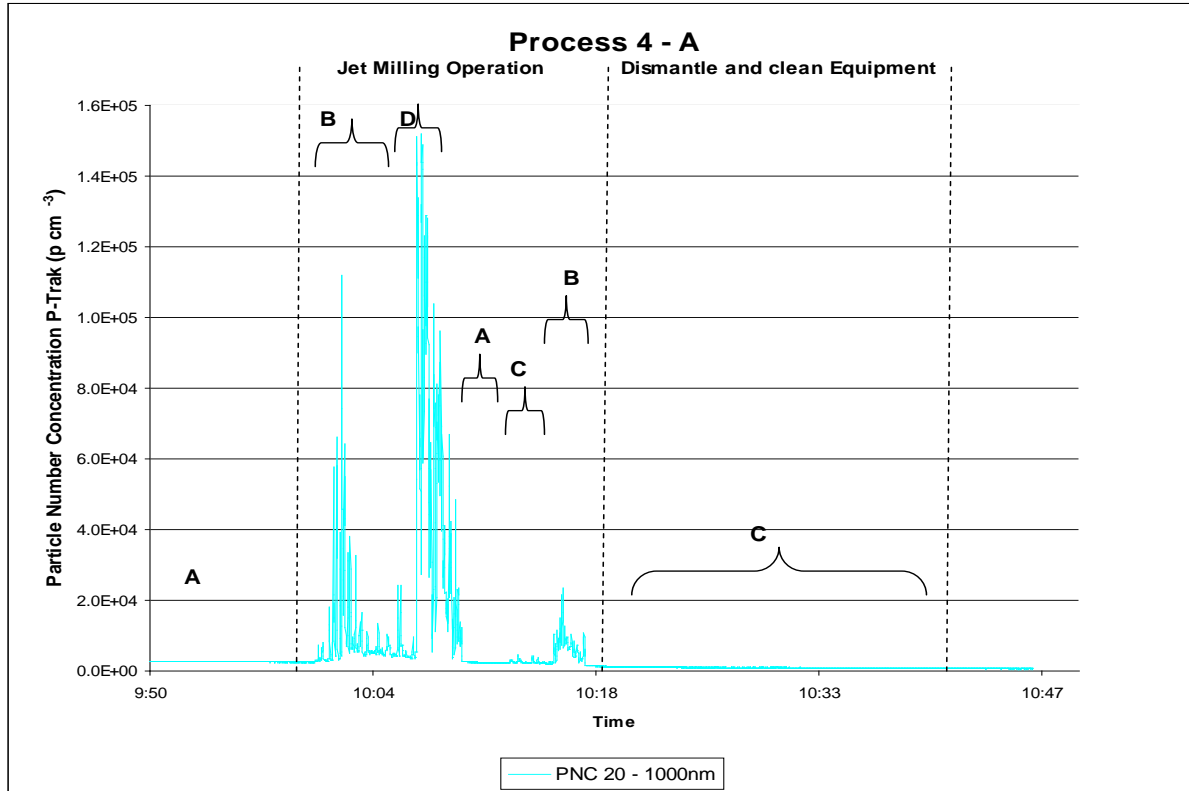
Figure 18: Particle number concentration (PNC) at different locations during the jet milling of a modified clay product during the first jet milling event. A P-Trak CPC was used in portable mode with the different measurement locations identified by the letters A to D. A = background concentration located 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 90⁰ 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.
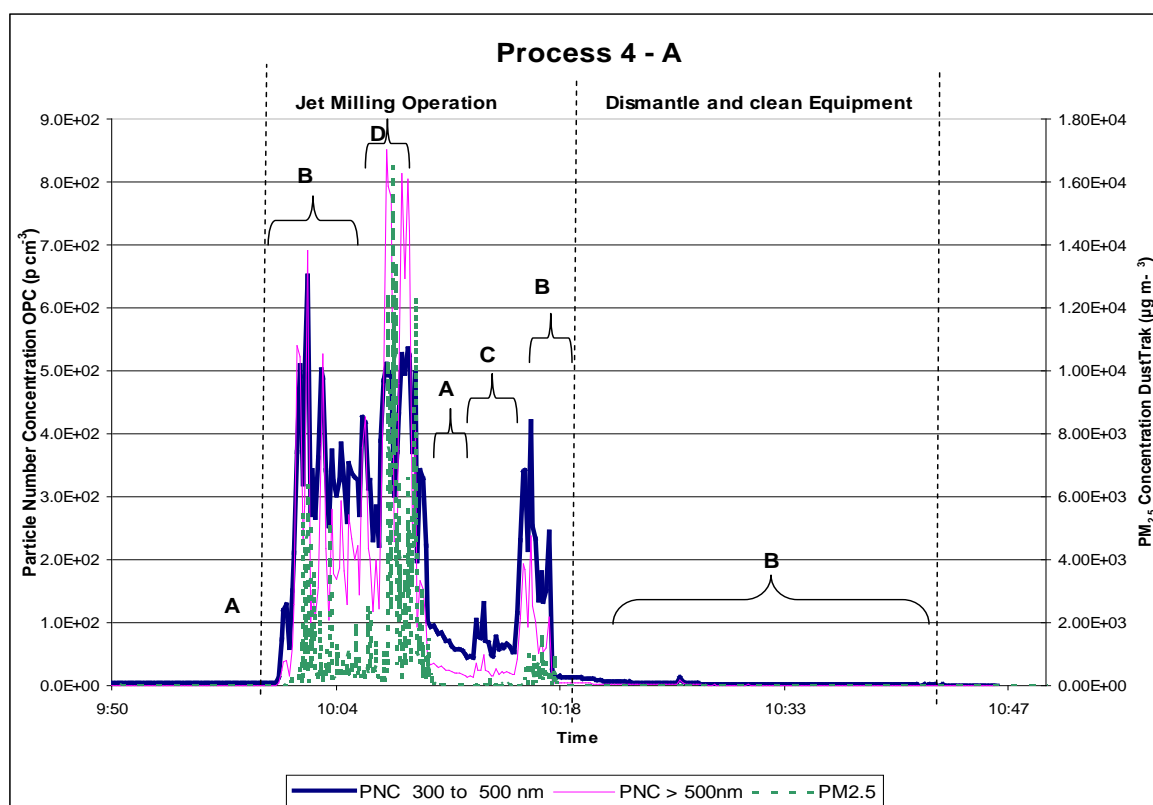
Figure 19: Particle number concentration (PNC) > 300nm and particle mass (PM$_{2.5}$) concentration at different locations during the jet milling of a modified clay product during the first jet milling event. An OPC and DustTrak were used in portable mode with the different measurement locations identified 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 90^0 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}.

It can clearly be seen from Figures 18 and 19 that the jet milling process is a strong source of particles when compared to the *local background particle exposure* . 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 18) is three orders of magnitude greater than that of the PNC in the size range of > 300 nm (OPC values in Figure 19) 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.

8.5.2.2   *Influence of local mechanical dilution ventilation upon the particle concentration within the work area*

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 18 and 19. 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

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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 heating, ventilation and air-conditioning (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.

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.

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 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.

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.

8.5.2.3   Discussion

The time-series plots from Figures 18 and 19 are reflective of the process operation and the *local background particle exposure*, and have been used in Table 10 to examine variability in peak PNC, mass concentration, CMD, and alveolar deposited surface area associated with Process 4.

Table 10: Summary of peak particle metrics at emission source during Process 4 operation compared to the peak associated with *local background particle exposure* (LBPE)

PNC 20 to 1000nm [p cm^{-3}] **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**		CMD [nm] **SMPS**		alveolar surface area [µm^2 cm^{-3}] **NSAM**	
Peak during	Peak of LBPE	Peak during	Peak of LBPE	Peak during	Peak of LBPE	Peak during	Peak of LBPE	Peak during	Peak of LBPE	Peak during	Peak of LBPE
1.5×10^5	5.5×10^2	8.0×10^2	< 1	2.0	<1	1.6×10^3	1	#	#	#	#
# not measured											

The data from Table 10 shows that Process 1B is a peak emitter of both sub- and supermicrometre particles, with the differences in values during and between process operations being greater than the manufacturer stated inaccuracy of the P-Trak, OPC, and DustTrak, and the normal variation in the background.

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 18 and 19, indicate the particle source is not strong enough to influence the *local background particle exposure* 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 section 8.5.2.2.

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$_{300-1000nm}$ 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.

8.6   Process Five – Decanting of single and multi-walled carbon nanotubes

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

8.6.1   Experimental Design and Conditions

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.

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 20 presents a picture of this sampling chamber and instrument setup.
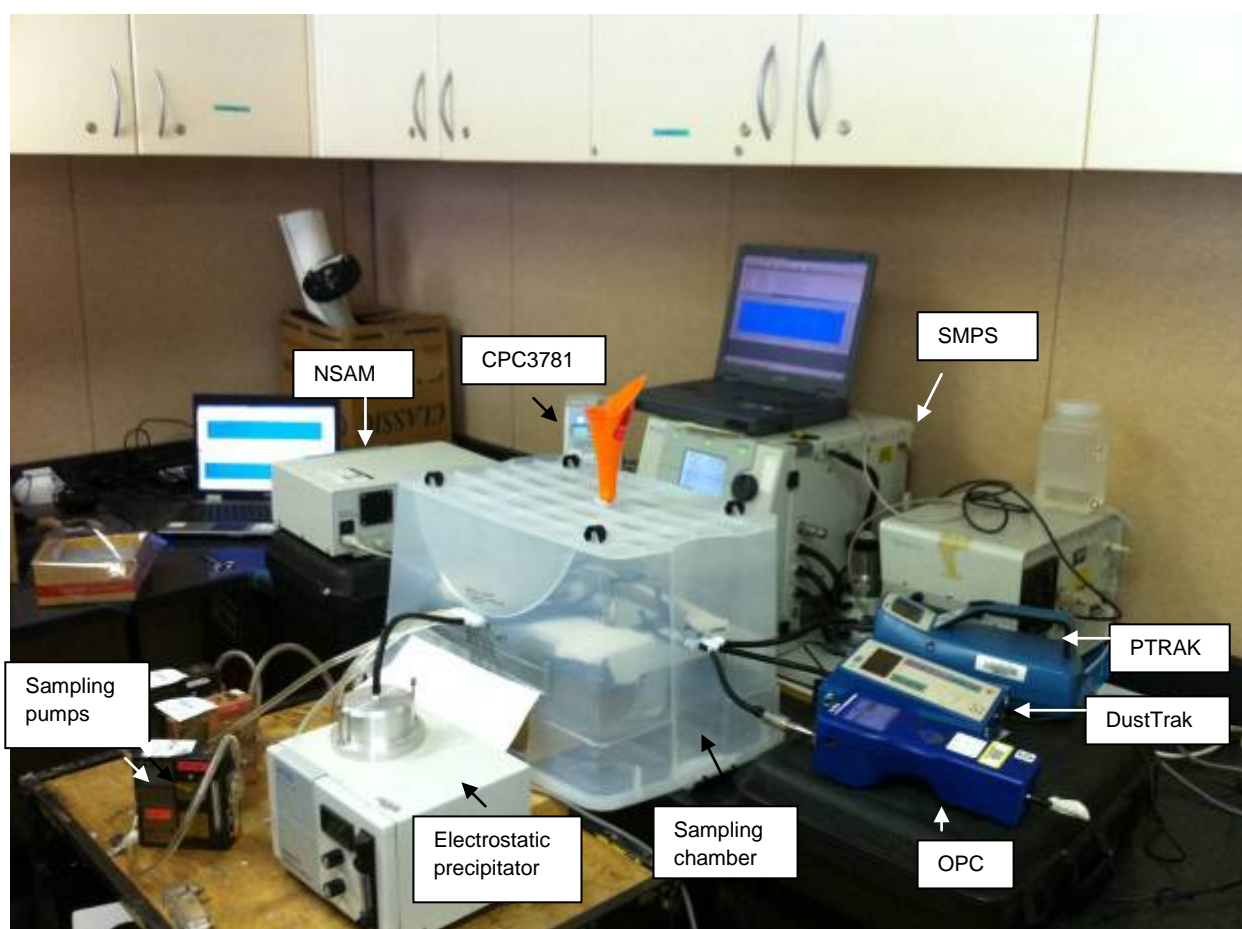
Figure 20: Sampling chamber and instrument configuration

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.

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/cm3 at 25 ºC, and produced by CoMoCAT® Catalytic Chemical Vapor Deposition (CVD) method, and
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 nanoparticles and amorphous and graphitic carbon nanoparticles, 7-15 nm diameter x 0.5-10 µm length, and produced by Electric Arc Discharge Method.

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.

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.

Because the material 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.

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.

8.6.2 Results

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.

8.6.2.1 *Time series of particle number and mass concentration, count median diameter, and alveolar deposited surface area*

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.

Figures 21 and 22 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. 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.
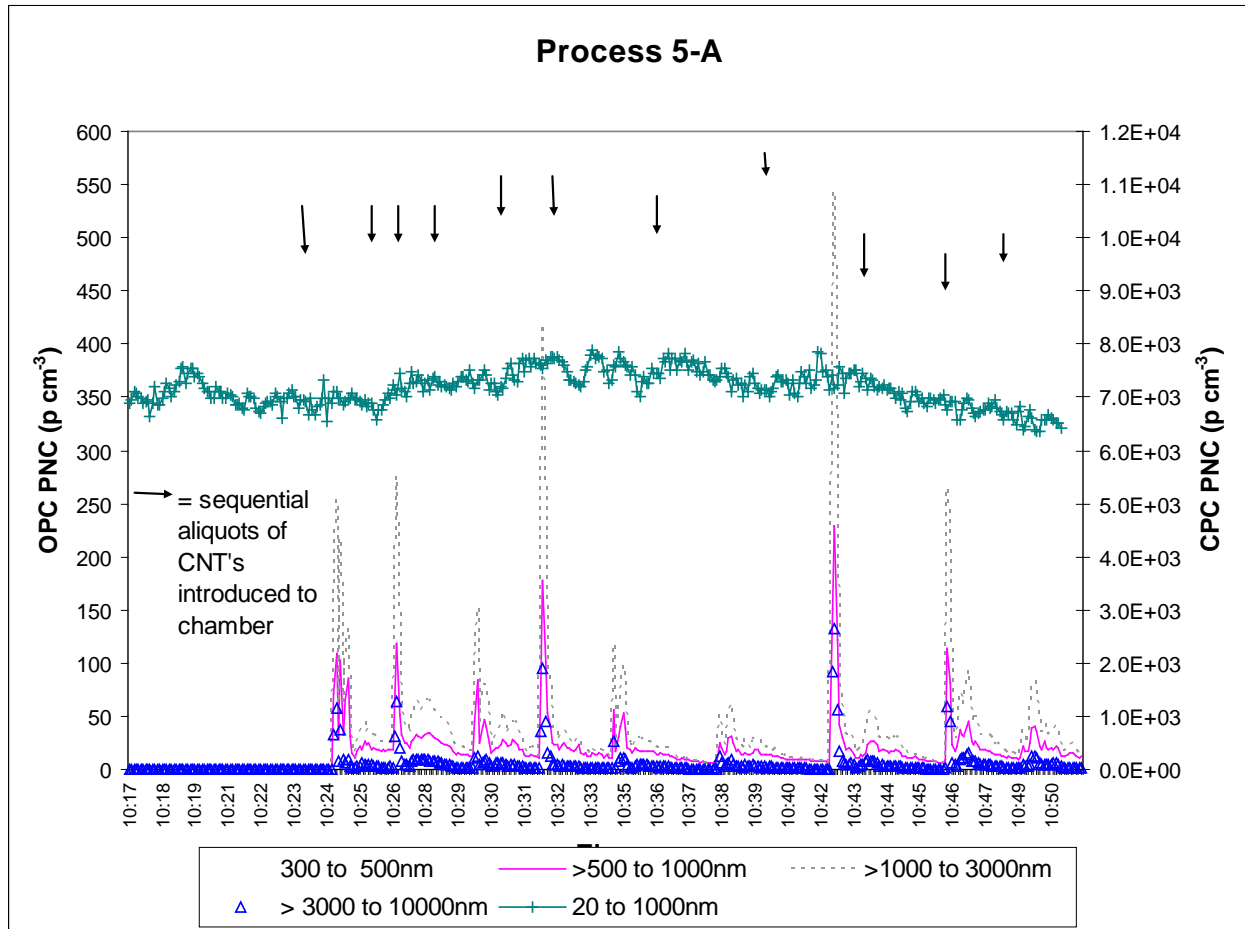
Figure 21: Particle number concentration in submicrometre and supermicrometre size range for single-walled carbon nanotubes
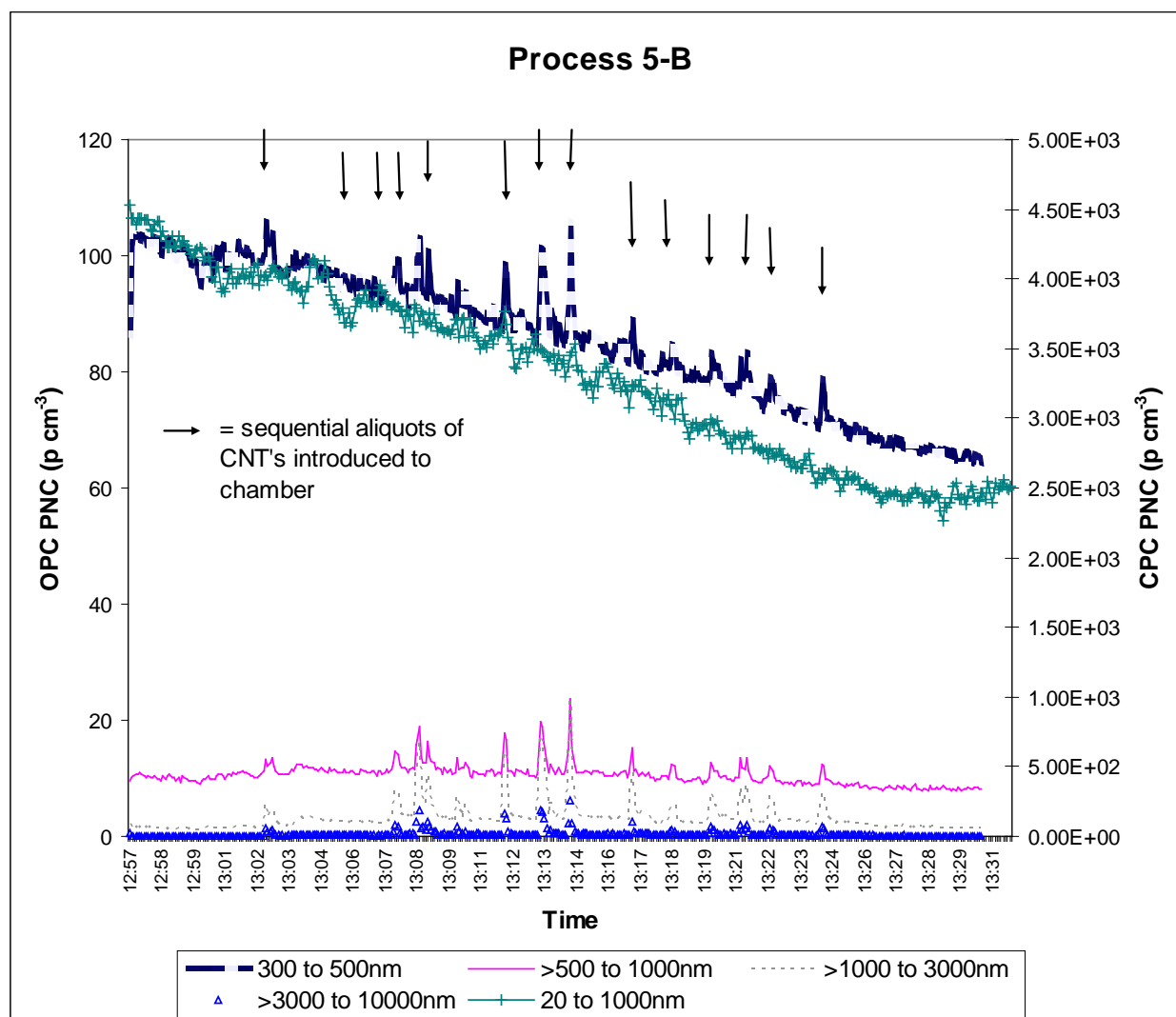
Figure 22: Particle number concentration in submicrometre and supermicrometre size range for multi-walled carbon nanotubes

From Figures 21 and 22 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 2 for data on instrument accuracy) and likely reflect normal fluctuations in background PNC.

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.

Figures 23 and 24 provide a comparison of particle number and mass concentration for both SWCNT and MWCNT respectively. In Figure 23, 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.
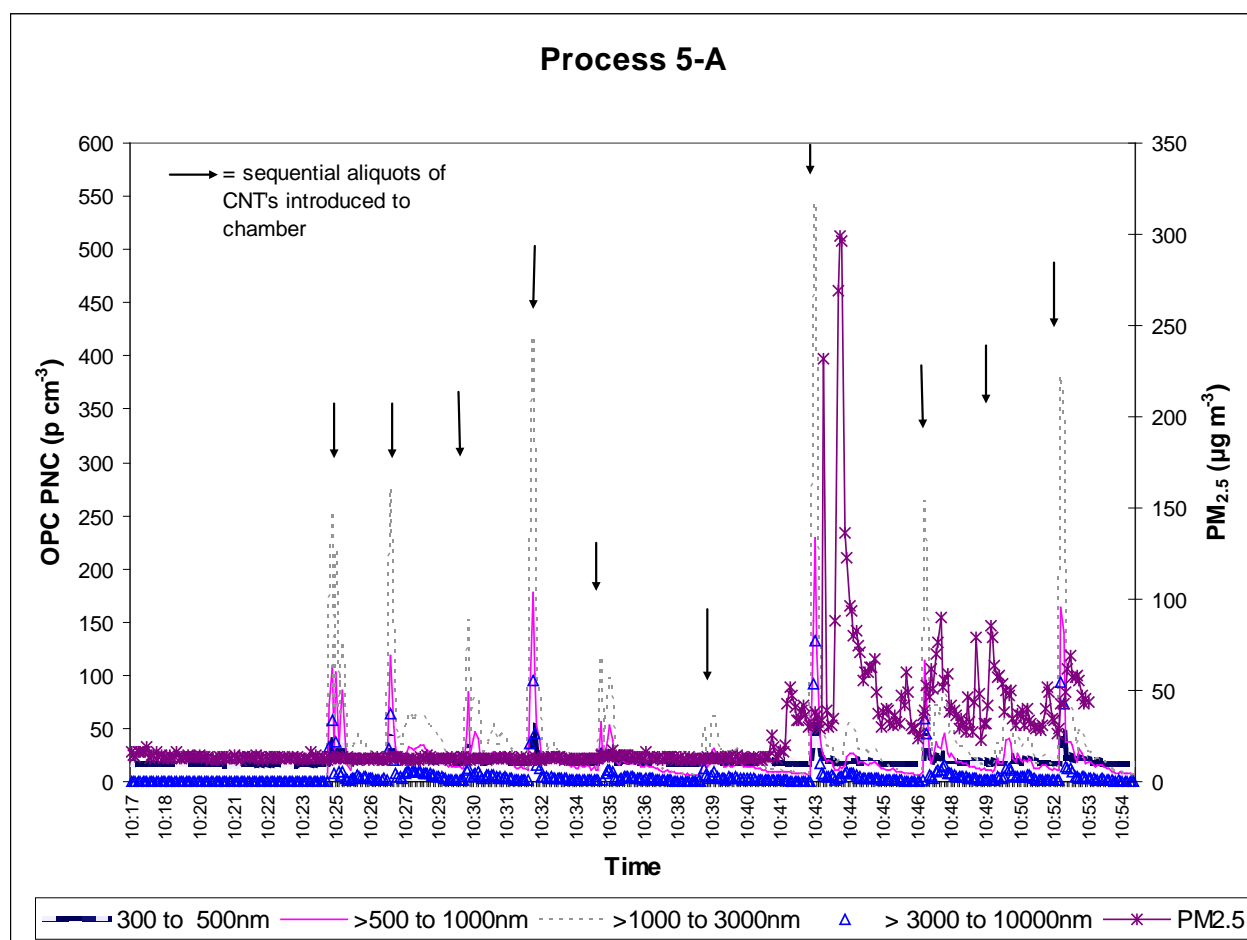
Figure 23: Particle number and mass concentration in submicrometre and supermicrometre size range for single-walled carbon nanotubes
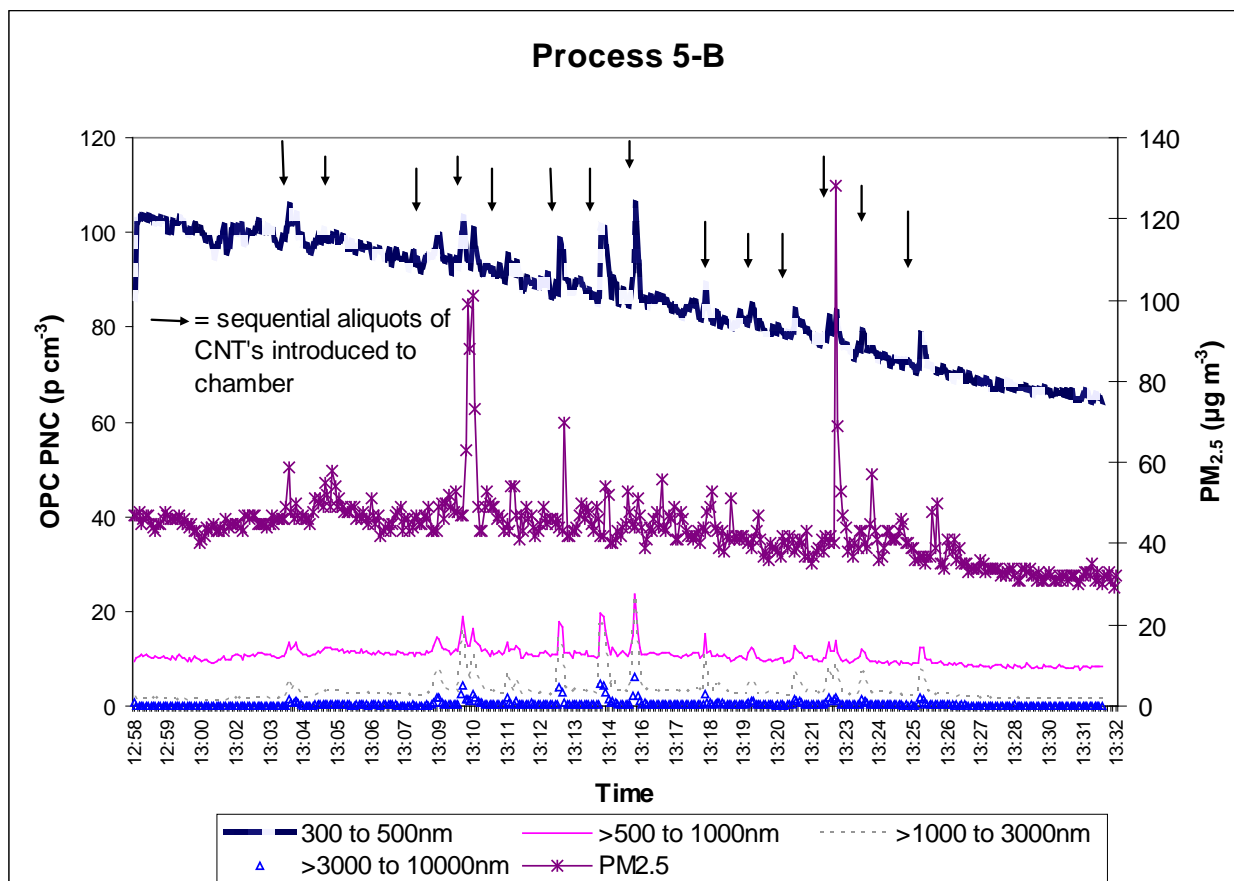
Figure 24: Particle number and mass concentration in submicrometre and supermicrometre size range for multi-walled carbon nanotubes

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.

Figures 25 and 26 compare the alveolar deposited surface area and PNC > 300 nm for the SWCNT and MWCNT aerosols respectively.
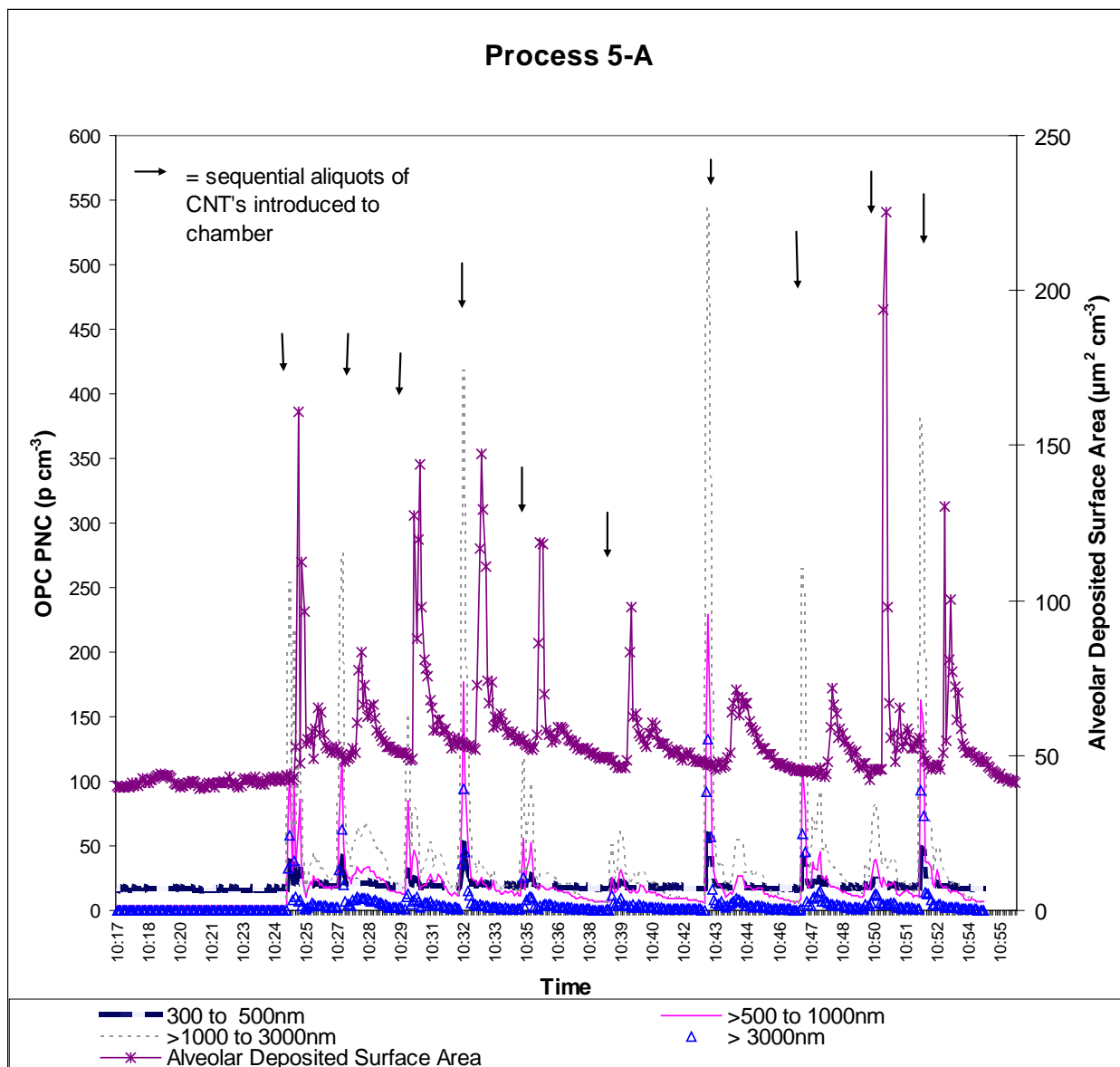
Figure 25: Particle number concentration in submicrometre and supermicrometre size range and alveolar deposited surface area for single-walled carbon nanotubes
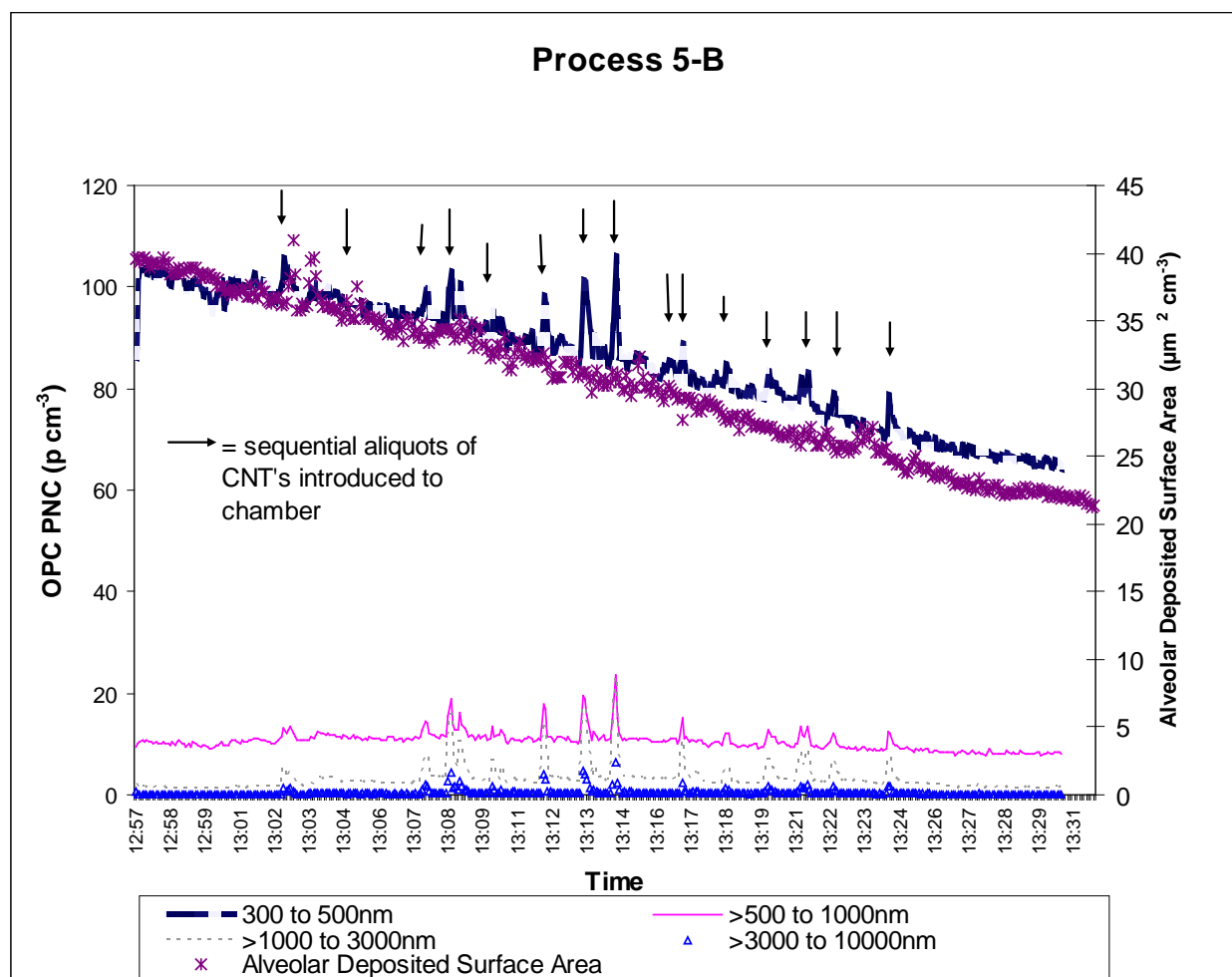
Figure 26: Particle number concentration in submicrometer and supermicrometre size range and alveolar deposited surface area for multi-walled carbon nanotubes

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 MWCNTs 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.

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.

The count median diameter (CMD) of the single- and multi-walled carbon nanotube aerosols are presented in Figures 27 and 28 respectively.
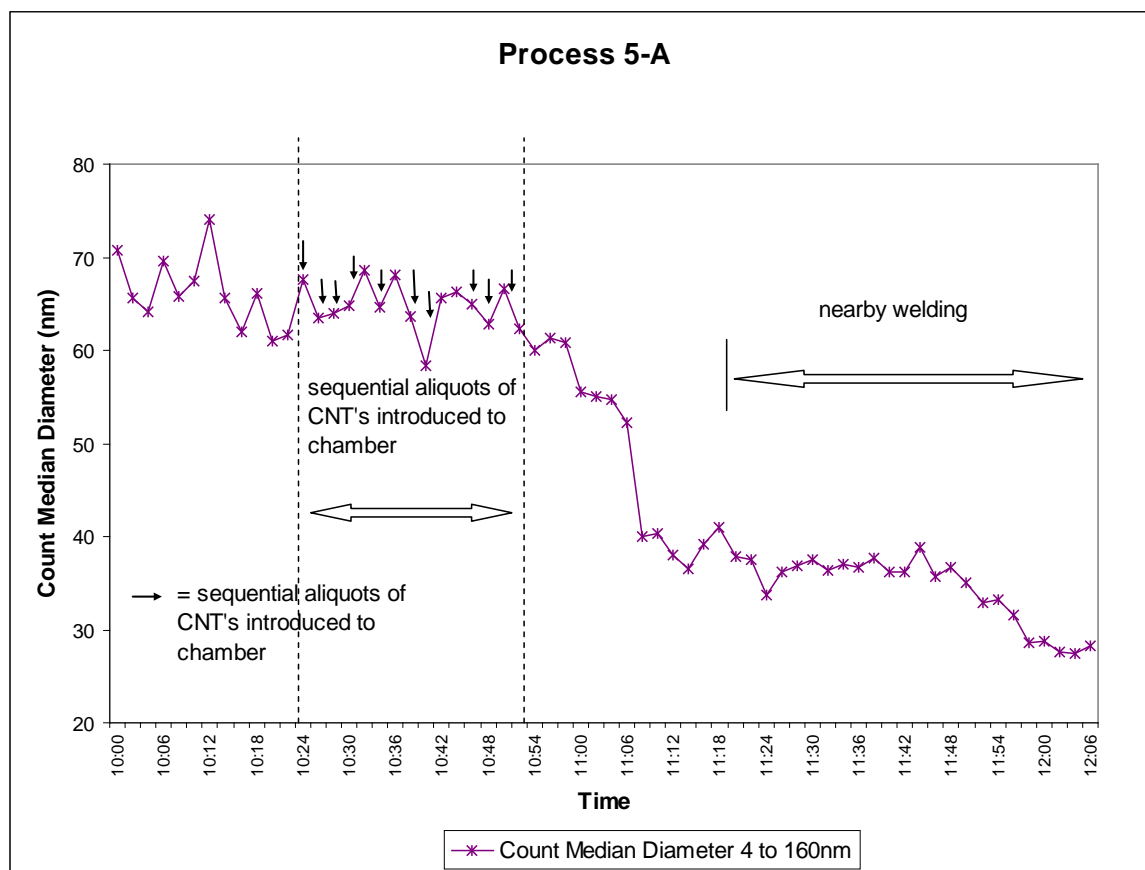
Figure 27: Count median diameter size range of 4 to 160nm for single-walled carbon nanotubes
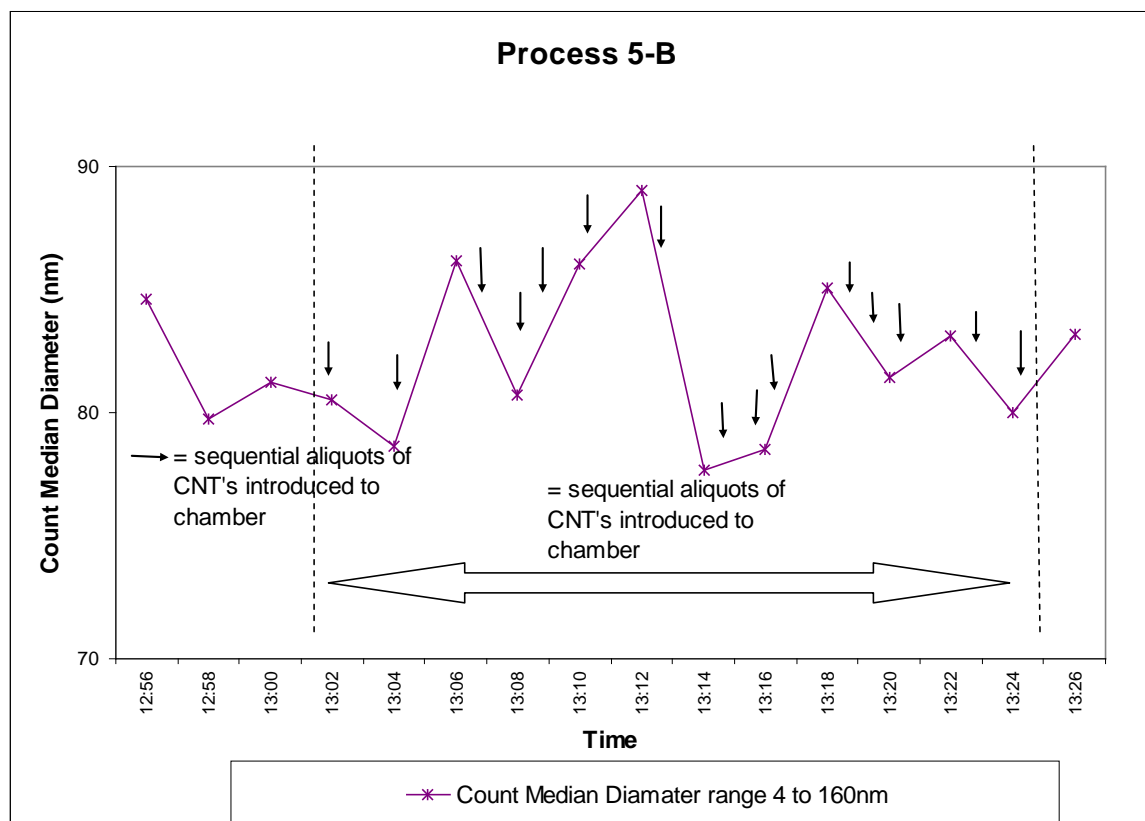
Figure 28: Count median diameter size range of 4 to 160nm for multi-walled carbon nanotubes

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 to 160nm and the particle number and mass concentration data presented in Figures 23 and 24 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.

Although a time related trend in reduction of CMD over time is evident in Figure 27 the scale of the y-axis is based on a very limited range thus over emphasising the fluctuation which is of the order of 10% max.

8.6.2.2   Electron microscopy analysis of particles

8.6.2.2.1 Methodology

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 scanning electron microscopy (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.

The filter samples were examined in a JEOL 7001F field-emission SEM. The TEM grid was examined using a Philips CM200 TEM at QUT 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.

8.6.2.2.2 Results

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.

The MCE filter used for the MWCNT aerosol showed scattered clusters consisting of both particles and MWCNTs (Figure 29 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 (Fig 29b).
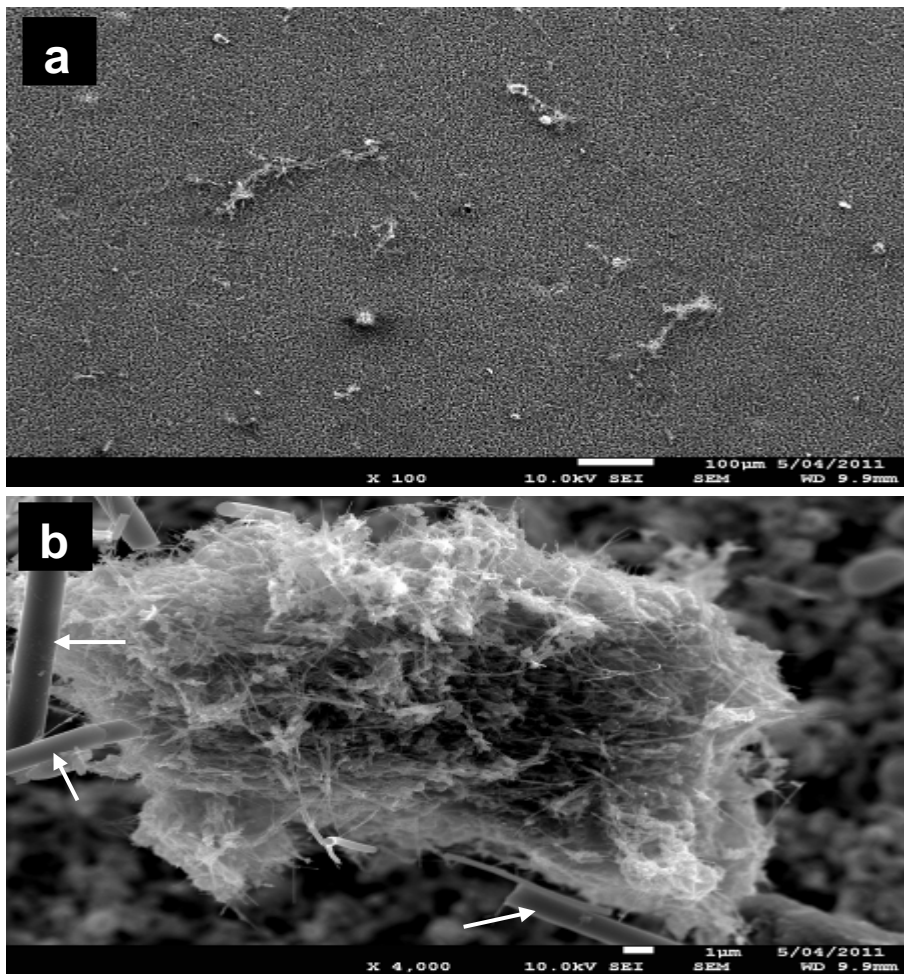
Figure 29: MWCNT sample on MCE filter; (a) scattered clusters of nanotubes and amorphous material, (b) a cluster of amorphous carbon and nanotubes, together with some fibreglass fibres (arrows).

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 30 a, b).
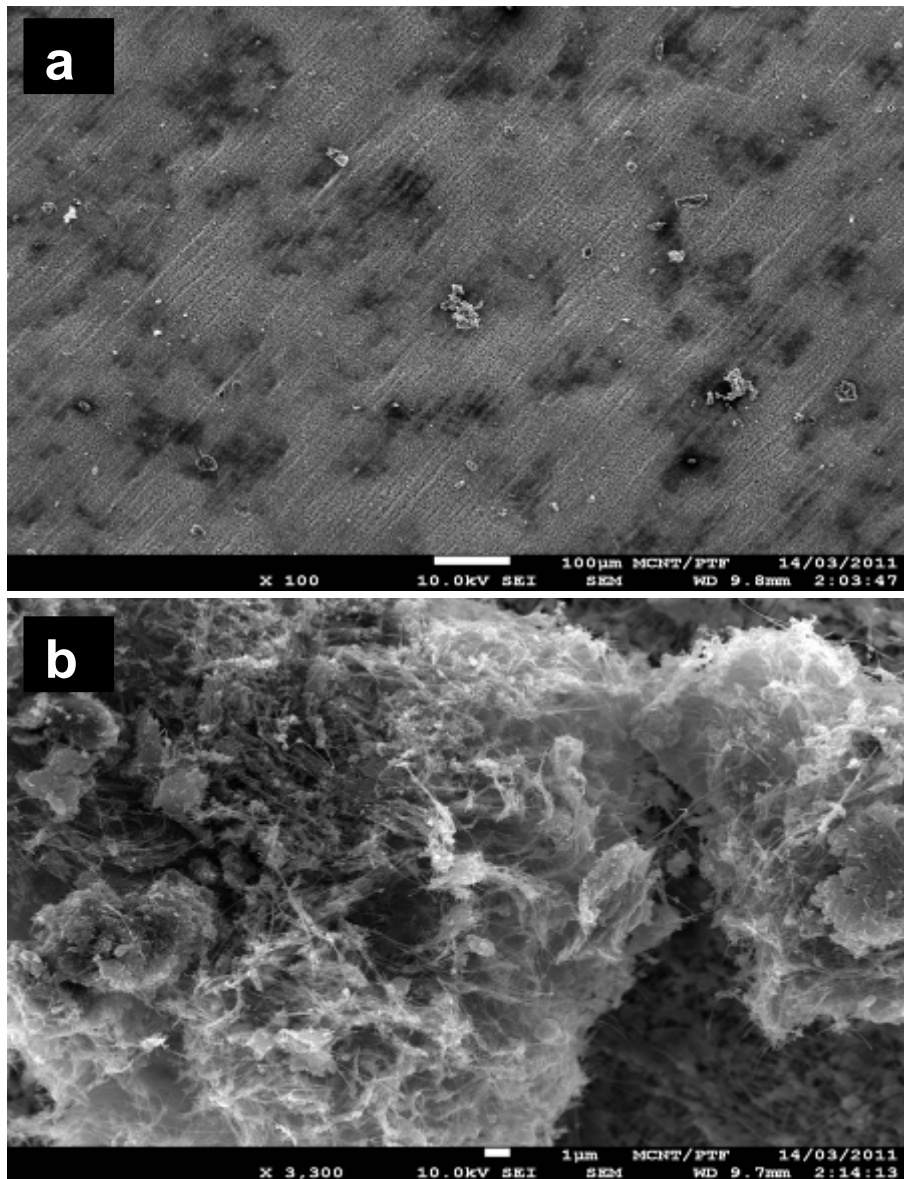
Figure 30: MWCNT sample on PTFE filter; (a) scattered clusters of nanotubes and amorphous material on the filter; (b) a large cluster of amorphous carbon material and nanotubes.

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 24.

The SWCNT samples collected on the MCE and PTFE filters showed a greater concentration of clusters than was observed with the MWCNT samples (Figures 31 and 32). 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.
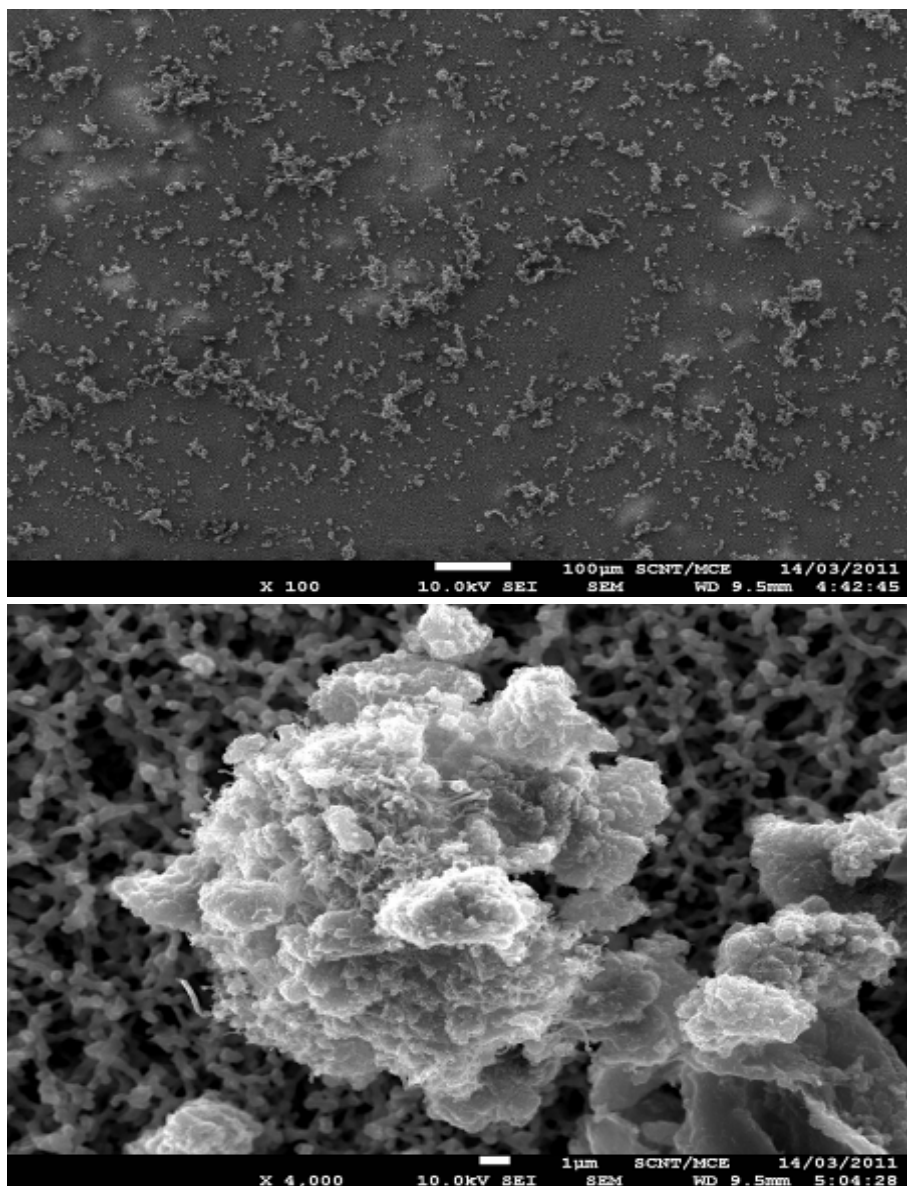
Figure 31: SWCNT sample on MCE filter; (a) clusters observed on the filter; (b) a large cluster of mainly amorphous carbon with some nanotubes.
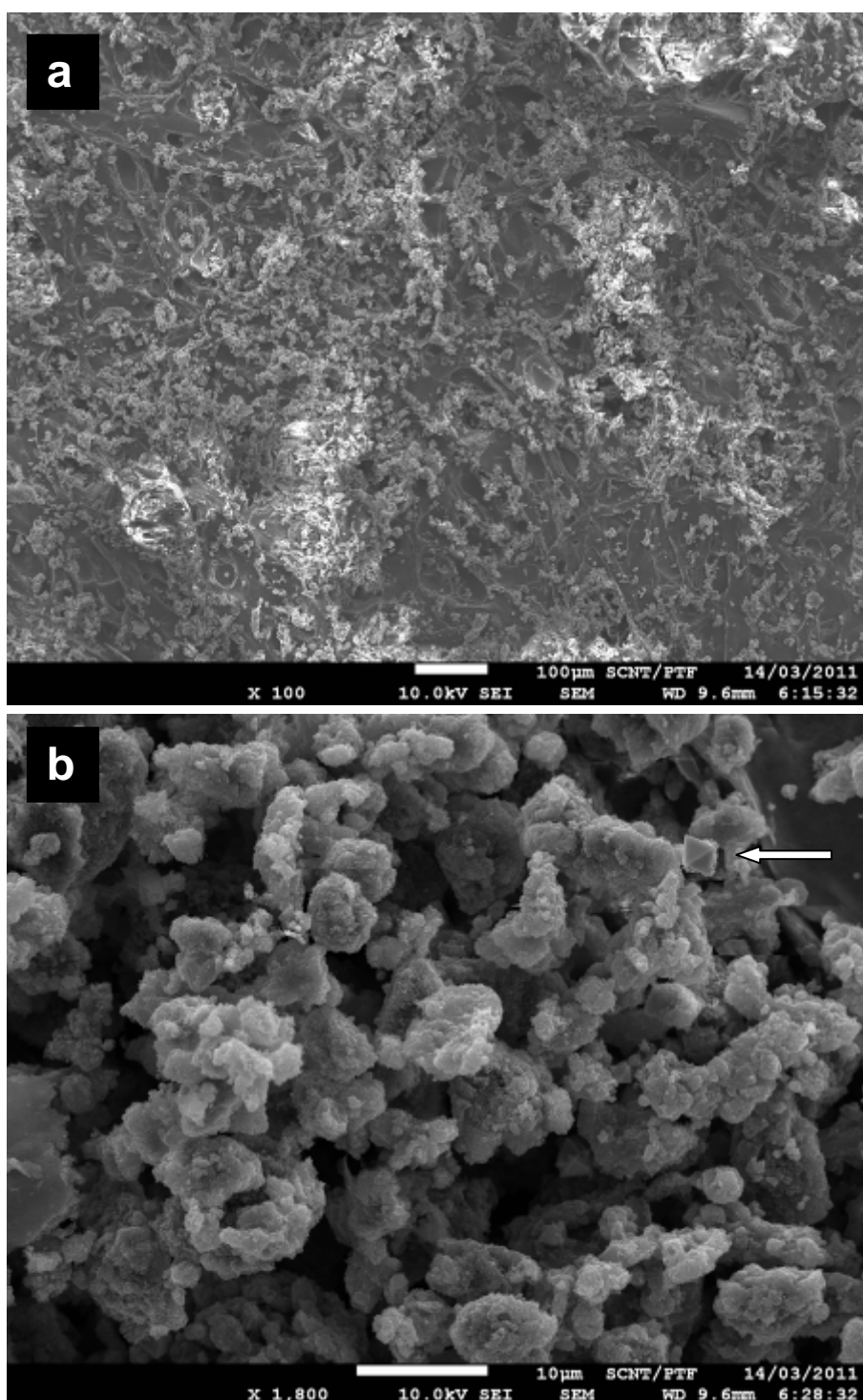
Figure 32: SWCNT sample on PTFE; (a) dense coating of clusters on the filter; (b) details of a large cluster showing smaller aggregates; the arrow indicates a Mo crystal.

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.

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.

A TEM examination of the SWCNT sample (Figure 33) showed that although SWCNTs were present, many of the nanotubes were of the MWCNT type, and 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.
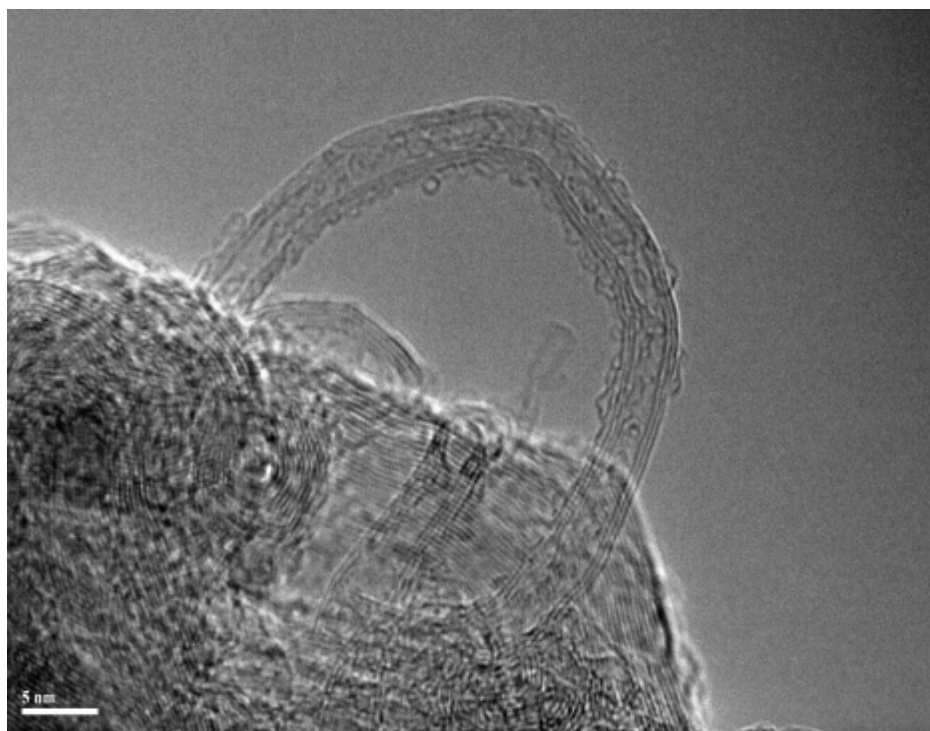
Figure 33 A high resolution TEM image of the SWCNT sample on a TEM grid.

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 also be a component of MWCNTs formed.

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.

8.6.2.3 *Estimating mass concentration of carbon nanotube aerosols - elemental carbon analysis and real time mass concentration measurements*

In December 2010 the National Institute for Occupational Safety and Health (NIOSH) proposed a mass based Recommended Exposure Limit (REL) of 7 µg m^{-3} of Elemental Carbon (EC), as an eight-hour time-weighted average exposure standard, for worker protection regarding exposure to airborne carbon nanotubes [79]. The NIOSH recommendation represents a divergence from the dominant paradigm of particle number or size for exposure assessment within the scientific literature regarding nanoparticles [14, 17, 38, 41, 42].

This NIOSH REL is based on the analytical detection limit of 7 µg m^{-3} of Elemental Carbon (EC). Sub-chronic and short-term animal dose-response data shows quantifiable excess risk of early-stage fibrotic and inflammatory lung responses to CNT exposure at a concentration of 7 µg m^{-3} of [79].

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.

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 8.6.1 and as such, the measurement results do not represent particle concentrations likely to be encountered within a workplace environment. These measurement results can be found in Table 4.

From Table 3 the elemental carbon (EC) mass concentration obtained using NIOSH Method 5040 was 1474 µg m^{-3} for Process 5A, and < 2 µg m^{-3} for Process 5B. 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, and 35 µg m^{-3} for Process 5B, with both these concentrations significantly higher than background values.

The mass concentration of the SWCNT aerosol was clearly higher than that of the MWCNT aerosol and the external laboratory reported 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 34. 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 34: 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.

The data from this experiment, albeit from only two samples, indicates that both the NIOSH Method 5040 and the DustTrak are valid 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. Therefore, the methods are best utilised to indicate relative changes rather than absolute concentrations.

8.6.2.4   *Discussion*

The data from Figures 21 and 28 has been used in Table 11 to examine variability in peak PNC, mass concentration, CMD, and alveolar deposited surface area, both during and between operation of Processes 5A and 5B.

Table 11: Summary of peak particle metrics at the point of emission during and between operation of Processes 5A and 5B

	PNC 20 to 1000nm [p cm^{-3}] 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		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

The data in Table 11 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.

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 finding are relevant as they suggest the SWCNT may have a greater likelihood of influencing the work environment and worker exposure.

Under the experimental conditions generated in the chamber the CNT particles did 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.

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 nanoparticle sources is limited when concentrations are not significantly different to background levels.

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.

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

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.

The dominant particle size of both the SWCNT and MWCNT aerosols were in the supermicrometre range of between 300 and 3000 nm. This conclusion was deducted 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 change in PNC and CMD respectively.

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.

The particle number and mass concentration, and alveolar deposited surface area was 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.

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 than the results cannot be used in regard to actual lung deposited surface area dose.

8.7 Process 6 – Synthesis of carbon nanotubes using Chemical Vapour Deposition

8.7.1 Experimental Design and Conditions

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.

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.

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.

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.

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.

8.7.2   Results

8.7.2.1   *Time series of particle number and mass concentration*

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.

Figure 35 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 in the 300 to 500 nm size range. Process 6-B produces a PNC of four orders of magnitude greater than 6-A. 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.
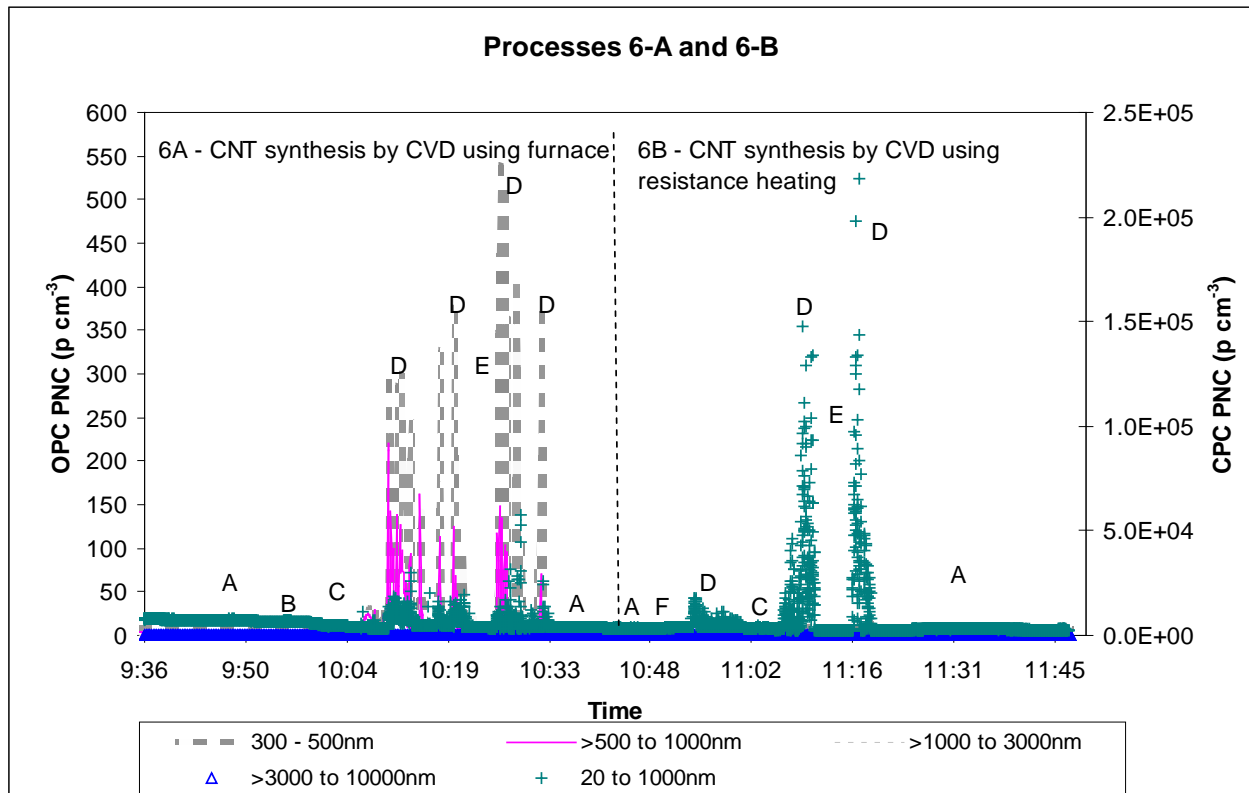
Figure 35: Particle number concentration (PNC) measured at various locations during two different condensation vapour deposition CNT synthesis processes. Measurement locations, marked A to F in the figure, were as follows: A = Background ambient PNC at various locations around the room; B = commencement 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

Figure 36 provides data PM$_{2.5}$ concentration data measured simultaneously with that of the PNC. This data shows 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 also correspond well with the peaks in PNC in size band 500 to 1000nm as shown in Figure 35.
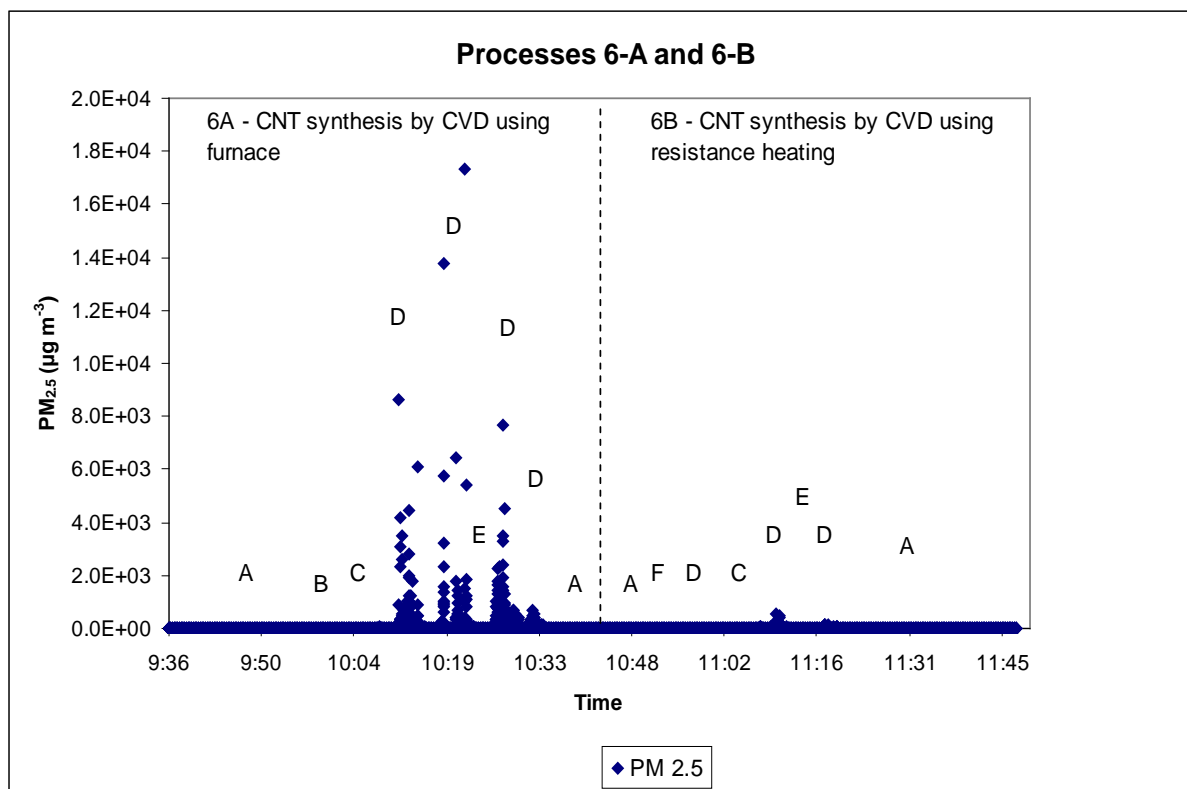
Figure 36: Particle mass concentration (PM$_{2.5}$) measured at various locations during two different condensation vapour deposition CNT synthesis processes. Measurement locations, marked A to F in the figure, were as follows: A = Background ambient PNC at various locations around the room; B = commencement 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

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.

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

The time-series plots from Figures 35 and 36 are reflective of the process operation and the *local background particle exposure*, and have been used in Table 12 to examine variability in 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 12: Summary of peak particle metrics at emission source during Process 6 operation compared to the peak associated with *local background particle exposure* (LBPE)

	PNC 20 to 1000nm [p cm^{-3}] **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**		CMD [nm] **SMPS**		alveolar surface area [µm^2 cm^{-3}] **NSAM**	
	Peak during	Peak of LBPE	Peak during	Peak of LBPE	Peak during	Peak of LBPE	Peak during	Peak of LBPE	Peak during	Peak of LBPE	Peak during	Peak of LBPE
6A	5.7×10^4	2.9×10^3	550	8	< 1	<1	1.8×10^4	8	#	#	#	#
6B	2.1×10^5	2.9×10^3	4	4	1	< 1	550	8	#	#	#	#
# not performed												

From Table 12 it is apparent that the CVD is a strong source of both sub and supermicrometre particles.

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 34 and 35 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.

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 a 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 35 and 36 where at measurement point E (along the edge of the fume cabinet sash opening) the particle metrics are similar to the *local background particle exposure* (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.

8.7.2.3 Discussion

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 the main CVD parameter that controls the relative production 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 that aimed to generate a predominance of MWCNT. SWCNT are by definition a smaller particle than MWCNT [89]. Therefore the characterisation of particles < 300nm for Process 6-B is likely to reflect a predominance of un-agglomerated SWCNT

within the chamber aerosol, whilst the particle size characterised from Process 6-A likely reflects the larger MWCNT.

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 37 and 38.
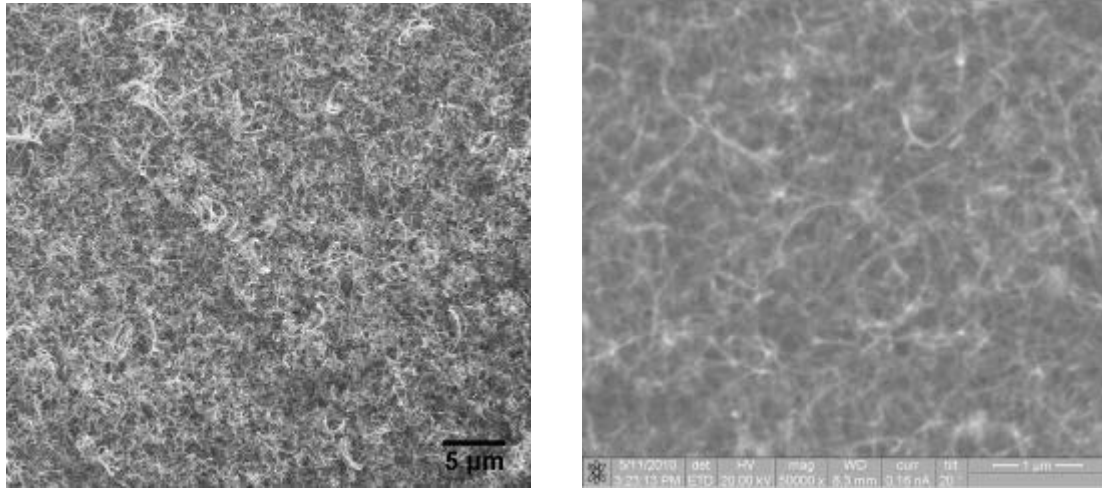
Figure 37: SEM micrographs of CNTs generated with CVD condition similar to Process 6-A (left) and Process 6-B (right), respectively [91].
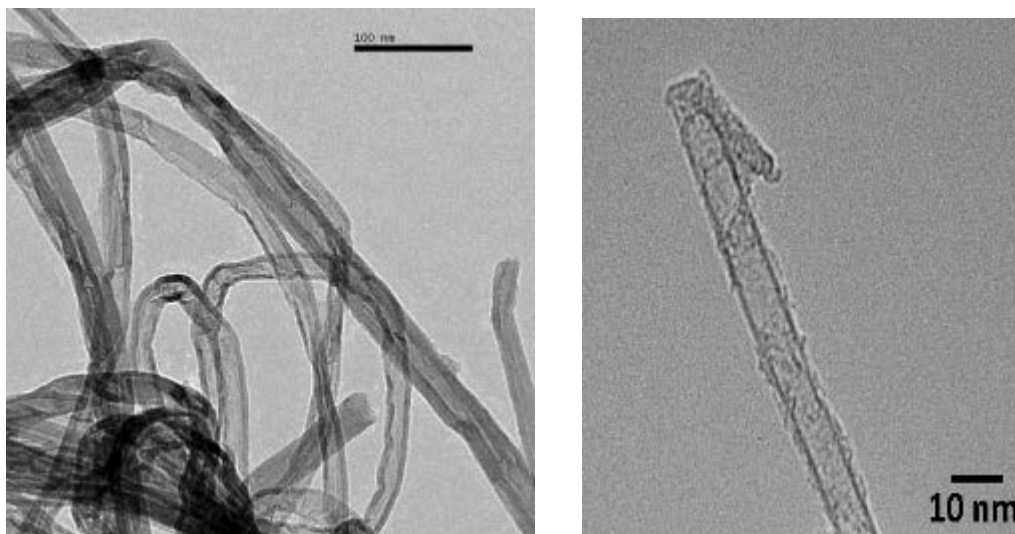
Figure 38: TEM images of CNTs collected from samples generated with CVD conditions similar to Process 6-A (left) and Process 6-B (right), respectively [91].

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.

In addition, the difference in particle size between the processes might be explained by the difference in the heating mechanisms for each process. 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 only the conductive sample holder (50x10 mm in size) 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.

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.

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.

9 Comparison and Evaluation of the Response of Different Instrumentation and Measurement Methodology to a Range of Airborne Engineered Particles

9.1 Methodology

In order to evaluate the correlation between instrument responses the inter-instrument Pearson's Correlation[16] matrix for different particle sources were calculated and the resultant r-values summarised in Tables 16 to 22 at Appendix B.

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.

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.

9.2 Discussion

The calculated r-values indicate 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

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[16] Pearson's correlation is also referred to as the correlation coefficient, or more formally as the Pearson product-moment correlation coefficient. It is a measure of the strength of the linear relationship between two variables, in this case the particle metric results from two instruments. The symbol "r" is used to represent the Pearson's correlation for the two variables. Pearson's r can range from -1 to 1. An r of -1 indicates a perfect negative linear relationship between variables, an r of 0 indicates no linear relationship between variables, and an r of 1 indicates a perfect positive relationship between variables.

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, 5, and 6 the P-Trak showed a 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 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.

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

The NSAM and the P-Trak exhibited a consistent positive linear relationship 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.

The SMPS consistently exhibited a positive linear relationship with all CPC's and the NSAM, but a poor linear response with the DustTrak and the OPC. This is as expected considering the SMPS particle size range of 5 to 160nm is within the range of the CPCs but below the minimum particle size of the OPC, and at the lower limit of the DustTrak. This also suggests the particle size across the processes was predominantly greater had greater CMD than 160nm.

These Pearson's correlation r-values indicate the P-Trak, OPC, DustTrak, and NSAM exhibit a consistent and positive linear relationship to one another across a variety of nanomaterial aerosols, including fibrous and non-fibrous particles. 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.

10 Discussion of, and Recommendations for, Characterisation and Reporting of Temporal and Spatial Concentrations of Airborne Engineered Nanoparticles

Our results clearly indicate that when used as a complimentary 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.

In addition, our results 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.

10.1 Recommendation 1: Utilise Particle Control Values when evaluating particle emission and exposure

In Section 7.1, issues relating to *Particle Control Values* that might be used for nanomaterials were considered. It was proposed that these might be used in the following order of priority, using the highest available:

1. A company or laboratory's in-house control limits – if these are lower, i.e. more stringent, than applicable regulatory limits
2. Australian Workplace Exposure Standards (WES)
3. National exposure limits or recommended national exposure limits from another country, e.g. Recommended Exposure Limits (REL) (US NIOSH)
4. Proposed workplace exposure limits – from research results
5. Benchmark Exposure Levels (BEL) – which include some consideration of health effects
6. Local particle reference values based on background nanoparticle levels

Based on this thinking, the use of following *Particle Control Values* is proposed.

10.1.1 Hierarchy of *Particle Control Values* for nanomaterials

1. Based on Australian Workplace Exposure Standards

Material	WES (8 hr TWA), mg m^{-3}
Carbon black	3
Fumed silica	2

2. Based on US NIOSH Recommended Exposure Limits

Material	Recommended exposure limit (REL), (8 hr TWA), mg m^{-3}
Ultrafine TiO$_2$	0.3
Fine TiO$_2$	2.4

3. Based on proposed workplace exposure limits

Nanomaterial	Proposed exposure limit, (8 hr TWA), mg m^{-3}
Carbon nanofibres, including carbon nanotubes (NIOSH)	0.007
Fullerenes (AIST)	0.39

4. Based on Benchmark Exposure Levels

Nanomaterial group	BEL	Basis
As measured: Fibre-like particles, or fibre-like structures	0.1 fibre/ml	Benke et al., [82] Using WHO fibre definition, Aspect ratio > 3 Length > 5 µm
Carcinogenic, Mutagenic, Asthmagenic, or Reproductive Toxins (CMAR)	0.1xAustralian WES for bulk (or REL or other ES) As default - 0.003 mg m^{-3}	BSI Guide [81] Australian WES for Category 1 Carcinogens (mg m^{-3}) Cd – 0.01 Be – 0.002 As – 0.05 Cr (VI) – 0.05 Zn chromate - 0.01 BEL = (mean value)/10
Insoluble	0.03xAustralian inhalable WES for bulk, (or REL or other ES) or 0.1xAustralian respirable WES for bulk, (or REL or other ES) As default - 0.3 mg m^{-3}	TiO_2 Ultrafine REL/Australian WES 0.1xACGIH TLV for respirable particles not otherwise specified (PNOS) of 3 mg m^{-3}
Soluble	0.5xAustralian WES for bulk (or REL or other ES) As default – 1.5 mg m^{-3}	BSI Guide [81] 0.5xACGIH TLV for respirable particles (PNOS) of 3 mg m^{-3}

Note, this includes BELs for the default situation where there is no WES, REL or proposed ES for the corresponding macrosized material.

5. Local Particle Reference Values

Australian WES, RELs, proposed workplace exposure limits, and BELs are in place for only very few nanomaterials. Therefore, in the absence of more widespread limits, measurement should be focussed upon 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 exposure.

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) $PNC_{20-1000nm}$, (b) $PNC_{300-3000nm}$, (c) $PM_{2.5}$.

The upper range of 3000nm has been used for the PNC because, from our 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.

10.2 Recommendation 2: Minimise the number of particle metrics to be characterised

The number of particle metrics should be minimised for the following reasons.

First, instrument and operator error must be minimised. As outlined in Table 3 particle concentration inaccuracy is inherent in all instrumentation. The more instrumentation utilised, the more instrument and operator error that has to be accounted for.

The second reason for limiting the number of instruments used relates to the need to ensure all instruments are sampling 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.

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 39 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 40 contrasts this with minimalist approach that does not require use of sample tubing.
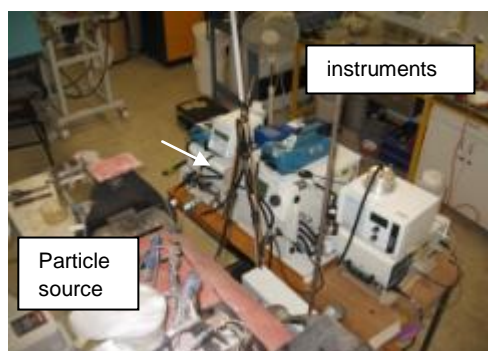
Figure 39: complex instrument method
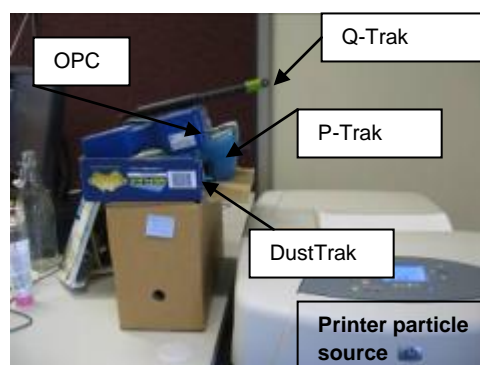
Figure 40 : minimalist instrument method

Section 10.3 provides further rationale for the selection of particle number and mass concentration.

10.3 Recommendation 3: Utilise real-time particle number and mass concentration data to identify sources of particle emission, spatial variation, and to validate effectiveness of engineering controls in containing particle emissions

Our research included the measurement of particle number and mass concentration, count median diameter, and alveolar deposited surface area for six different nanotechnology processes, and included both fibrous and non-fibrous particles. 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. Pearson correlation values showed a consistent positive relationship between particle number and mass concentration values.

Particle number and mass concentration measurements clearly identified points of particle emission. For example, significant peaks in $PNC_{20-1000nm}$ were evident for Processes 1B, 2, 3, 4, 6A, and 6B. Significant peaks in $PNC_{300-3000nm}$ were evident for Processes 4, 5A, and 6A. Significant peaks in particle mass concentration were evident for processes 1A, 1B, 2, 3, 4, 5A, 6A, and 6B. In addition, correlated peaks in both $PM_{2.5}$ and $PNC_{300-3000nm}$ were evident for Processes 4, 5A, and 6A.

As part of the assessment of Process 4 (see section 8.5), a P-Trak, OPC, and DustTrak were utilised to characterise sources of particle leakage during operation of the jet-milling machine. The instruments were used at different locations as signified in time-series plots of the PNC and $PM_{2.5}$ concentration illustrated in Figures 18 and 19 (see section 8.5.2). As can be seen in these figures the instruments were able to show (1) the emission aerosol as including both sub and supermicrometre sized particles, (2) the specific particle leakage point, in this case the "o" ring connecting the dust collection bag to the venturi outlet, and (3) that the "dismantling and cleaning" stage was not an emitter of particles when compared to the background. Analysis of both the P-Trak and OPC data shows the submicrometre PNC was up to three orders of magnitude greater than that of the supermicrometre PNC, and the maximum particle size to be 1000nm (PNC in OPC bin sizes > 1000nm were all < 1 p cm^3, which was similar to the background). In addition, it is clear that there was good correlation between the OPC response and the DustTrak response. The Pearson's correlation r-values, calculated in Section 9, showed a positive correlation ($r = 0.48$) for these two instrument particle responses.

Clearly the aerosol emission was dominated by sub-1000 nm sized particles with the P-Trak able to characterise these particles. However the particle signature from the process also includes particles within the 300 to 1000nm size range as characterised by the OPC, and the correlating mass concentration less than 2500nm as characterised by the DustTrak. Therefore using the data obtained from the P-Trak, OPC, and DustTrak it can be concluded that both sub and supermicrometre particles are emitted from this process and that the measurement methods are capable of characterising particles.

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 9 that turning off the extraction ventilation for Process 2 resulted in an immediate and significant increase in PNC. From Figure 35 it is clear the fume cabinet was able to effectively prevent 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.

The data in Figures 18 and 19 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 are significantly lower than at the particle emission points, B and D.

Significant peaks in alveolar deposited surface area were evident for processes 1B, 2, 3, and 5A. However, 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. However, significant peaks in $PM_{2.5}$ concentration were evident during operation of Process 1B, 2, 3, and 5A. 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 can be utilised in identifying sources of particle emission that are within size range of 20 to 1000nm.

The upper particle size of the SMPS used during the research was purposely limited to approximately 160nm so as to identify the contribution of ultrafine particles to the total aerosol particle size distribution. Mean CMD results did not vary significantly during operation of the various nanotechnology processes when compared to background. However, particle number and mass concentration did vary across a size measurement band between 20 nm and 3000 nm. This strongly suggests a narrow focus upon characterising ultrafine size range on its own is not valid for identifying particle emission and spatial distribution.

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. Recommended instrumentation 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.

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. Subtracting OPC and CPC measurement results from one another is not recommended because of the fundamental differences in operating principles of both instruments.

10.4 Recommendation 4: comprehensively characterise background and incidental particle number and mass concentration

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.

For example, it is clear from Figure 10 that there was significant variability in background PNC prior to operation of Process 2. It is also clear from Figure 15 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 18 for Process 4A.

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 9 in section 8.3.2.2. 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.

It is clear from Figures 41 and 42 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.
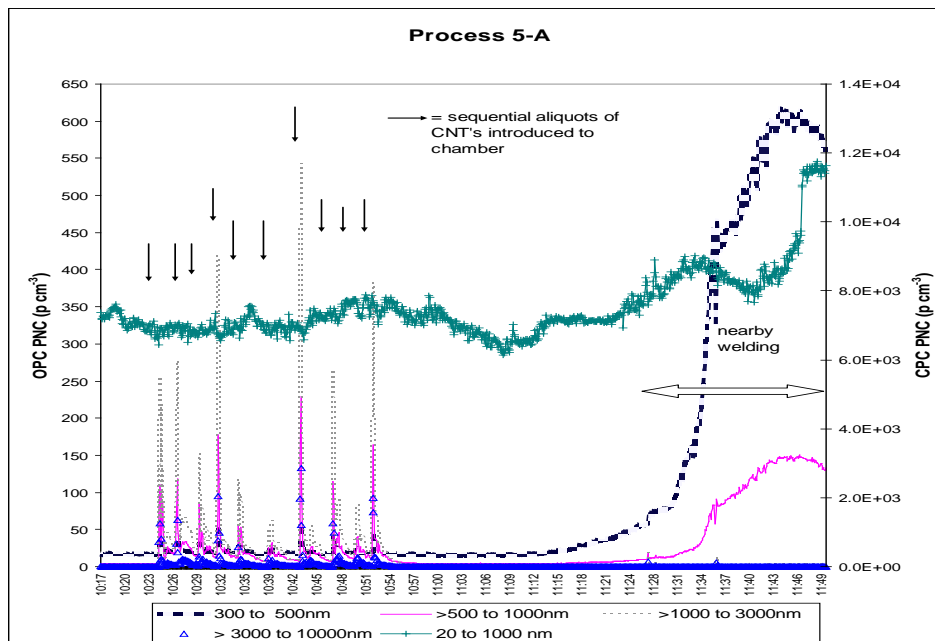
Figure 41: Particle number concentration both during and after the introduction of CNT's to the chamber
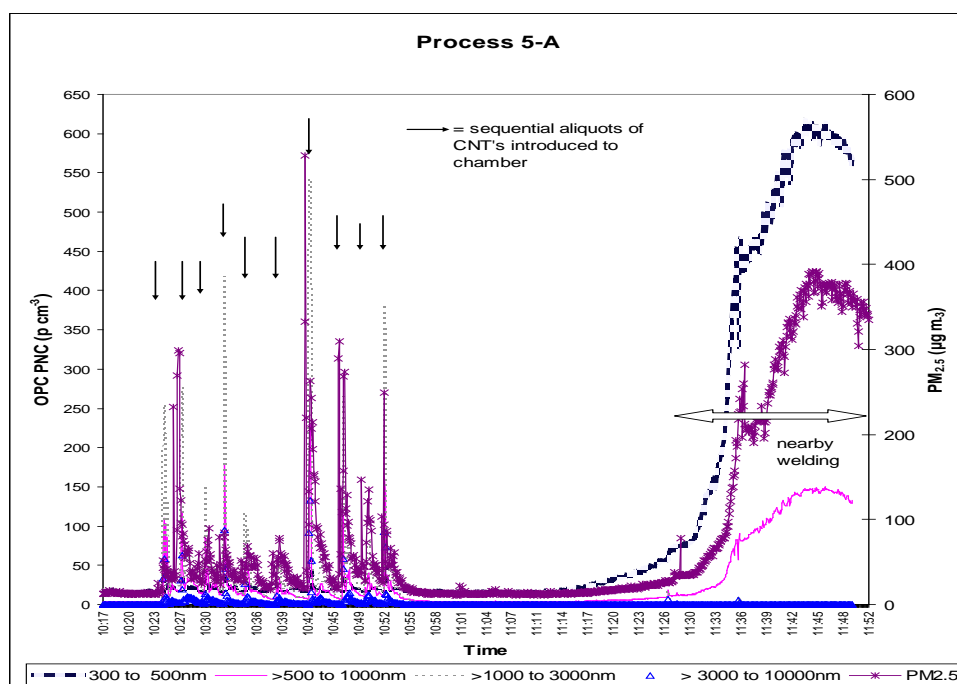
Figure 42: Particle number and mass concentration response of OPC and DustTrak to carbon nanotube aerosol and nearby welding

In addition, analysing the particle concentrations recorded during the operation of processes 1B, 2A, 2B, and 2C, the probability of the extrusion machine, which was operating at a temperature of approximately 200ºC, contributing particles associated with vapour generation, must be considered as high.

The influence of incidental particle sources is further illustrated in the data contained in Figure 43. 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].
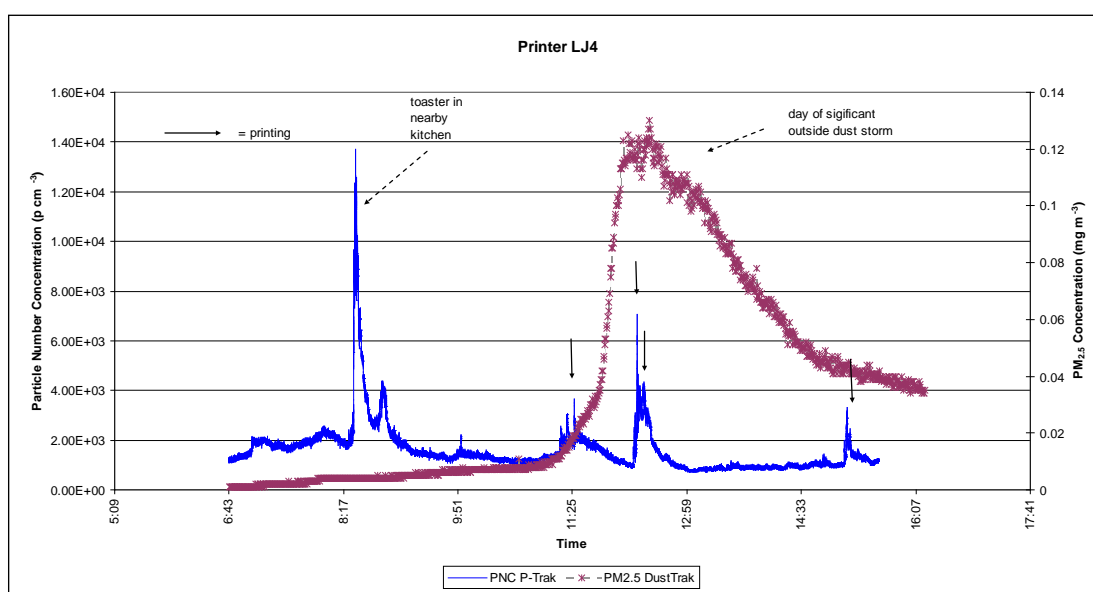
Figure 43: Particle number and mass concentrations associated with incidental background particle sources

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.

10.5   Recommendation 5 – utilise excursion guidance criteria relative to particle background to evaluate significance of temporal and spatial particle variation

As described in Section 7.2, *excursion guidance* criteria should be utilised so as to inform decisions as to whether particle concentration emission and exposure relative to background values are acceptable or require further assessment. The *excursion guidance criteria* model cannot be used to make conclusions about exposure related health effects. The excursion criteria model provides for replicable decision making.

A nanotechnology process can be considered to require control or further assessment if the:
    (a) eight-hour TWA exposure > *particle control value*, or
    (b) 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
    (c) a single short term value for emission or exposure exceeds five times the *particle control value.*

A pragmatic argument supporting the utility of the excursion criteria model is presented below. Here, the *excursion guidance criteria* are applied to Processes 1A, 1B, 2, 3, 4, 6A, and 6B. Based upon these excursion criteria, a nanotechnology process could be considered to require further assessment if:
    a. short term exposures exceed three times the *local particle reference value* for more than a total of 30 minutes per eight-hour working day, or
    b. if a single short term value exceeds five times the *local particle reference value.*

However, the values of 'three times' and 'five time' are arbitrary. Indeed, a more precautionary approach could also be utilised. For example, examination of the real-time particle concentrations presented in the graphs in Section 8 for Processes 1 to 6, reveals variation in background particle concentration was typically no greater than twice that of the average background particle concentrations. Therefore, "any single value > two times the particle reference value" and "> 3 times the *local particle reference value* for more than 30 minutes in an eight hour period" could be utilised for these processes.

Regardless of which *excursion guidance criteria* values are chosen, the value chosen must be able to account for typical fluctuations in the background particle concentration so as particle emission associated with the process of interest can be clearly identified.

For this reason it is important the typical variation in background particle concentration is carefully and comprehensively characterised during period when the process of interest in not in operation.

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 in relation to the *excursion guidance criteria*.
4. Conclude whether:
   a) the particle *exposures* were significant, and
   b) the particle *source emissions* were significant.

10.5.1 Application of *excursion guidance criteria* to research data contained in this report

The utilisation of *excursion guidance criteria* values relative to each of the nanotechnology environments studied is examined below. The *excursion guidance criteria* are applied to Processes 1A, 1B, 2, 3, 4, 6A, and 6B, as shown in Table 13.

Process 5 has been excluded because the particle data was generated within a chamber, whereas data for the other processes was generated within actual work environments.

Table 13 has been divided along the lines of "Tier Two" and "Tier Three" assessment to reflect the three-tiered particle assessment process recommended in Section 10.6.

In relation to the *local particle reference value*, where the excursion criteria have been exceeded the relevant cell within Table 13 has been shaded to signify that this is a significant Tier Two assessment finding. 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 Workplace Exposure Standards and similar.

As part of the Tier Two assessment, *local particle reference values* have been assigned in following three bands: (a) $PNC_{20-1000nm}$, (b) $PNC_{300-3000nm}$, (c) $PM_{2.5}$. The upper range of 3000nm has been used for the PNC because all background and nanomaterial aerosol concentrations > 3000nm were <1 particle cm^{-3} and therefore of insignificance. 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. Also in such circumstances, the PM_{10} rather than $PM_{2.5}$ particle size impactor should also be used for the DustTrak.

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.

Table 13: Summary of assigned local particle reference values and calculation of excursions above such at the point of particle emission and within breathing zones

P R O C E S S	Local particle reference values a) $PNC_{20-1000nm}$ [p cm^{-3}] b) $PNC_{300-3000nm}$ [p cm^{-3}] c) $PM_{2.5}$ [µg m^{-3}]	Tier Two assessment				Tier Three assessment	
		Application of excursion criteria using measured particle concentrations relative to local particle reference values				Actual Tier Three assessment conducted for the nanomaterial	Other options for Tier Three Assessment using Workplace Exposure Standards (WES), Recommended Exposure Standards (REL), proposed exposure standards, or Benchmark Exposure Limits (BEL)
		Is *source emission* > 3 times the local particle reference value for more than 30 minutes in 8 hour day?	Is any single *source emission* peak value > 5 times the local particle reference value?	Is *breathing zone* value > 3 times the local particle reference value for more than 30 minutes in 8 hour day?	Is any *breathing zone* peak value > 5 times the local particle reference value?		
1A	a) 5.2×10^3	no	No	no	no	SMPS data – no significant difference in count media diameter during or between process operation at emission point	REL Ultrafine TiO_2 300 µg m^{-3}
	b) #	n/a	n/a	n/a	n/a		
	c) 6.5	no	yes = 50 µg m^{-3}	no	no		
1B	a) 1.2×10^4	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}
	b) #	n/a	n/a	n/a	n/a		
	c) 7.4	no	No	no	no		
2*	a) 6.6×10^3	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}	no	no		
3^	a) 2.7×10^3	no	yes = 1.1 x 10^4 p cm^{-3}	no	no	SMPS data – no significant difference in count media diameter during or between process operation at	REL Ultrafine TiO_2 300 µg m^{-3}
	b) #	n/a	n/a	n/a	n/a		

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				Actual Tier Three assessment conducted for the nanomaterial	Other options for Tier Three Assessment using Workplace Exposure Standards (WES), Recommended Exposure Standards (REL), proposed exposure standards, or Benchmark Exposure Limits (BEL)
		Is *source emission* > 3 times the local particle reference value for more than 30 minutes in 8 hour day?	Is any single *source emission* peak value > 5 times the local particle reference value?	Is *breathing zone* value > 3 times the local particle reference value for more than 30 minutes in 8 hour day?	Is any *breathing zone* peak value > 5 times the local particle reference value?		
	c) 10	no	yes = 70 µg m^{-3}	no	no	emission point	
4$^\triangle$	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}		
	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 ES 7 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 ES 7 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 particle concentration measurements 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

$\triangle$ values reflect jet milling phase only, and do not include cleaning phase because cleaning phase did not emit particles above background values

10.5.2 Examination of findings in relation to background particle reference values

It is clear from Table 13, column 3, that particle emission from Processes 1A, 1B, 2, and 3 were not strong enough to cause any sustained increase in the local background particle exposure. This is despite peak PNC and $PM_{2.5}$ concentrations of greater than five times the *local particle reference value* being recorded at locations close to the process. This indicates that these peak particle concentrations were of insufficient strength and frequency to cause significant prolonged elevation of the background particle concentration at the point of emission or in breathing zone of workers.

Although SEM-EDX and TEM-EDX analysis of the emission aerosols for Processes 1B and 2 revealed the presence of airborne particles consistent with the raw nanomaterials, breathing zone particle concentrations were found to be insignificant when compared to background. Likewise, breathing zone particle concentrations were not significantly elevated above the particle reference value for Processes 1A and 3.

In contrast, it is evident that Process 4 was a strong emitter of both sub and supermicrometre particles at greater than five times the *local particle reference values*, and the strength was sufficient to sustain an elevation in particle concentration relative to background. The extraction ventilation at the emission points and the mechanical dilution ventilation were sufficient to maintain peak and average submicrometre exposure at background levels. However, the process operator was exposed to peak $PNC_{300-3000nm}$ and $PM_{2.5}$ greater than five times the background particle reference values.

Processes 6A and 6B were strong emitters of particles at greater than five times the *local particle reference value*. In addition, the strength of the particle emission was such that the average $PNC_{300-3000nm}$ and $PM_{2.5}$ at the emission point for Process 6 was three times the background particle reference value for more than 30 minutes. For Process 6B the $PM_{2.5}$ at the emission point was elevated for more than 30 minutes. As the particle concentrations within the breathing zone of workers was below the *excursion guidance criteria* it is clear the enclosures and extraction ventilation utilised for Processes 6A and 6B are effective emission controls.

The excursion criteria model provides for replicable decision making. It is clear 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 emission and exposure that required control and/or further assessment.

10.5.3 Approach summary

In summary the steps to follow are:
- a) Measure real-time *local background particle exposure* in terms of number and mass concentration during periods when the process of interest in not in operation.
  - a. Plot the time-series data.

      b. Calculate the average of the *local background particle exposure* particle number and mass concentration – this is the *local particle reference value*.

      c. Identify the presence of peak particle concentration values. Exclude particle values that are within ± of the manufacturer stated accuracy of the instrument, i.e. peak values that are within ± of *the local particle reference value*.

      d. Calculate the peak particle and mass concentration values for the *local background particle exposure*

b) Measure real-time particle number and mass concentration data at emission points, within breathing zone of worker, and at the perimeters of process enclosures and extraction ventilation, during operation of the process.

      a. Plot the time-series data –

      b. Calculate the time-weighted average of the real-time particle number and mass concentration

      c. identify the presence of peak particle concentration values. Exclude particle values that are within ± of the manufacturer stated accuracy of the instrument, i.e. peak values that are within ± of the time-weighted average of the real-time particle number and mass concentration

      d. Calculate the peak particle number and mass concentration values for the process operation

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

d) Compare this ratio to the general *excursion guidance criteria* as a trigger for to review of particle controls and/or conduct further assessment.

e) General *excursion guidance criteria* - a nanotechnology process could be considered to require further assessment if:

      a. Short term exposures/emissions exceed three times the *local particle reference value* for more than a total of 30 minutes during a work day; and/or

      b. If a single short term value exceeds five times the *local particle reference value*.

The excursion criteria model allows decision to be made as to whether particle emissions relative to the background are acceptable or unacceptable. The excursion criteria model does not allow conclusions to be made about potential health effects arising from exposure to airborne engineered nanoparticles. The excursion criteria model is a pragmatic approach that can be used in the absence of health based particle exposure standards, and therefore is currently applicable to nearly all nanomaterials. Therefore, as this is not a health exposure model, the ratio of particle emission to background that is of relevance.

However, absolute particle concentration values are of importance where relevant exposure standards exist, and also for future epidemiological studies.

10.6 Recommendation 6: Utilise a three-tiered particle evaluation process

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

10.6.1   Tier One - comprehensive survey of the process environment

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. The information gathered during Tier One is used to inform the Tier Two measurement process.

10.6.1.1 Qualitative survey

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.

10.6.1.2 Quantitative survey

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.

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 40 contains a picture of such set-up of instruments.

The time series data described in section 8.5 for Process 4, and section 8.7 for process 6, illustrates how to conduct and document the quantitative survey. Figures 18, 19, 35, and 36 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 35 and 36 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.

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

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

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, exposure, or validation of 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.

10.6.2.1 Characterisation of particle source emission

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.

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 so as to characterise any residual impact upon the background following shut-down of the process of interest.

For example, as part of the assessment of Process 1B (see section 8.2), a P-Trak was used to characterise the PNC, and a DustTrak was used to characterise the $PM_{2.5}$ concentration, relative to the *local background particle exposure*. Both instruments were located with their sampling orifices ~ 20 cm from the point of powder crushing. Figure 2, in section 8.2, provides the time-series plot of particle number and mass concentration related to Process 1A which included the manual crushing of a modified TiO_2 powder. It is clear from Figure 2 that both instruments were able to characterise both the particle number and mass concentrations, relative to the process and the background. The increase in PNC during the process was relatively small when compared to the background, with peak PNC of 7.0×10^3 p m^{-3} during the process being similar to that of the background, and to the accuracy of the instrument, ±20% of each reading. However, peaks in $PM_{2.5}$ concentration were evident, although only 5 µg m^{-3} above background.

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 upon the general workplace atmosphere and therefore potential exposure of workers. Figure 9 illustrates the time series data obtained from using two CPC's.

Further information on the utility of mulitiple 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]

10.6.2.2 Estimation of exposure

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.

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.

Relative 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 40 contains a picture of such set-up of instruments.

Peak particle number and mass concentration exposure are more reliably obtained using instrument 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 14.

Table 14: Peak particle number and mass concentrations in process operator breathing zone during process operation compared to the *local background particle exposure* (LBPE)

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	LBPE	Peak during	LBPE	Peak during	LBPE
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$^\Delta$	5.0 x 10^2	5.0 x 10^2	100	< 1	2	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						

10.6.2.3 Validation of effectiveness of particle emission controls

The goal of this measurement is to validate if engineering controls such as enclosure and extraction ventilation are containing 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.

Figures 9, 18, 19, 35 and 36 contain information obtained from using the instruments in to assess the effectiveness of enclosures, mechanical dilution ventilation, and extraction ventilation in containing and entraining particles. Note the specific times and locations of the measurements have been correlated to the measurement data within these figures.

Local extraction ventilation

Figure 9 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

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 18 and 19 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 section 8.5.2.2. This demonstrates the utility of the P-Trak and OPC in assessing and validating the effectiveness of mechanical dilution ventilation to disperse particles from the breathing zone of process operators.

Enclosures

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 35 and 36 (section 8.7.2). 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.

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.

Historic performance levels of engineering control options for airborne dusts

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 15. These data support the conclusions from the research data that it is feasible in practice to achieve acceptable airborne concentrations.

Table 15: 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

10.6.2.4 Summarising overall findings of Tier Two assessment

From Table 13, a comparison of short term and peak emissions and exposures with the corresponding *local particle reference values* indicates that:

- the controls for processes 1A do not require further assessment
- Processes 2, 3, and 4 require either further control, or a Tier Three assessment
- process 6 is a strong emitter of CNTs, but the existing controls in place prevent exposure, and therefore further assessment is not required.

10.6.3 Tier Three - utilise sampling methods for off-line analysis of particle morphology, chemical composition, and mass concentration, and real-time SMPS

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:

- 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 more comprehensive particle sampling should occur as part of a tier three assessment in order to inform the review of controls.

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 particle morphology and chemical composition. The results of the off-line particle morphology and chemical composition analysis can also be compared to real-time measurement results.

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. Section 10.6.3.1 includes a description of successful use of the above particle sampling and analysis methods.

In addition, where an Australian 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.

A scanning mobility particle sizer with a lower size measurement point within the ultrafine particle size range, and as small as possible, could also 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 exposure* would suggest the nanotechnology process is emitting particles. These particles may be within the ultrafine size fraction but could also be of larger particle sizes due to agglomeration of particles.

The results of our off-line analysis of particles 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.

Particles can be collected at both the emission point and in the breathing zone of workers as described below.

10.6.3.1 Collection of particles at emission point

As part of the assessment of Process 2 (see section 8.3), 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 operations of the process. The aerosol at the point of particle emission was also simultaneously collected onto a filter membrane connected to a sampling pump, TEM grid within an electrostatic precipitator, with analysis SEM/XRD and TEM/XRD respectively.

It is clear from the data presented in sections 8.2 and 8.3 that filter membranes within open-faced cassettes attached to sampling pumps, and TEM grids utilised within electrostatic precipitators can entrain airborne engineered nanoparticles 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.

For example, where the results of real-time particle concentration measurement revealed the particle emission to be weak, such as with Process 1A, 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.

As part of the assessment of Process 1A (see section 8.2), 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.

The collection of particles for such off-line analysis is particularly pertinent for processes 1B, 2A, 2B, and 2C, because the probability of the extrusion machine, which was operating at a temperature of approximately 200ºC, contributing particles associated with vapour generation, must be considered as likely. Without such off-line analysis of paticle composition, it could not be concluded that any elevation in particle concentrations during the operation of the process originated from the nanomaterial of interest.

Where real-time measurement results indicate a process to be a likely emitter of significant peak concentrations of particles, such as with process 2, both SEM-EDX and TEM-EDX analysis of aerosol particles clearly verified the process was an emitter of particles to the work area atmosphere.

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 at the point of emission.

10.6.3.2 Collection of particles in the breathing zone of workers

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

As outlined in section 7.1 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 7 μg 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 must 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 300 μg m^{-3}, the aerosol should 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 TiO$_2$ of 300 μg m^{-3}, 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 300 μg/m^3, then no further action is required. If the exposure concentration exceeds 300 μg/m^3, then additional characterization of the sample is needed to determine the particle size and percentage of TiO$_2$ and other extraneous material on the sample. 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 fine (> 0.1 μm) and ultrafine (< 0.1 μm) TiO$_2$.

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.

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.

10.6.3.3 Case study of tier three assessment

As part of the assessment of Processes 5A and 5B (discussed in detail in section 8.6), 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 SEM and XRD, and (3) a quartz filter connect to a sampling pump and analysed for elemental carbon mass using Evolved Gas Analysis by thermal-optical analyser.

Figures 20, 21, 22, and 23 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 10, confirmed an overall positive correlation for these two instrument particle responses.

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.

10.7 Recommendation 7: calculate impact of instrument accuracy on measurement results

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 reasons. 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. Because such increases were consistent with normal fluctuation in background and the manufacturer stated accuracy of the instrument (in this case < ±20% of the background), it could not be concluded with confidence that these increases in particle concentration were associated with the process.

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. 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.

10.8   Recommendation 8: calibrate equipment

This 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.

The CPC, OPC, and photometer should be calibrated and adjusted to National Measurement Institute (NMI) 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.

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.

Knowledge of the typical values of the particle values of the ambient environment used for field calibration can also be used to judge if the instrumentation is operating correctly. This then requires detailed 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.

10.9   Recommendation 9: utilise same equipment for on-going measurement of same process

Figures 7 and 10 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.

10.10   Recommendation 10: record and report the relative humidity and temperature of the work area

Increases in relative humidity can cause an increase 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.

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.

An example of graphed relative humidity and temperature data is provided in Figure 44.
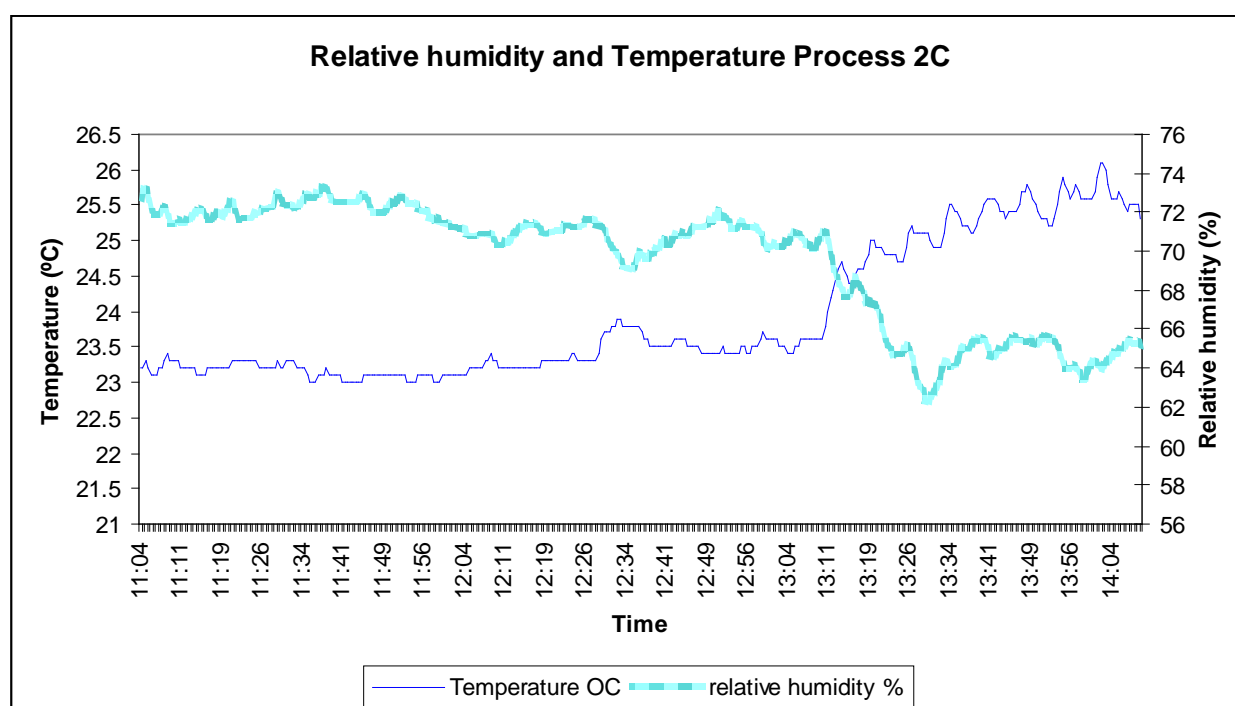
Figure 44: Relative humidity and temperature variation during the operation of process 2C

10.11   Recommendation 11: A minimum data set should be included in all reports of assessment of nanomaterial aerosol

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 aersols.

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

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- 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.

Tier Two Assessment data including:

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- 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

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 an Australian 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.

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, etc of ventilation controls, personal protective equipment being used
- Details of environmental and area conditions, for example room dimensions, sources of natural ventilation.

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12 Appendix A

Schematics of extrusion machine [5]
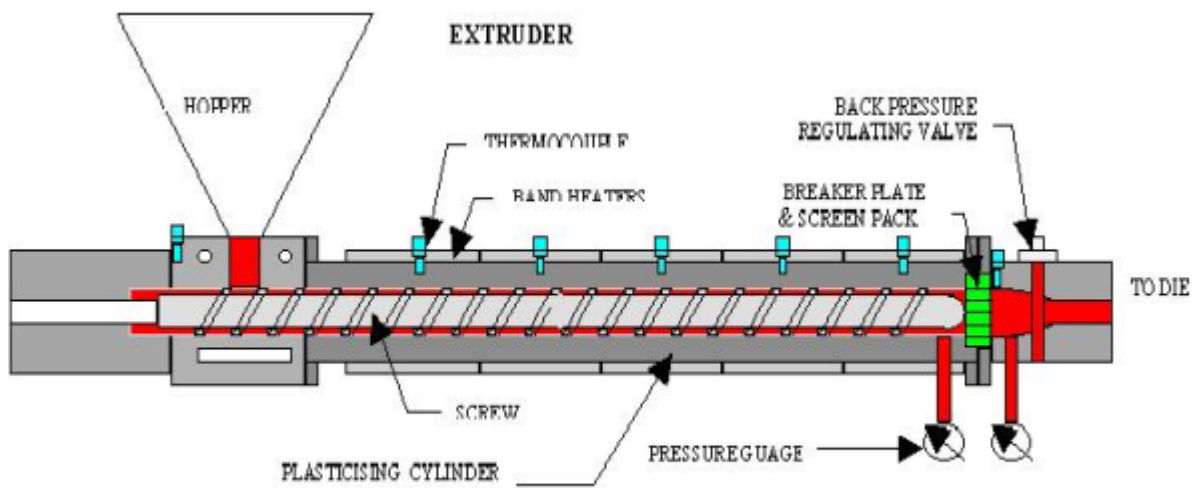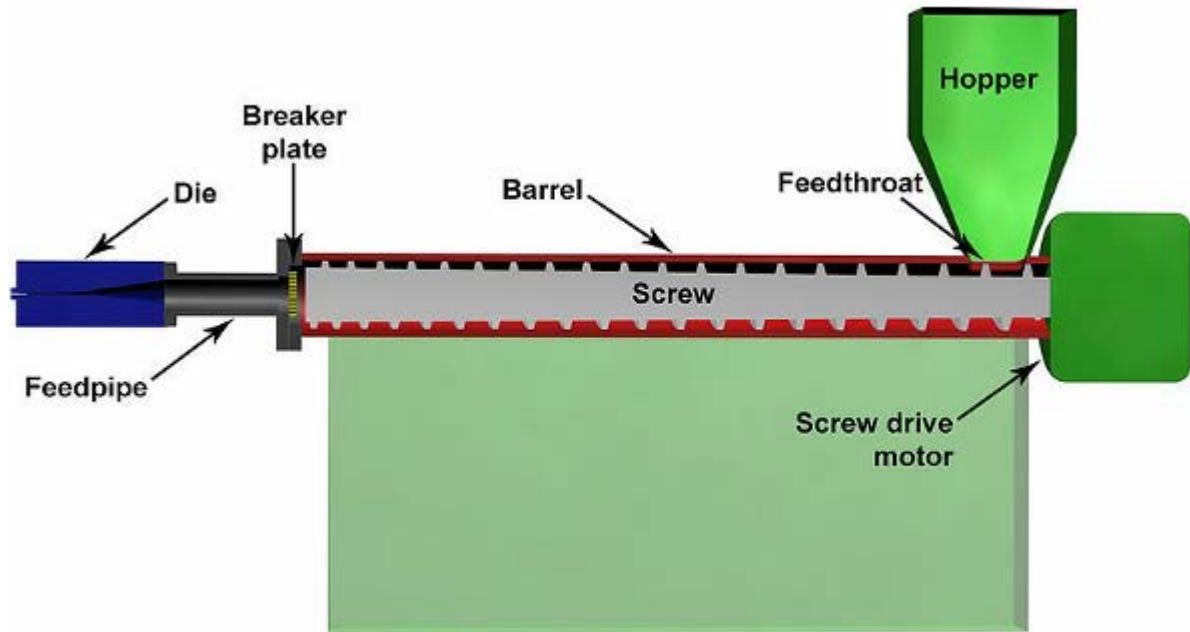
13 Appendix B – Pearson's Correlation Results

13.1 Grinding of titanium dioxide powder

Table 16 provides the Pearson's Correlation r-values for selected instruments used to characterise airborne particles during the grinding of titanium dioxide powder.

Table 16: 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

From Table 16 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 strong 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.

13.2 Extrusion of titanium dioxide and polyethylene materials

Table 7 provides the Pearson's Correlation r-values for selected instruments used to characterise airborne particles during the measurements.

Table 17: Inter-instrument Pearson's Correlation matrix for Process 1-B - extrusion of titanium dioxide & 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

From Table 17 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.

13.3 Extrusion of clay platelets and polyurethane materials

Table 18 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 18: Inter-instrument Pearson's Correlation matrix for Process 2 - extrusion of clay platelets and polyurethane materials

	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

From Table 18 it can be seen that there is a strong correlation between all four CPC responses to this aerosol, and also a 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.

13.4 Grinding of titanium dioxide powder

Table 19 provides the Pearson's Correlation r-values for selected instruments used to characterise airborne particles during the grinding of titanium dioxide powder

Table 19: 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

From Table 19 it can be seen that there is a weakly positive linear relationship between the two CPC's, the SMPS, and the NSAM. The DustTrak also exhibits a poor linear correlation with the other instruments.

13.5 Jet milling of clay platelets

Table 20 provides the Pearson's Correlation r-values for selected instruments used to characterise airborne particles during the jet milling of clay platelets.

Table 20: 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

From Table 20 it can be seen that for the portable hand-held instruments there is a strong 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.

13.6 Decanting of single-walled carbon nanotube powder

Table 21 provides the Pearson's Correlation r-values for selected instruments used to characterise airborne particles during the decanting of SWCNT powder.

Table 21: 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)	Ptrak (source)	SMPS (source)	NSAM (source)	DustTrak (source)
Ptrak (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

From Table 21, a 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, and strong correlation with the DustTrak and a poor linear relationship with the other instrumentation.

13.7 Decanting of multi-walled carbon nanotube powder

Table 22 provides the Pearson's Correlation r-values for selected instruments used to characterise airborne particles during the decanting of MWCNT powder.

Table 22: 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)	Ptrak (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

From Table 22, a strong linear relationship exists between the P-Trak and the OPC (300 to 500nm) but is weakly positive between the P-Trak and OPC (> 500nm). The SMPS exhibits a poor linear relationship with all instruments. The DustTrak and NSAM exhibit a weakly positive relationship with the OPC (particle 300 to 1000nm).   The NSAM exhibits a strong relationship with the P-Trak.

Appendix C

Table 23: 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 (C_{60})	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