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## TITLE PAGE

**Title:** Excursion guidance criteria to guide control of peak emission and exposure to airborne engineered particles

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## **Abstract**

The overall aim of our research was to characterise airborne particles from selected nanotechnology processes and to utilise the data to develop and test quantitative particle concentration based criteria that can be used to trigger an assessment of particle emission controls.

We investigated particle number concentration (PNC), particle mass (PM) concentration, count median diameter (CMD), alveolar deposited surface area, elemental composition, and morphology from sampling of aerosols arising from six nanotechnology processes. These included fibrous and non-fibrous particles, including carbon nanotubes (CNTs).

We adopted standard occupational hygiene principles in relation to controlling peak emission and exposures, as outlined by both *Safe Work Australia* [1], and the *American Conference of Governmental Industrial Hygienists* [2]. The results from the study were used to analyse peak and 30-minute averaged particle number and mass concentration values measured during the operation of the nanotechnology processes.

Analysis of peak (highest value recorded) and 30-minute averaged particle number and mass concentration values revealed: Peak PNC<sub>20-1000nm</sub> emitted from the nanotechnology processes were up to three orders of magnitude greater than the local background particle concentration (LBPC). Peak PNC<sub>300-3000nm</sub> was up to an order of magnitude greater, and PM<sub>2.5</sub> concentrations up to four orders of magnitude greater. For three of these nanotechnology processes, the 30-minute average particle number and mass concentrations were also significantly different from the LBPC (p-value < 0.001).

We propose emission or exposure controls may need to be implemented or modified, or further assessment of the controls be undertaken, if concentrations exceed three times the LBPC, which is also used as the *local particle reference value*, for more than a total of 30 minutes during a work day, and/or if a single short-term measurement exceeds five times

the *local particle reference value*. The use of these quantitative criteria, which we are terming the universal excursion guidance criteria, will account for the typical variation in LBPC and inaccuracy of instruments, whilst being precautionary enough to highlight peaks in particle concentration likely to be associated with particle emission from the nanotechnology process. Recommendations on when to utilise local excursion guidance criteria are also provided.

## **INTRODUCTION**

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. Coinciding with the increased penetration of nanotechnology across many sectors of the world-wide economy, there has been a corresponding increase in scientific literature over the last decade on the subject of characterising emission of, and exposure to, particles arising from nanotechnology processes.

There is strong agreement in the literature [3-5] that mass, or at least mass on its own, is not an adequate metric for evaluating exposure to nanoparticles (a nano-object with all three external dimensions in the nanoscale size range of approximately 1 to 100 nm [6]). Nanoparticle properties such as surface area and activity [3, 4, 7, 8], particle number concentration [4, 7], or fibre aspect ratio and length [7], are considered to be better metrics of exposure than mass. However, no single sampling method is available for measuring all of these nanoparticle traits in terms of workplace exposure and evaluation of effectiveness of emission controls.

To identify the wide array of aerosol measurement methodologies used to assess particle emission from nanotechnology processes, we reviewed 25 studies as outlined and referenced in the Supplemental Information - Table SI.

The review highlighted a mixture of relatively simple, as well as complex particle measurement techniques, both real-time and off-line, are commonly used. Most common in these studies was the characterisation of particle number and mass concentration, mostly as area sampling in contrast to personal sampling (sampling in a zone approximately 300mm from mouth/nose). It is evident from the variety of methods described in the literature that consensus has not yet been reached regarding which particle metric/s and sampling methods should be used to characterise aerosols arising from nanotechnology processes. This is partly because it has not been agreed how these particle metrics reflect disease risk. A similar review of measurement methods was conducted by Kuhlbusch et al. [9].

Whilst the results of different measurement methods provide useful information about an aerosol, they differ markedly in complexity, precision, accuracy, and cost. The literature also reflects an over-emphasis on attempts to demarcate only the sub-100 nm (i.e. nanoparticle) fraction of aerosols, adding complexities to measurement methods. The use of the size range of less than 100 nm is simplistic and arbitrary when discussing health effects or emission characteristics of particles because (i) particles are never monodisperse [10], unless they are purposely generated as such and have not agglomerated, and (ii) there are no instruments which provide exclusive measurement of particle size below 100 nm, however this size fraction can be extracted from the particle measurements obtained using a scanning mobility particle sizer (SMPS). 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, 12]. However, this definition is not particularly useful for assessment of nanoparticle emission because particles are unlikely to persist in their initial particle size, but rather will agglomerate or aggregate into larger sized particles over time, including into the micrometre size range [4, 11, 13].

Given the present lack of dose response associations for many nanoparticle types and the scarcity of human exposure and toxicological data, the concept of having a single exposure standard for engineered nanoparticles based purely on a physical nanoparticle property would seem unrealistic. This would exclude the often interacting and heterogeneous factors (material, size, shape, surface reactivity, chemical composition) which contribute to their special functions as nanomaterials.

To date, only a small number of airborne concentration exposure standards have been established or proposed for engineered nanoparticles. A hierarchy of what we are terming *particle control values* (PCVs), which are currently used or have been proposed for assessing the significance of particle emission and exposure, in decreasing order of preference is:

1. A company or laboratory in house control limit - where these are lower (i.e. more stringent), than applicable regulatory limits. For example, Multi-Walled Carbon Nanotubes –  $0.05 \text{ mg m}^{-3}$  [14]
2. National workplace exposure standards. For example, carbon black ( $3 \text{ mg m}^{-3}$  [15]) and fumed silica ( $2 \text{ mg m}^{-3}$  [15])
3. Recommended Exposure Limits. For example, ultrafine  $\text{TiO}_2$  ( $0.3 \text{ mg m}^{-3}$  [16]), and fine  $\text{TiO}_2$  ( $2.4 \text{ mg m}^{-3}$  [16])
4. Proposed workplace exposure limits – from research results. For example,  $\text{TiO}_2$  ( $0.6 \text{ mg m}^{-3}$  [17]), fullerenes C60 ( $0.39 \text{ mg m}^{-3}$  [17]), carbon nanotubes (CNTs) ( $0.03 \text{ mg m}^{-3}$  [17],  $0.001 \text{ mg m}^{-3}$  [18])
5. Benchmark exposure levels (BEL) – which have some consideration of health effects. For example, fibrous nanomaterials : BEL =  $0.01 \text{ fibres/ml}$  [19]; nanomaterials classified as Carcinogenic, Mutagenic, Asthmagenic, or Reproductive Toxins (CMAR): BEL =  $0.1 \times \text{Workplace Exposure Limit (WEL)}$  of the bulk material [19]; insoluble

nanomaterials: BEL = 0.066 x WEL of the bulk material [19]; soluble nanomaterials:

BEL = 0.5 x WEL of the bulk material [19]

6. *Local particle reference values.* For example, derived from characterising background particle number and mass concentrations [20, 21].

It can be concluded from the above that there are relatively few *PCVs* currently established or proposed for nanomaterials, and these are all eight to ten-hour time-weighted average (TWA) standards. In addition, with the exception of local particle reference values, they are exposure (in contrast to emission) limits, mass based (except for the fibrous nanomaterial BEL), and require sampling for off-line analysis. However, also required is guidance on when excursion above these averages for shorter periods require control, such as Peak or Short Term Exposure Limits (STELs). This is particularly relevant for nanotechnology processes of short duration and those with large variability in particle emission. Such comparison of peak values to *particle control 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.

The purpose for limiting some excursions of airborne contaminant exposures above time-weighted average (TWA) exposure standard values within the occupational environment is explained by both *Safe Work Australia* [1], and the *American Conference of Governmental Industrial Hygienists* [2]. Although McGarry et al. [20, 21] described the use of excursion guidance criteria in relation to (nano)particle emission from laser printers, there is limited reference in the scientific literature to the use of excursion guidance criteria for assessment of engineered nanoparticle emissions.

Debate in the scientific and occupational health community regarding which particle metric/s should underlie health based exposure standards is ongoing while equipment/instrumentation that allows breathing zone assessment of exposure of a wide range of possible health related particle characteristics remains in its developmental

infancy. Whilst waiting for this knowledge to mature, exposure should be controlled by assessing and controlling particle emission at its source. Further, such assessment and control should not be narrowly focussed at the nanoparticle size range, but rather a holistic approach that targets a larger range of particle sizes should be employed. For such an approach to have utility at the workplace level any assessment must incorporate relatively inexpensive and easy to use instruments supported by criteria that inform decisions on when to control particle emission.

To address this need, we measured a range of particle number and mass concentration values during the operation of nanotechnology processes relative to background concentration, and used this data to answer the following questions: (i) in the absence of quantitative exposure standards for most engineered nanomaterials, can background particle reference values be used as benchmarks to examine relative emission of, and exposure to, particles arising from a nanotechnology process? (ii) which particle metrics should be used at a workplace level to identify particle emission from a nanotechnology process? (iii) can excursion guidance criteria be used to inform decisions on when particle emission needs further assessment and/or control?

## **METHODS**

Both real-time and off-line data was collected and analysed to characterise the emission and transport of particles associated with nanotechnology processes during the operation of six processes involving engineered nanoparticles. Temporal and spatial particle data were collected at likely sources of particle emission, and where possible within proximity of the breathing zone of workers both during and between operation of the processes, so as to characterise particles arising from the nanotechnology process and background particle sources.



## **Real-time sampling instrumentation and equipment**

Both real-time and off-line particle sampling was conducted. However, for this paper, only the real-time particle number and mass concentration data has been used to evaluate the use of excursion guidance criteria. This data was obtained using a:

- TSI (United States) Model 8525 P-Trak, condensation particle counter (CPC), for PNC in particle size range of 0.02 - 1  $\mu\text{m}$
- TSI Model AeroTrak 9306 optical particle counter (OPC) for PNC in six channels, over the particle size range of 0.3  $\mu\text{m}$  to 10  $\mu\text{m}$ , and
- TSI Model 8520 photometer (DustTrak) for particle mass concentration - fitted with a 2.5  $\mu\text{m}$  impactor ( $\text{PM}_{2.5}$ ).

A summary of the other data and sampling and analytical methods is included in Supplemental Information - Table SII. Further analysis and reporting of other data will be the subject of future work. To ensure the comparability of the instruments, they were periodically co-located and sampled in outdoor air and the values compared to our dataset for this ambient environment.

Mass concentration was not measured directly (gravimetrically) in this study. It was inferred via the signal provided by a photometer. However, the response of a photometer to aerosols in these processes was sensitive enough to provide an indication of mass concentration.

## **Selection of nanotechnology processes**

The nanotechnology processes were selected following an expression of interest amongst relevant faculties at two universities in Brisbane, Australia. The expression of interest included the need for a range of different nanomaterials, including both fibrous and non-fibrous materials. The six processes selected, including laboratory research and commercial processes, were:

- **Process 1:** Hand mixing of *functionalised titanium dioxide* with other chemicals (Process 1A), followed by heating and homogenising (Process 1B) the mixture in an extruder to produce pellets that could then be used to blow photo-degradable thin film for use in agriculture.
- **Process 2:** Fine, *functionalised clay platelets and polyurethane plastic beads* were simultaneously added to an extrusion machine, designed to homogenise and heat the mixture so as to form a clay-polyurethane nanocomposite material.
- **Process 3:** A university laboratory process investigating electron transfer and nanotechnology to solar cells. Nanocrystalline *titanium dioxide* (TiO<sub>2</sub>) (99% Anatase) was manually ground, using a mortar and pestle, and mixed with a diluted acidic solution. The resultant TiO<sub>2</sub> solution was added to a slide using a dropper.
- **Process 4:** 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.
- **Process 5:** Proprietary manufactured *single walled (SW) and multi walled (MW) CNTs* in solid form were repeatedly introduced to a chamber from which the resultant aerosols were analysed.
- **Process 6:** Chemical Vapour Deposition manufacture of *CNTs*. Process 6A utilised a furnace for catalytic CNT synthesis, whilst Process 6B utilised a SabreTube™ Bench Top Thermal Processing System.

Because processes 1, 4, 5, and 6 involved distinct sub-processes, the measurement results were analysed as processes 1A, 1B, 4A, 4B, 5A, 5B, and 6A, 6B, respectively, resulting in nine distinct data sets.

## **Study design**

The particle measurement instrumentation and equipment was located and operated as follows. A P-Trak, OPC, and DustTrak were co-located on a tray and operated before and after the operation of each process in order to characterise the LBPC, and then within ~0.2m of the likely point of emission for the period of operation of each process. The duration of measurement of each process varied in accordance with the process operational plan on a particular day. Particle concentration within the breathing zone of process operators was also measured where possible. To assist in locating the aerosol inlets of the instrumentation, smoke tubes were used to identify the impact of local airflow to transport particles to the equipment.

Process 5 involved decanting aliquots of proprietary manufactured dry SWCNT and MWCNT in powder form, a common laboratory task. Because of the specific health concerns regarding CNTs, the experiment was carried out in a chamber. This experiment involved constructing a sampling chamber from a polyethylene storage container with a volume of approximately  $0.07\text{m}^3$ . The aerosol inlets of the instrumentation sampled the inside of the chamber using black conductive rubber tubing connected separately to each instrument, located outside the chamber.

To ensure the comparison of all measurement values was meaningful, each instrument was set to the same sampling interval where possible. In addition, because the ability to resolve the peak concentration is influenced by the sampling frequency, it was set to shortest period possible for that instrument. Therefore, the sampling frequency for the P-Trak, OPC, and DustTrak 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).

## **Data analysis**

To evaluate the contribution of particles from the nanotechnology process to the overall background particle number and mass concentration the following steps were followed.

Firstly, for each nanotechnology process, a time series of PNC and PM<sub>2.5</sub> concentration was plotted for the period prior to, during, and after operation of the process. Secondly, arithmetic averages (of the measurement results recorded by the instrument over the time series) were calculated, from grouped data of repeated measurements (repeated measurements were not done for Processes 5A, 5B, 6A, and 6B), for two periods - when the process was in, and prior to, operation. Thirdly, a LBPC value was assigned for each process. The LBPC is defined as the average of the local work area particle number or mass concentration that excludes any contribution of particles from the nanotechnology process. This value is specific to each work environment and represents the ambient particle exposure not associated with the nanotechnology process. It was calculated following repeated time-series of the particle number and mass concentration when the nanotechnology processes were not in operation. The number of repeated time-series for Processes 1A, 1B, 2, 3, and 4 were 2, 2, 3, 6, and 2, respectively. Fourthly, the peak particle number and mass concentration value recorded during and before operation of each process was identified from the plots of the time-series data. The manufacturer supplied particle concentration accuracy data for each instrument was applied when choosing a peak concentration value. Finally, excursion guidance criteria were utilised to conclude whether assessment, or control or additional control of particle emissions was required, and where relevant, specific recommendations were made to persons in control of a process for improvements in particle emission control.

## RESULTS

For this paper, only the real-time particle number and mass concentration data has been used to evaluate the use of excursion guidance criteria.

### **Time series of particle number and mass concentration**

Six time-series plots (Figures 1 and 2, and Supplemental Information - Figure S1) were selected to illustrate the variability in particle number and mass concentration, across a wide particle size range, associated with particles arising from different nanotechnology processes and background sources.

It can be seen from these Figures that peaks in particle number and mass concentration are associated with both the nanotechnology processes and background sources, and were clearly registered by the P-Trak, OPC, and DustTrak, respectively.

The introduction of each aliquot of single-walled CNTs corresponds to peaks in both  $\text{PNC}_{300-3000\text{nm}}$  and  $\text{PM}_{2.5}$ , as illustrated in Figures 1a and 1b, respectively. These were not evident in  $\text{PNC}_{20-1000\text{nm}}$  associated with the aliquots. This suggests that relative to the background, there are a significant number of particles emitted from the process in the larger size range whereas there is not a significant number in the smaller range. Nearby welding, which occurred after the CNT measurements were completed, contributed significantly to the background particle concentration. Therefore, to effectively utilise PCVs relative to LBPC, extraneous sources of nanoparticles must be removed prior to determining background concentrations.

For the process shown in Figure 2, the time series was started prior to the initiation of events that were suspected to cause nanoparticle concentrations. Therefore, the first values shown on the left side of the figure represent LBPC values. It is evident the jet milling process is a strong source of particles when compared to the LBPC (i.e. when the process was not in operation). In contrast, dismantling and cleaning the jet milling equipment was not a strong source of particles. Note that the  $\text{PNC}_{20-1000\text{nm}}$  was over two orders of

magnitude greater than that of PNC > 300 nm, indicating the predominant size range of the particles emitted from the jet milling process is likely to be < 300 nm. In addition, there was an expected similar trend for both the PNC<sub>>300-1000nm</sub> and the PM<sub>2.5</sub> concentration because of the overlap in the size range response of the OPC and DustTrak.

Comparison (Figure 2) of the PNC at locations B and D (both within ~0.2m of particle emission points of the jet milling machine) to the breathing zone (location C) of the machine operator, revealed - (i) a spatial reduction in PNC of up to two orders of magnitude for < 300 nm particles, and (ii) an approximately eight-fold reduction in > 300 nm particle concentration. There is a spatial reduction in PNC between the particle source and the operator breathing zone because the breathing zone (location C) is more distant from the jet milling machine and mechanical dilution ventilation is operating in the work area. This incidental finding 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.

It is also evident from Supplemental Information - Figure S1 that both sub and supermicrometre particles were generated in significant quantities within chemical vapour deposition (CVD) chambers, and up to four orders of magnitude higher than the laboratory work area. The three instruments were able to validate that both process enclosures and the fume extraction cabinet prevented particles escaping to the laboratory work area.

### **Mean and peak particle concentration**

To explore the effect of background and nanotechnology process contribution to total particle concentration, the data from repeated measurements were grouped, and the arithmetic means calculated. This allowed analysis of data that included and excluded particles from the nanotechnology processes. The mean value, as described in the Methods section, that excludes particles from the nanotechnology process, has been termed the LBPC. To analyse peaks in particle number and mass concentration associated with the

nanotechnology process and background sources of particles, the peak values were identified from the plots of real-time data. Table I provides a summary of these calculations.

It can be seen from Table I that the LBPC in terms of particle number and mass concentration varied by up to two orders of magnitude amongst the process locations. The LBPC also varied on a daily basis at the same location, for example, by an order of magnitude in PNC between processes 1A and 1B, both of which took place in sequence in the same room, but over different days. Daily variance in background particle concentrations at the same location and between locations is not uncommon, and is associated with local sources of particles such as fresh traffic emissions, industrial emissions, and natural events and has been reported elsewhere in the literature [5, 22, 23]. McGarry et al., [20] reported the LBPC varied by an order of magnitude amongst five different office locations within a central business district.

The difference in the mean values of  $\text{PNC}_{20-1000\text{nm}}$  (during process compared to LBPC) for processes 1A, 5A, and 5B were all within one order of magnitude, and within only several hundred particles  $\text{cm}^{-3}$  in absolute terms. For processes 4 and 6B the mean during the processes were an order of magnitude higher than the LBPC. For processes 6A, the difference in absolute particle concentration was less than an order of magnitude.

Likewise, for processes 1A, 1B, 2, and 3 the differences in the mean  $\text{PM}_{2.5}$  values (during process compared to LBPC) were within an order of magnitude of the LBPC, and all within only several  $\mu\text{g m}^{-3}$  in absolute terms. For processes 5A and 5B, the absolute difference in particle concentration was also relatively low and within one order of magnitude. For processes 4, 6A, and 6B the difference in the mean values (during process compared to LBPC) were an order of magnitude higher.

For processes 5A, 5B, and 6B the mean  $\text{PNC}_{300-3000\text{nm}}$  values (during process compared to LBPC) were all within an order of magnitude of the LBPC, and only within 10 particles

cm<sup>-3</sup> in absolute terms For Process 6A the mean during the process was an order of magnitude higher than LBPC, and for Process 4 the difference was two orders of magnitude.

Again from Table I, analysis of the peak particle concentrations associated with process operation relative to the LBPC, showed the peak value exceeded the LBPC by a factor of five or more as follows: PNC<sub>20-1000nm</sub> - six of nine processes, PNC<sub>300-3000nm</sub> - four of five processes, and PM<sub>2.5</sub> - six of nine processes. Simultaneous peaks in both PNC<sub>300-3000nm</sub> and PM<sub>2.5</sub> were also evident for four of the five processes. Apart from processes 5A and 5B, the peak particle concentrations during the operation of the processes were mostly greater by an order of magnitude than peak concentrations associated with LBPC (i.e. when process was not in operation).

## DISCUSSION

### **Which particle metrics should be used at a workplace level to identify particle emission from a nanotechnology process?**

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.

For example, from Table 1, significant peaks in PNC<sub>20-1000nm</sub> were evident for processes 1B, 2, 3, 4, 6A, and 6B. Significant peaks in PNC<sub>300-3000nm</sub> 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<sub>2.5</sub> and PNC<sub>300-3000nm</sub> were evident for processes 4, 5A, and 6A.

This is further illustrated in the data from process 4, Figure 2, where 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 the time-series plots of the PNC and PM<sub>2.5</sub> concentration illustrated in Figure 2. As can be seen in this Figure the instruments were able to show (i) the emission aerosol dominated by



submicrometre sized particles, (ii) 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  $1 \text{ p cm}^3$ , which was similar to the background). In addition, it is clear that there was good correlation between the OPC response and the DustTrak response.

Clearly this 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 included particles within the 300 to 1000nm size range as characterised by the OPC, and the correlating  $\text{PM}_{2.5}$  mass concentration as characterised by the DustTrak. This finding of particle signatures incorporating sub and supermicrometre particles was common to our dataset as a whole. It can be concluded that both sub and supermicrometre particles are emitted from these processes, particle signatures dominated by sub or supermicrometre particles are readily identifiable, and that concurrent characterisation of particle number and mass concentration are applicable for identifying particle emission.

Therefore, we recommend particle number and mass concentration data 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  $10 \text{ }\mu\text{m}$
- A photometer with a sensitivity over a size range that overlaps with the portable CPC and OPC, for example a DustTrak.

Although the mass concentrations reported in this study were estimates based upon the signal provided by a photometer, the results indicate the photometer is sufficiently sensitive in the sub and supermicrometre range to be useful for characterising relative mass concentrations before and during process operation, and therefore relevant when using excursion guidance criteria to identify particle emission.

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, combined with an understanding of the overlap in particle response bands of the three instruments allows sound conclusions to be made about the dominant particle signature. For example, a significant PNC in the range of 500 to 3000nm may correlate with significant PM<sub>2.5</sub> 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.

Particle number and mass concentration should be characterised as part of a Tier 1 and 2 assessment process to screen whether *emission* from a process may require control or further assessment. In contrast, where information is required on particle *exposure* in terms of mass or fibre concentration, agglomeration, aggregation, primary particles, fibre morphology, particle morphology and chemical composition, a Tier 3 assessment utilising sampling by more complex instruments and methods should be implemented.

**How can excursion guidance criteria, relative to background particle concentration, be used to inform decisions on when particle emission needs further assessment and/or control?**

Although the concept of characterising particle number and mass concentration during the operation of nanotechnology processes relative to background values is not unique to our study, and has been described as part of the United States National Institute of Occupational Safety and Health Nanoparticle Emission Assessment Technique (NEAT)

[24, 25], we have extended this approach by incorporating the concept of *excursion guidance criteria*.

Both sub and supermicrometre particles are ubiquitous in the environment. Therefore, excursion guidance criteria need to account for normal fluctuations in sources and levels of background particles. Indeed, more than 99% of the total number concentration of particles in the ambient atmosphere are < 300 nm in size [5].

The excursion guidance criteria values must be robust enough to account for the typical variation in LBPC, and be precautionary enough to capture peaks in particle concentration likely to be associated with the nanotechnology process. For example, as indicated from Table I, LBPC can vary by two orders of magnitude from location to location and this reflects particles arising from both natural and anthropogenic sources. It is also clear from Figure 1, that other sources of particles, such as nearby welding, contribute to the background particle concentration and can be a stronger source of particles than the process of interest.

There are two sources of particles that workers can be exposed to as a result of processes involving engineered nanomaterials: (a) engineered nanomaterials emitted from the process, and (b) incidental nanoparticles, e.g. combustion particles, resulting from operation of the process equipment. Therefore, it is important that the typical variation in background particle concentration is also carefully and comprehensively characterised during the period when the process of interest is not in operation, and also where possible, with the process of interest in operation but with no nanomaterials being introduced.

Excursion guidance criteria could be based upon the order of magnitude in difference between the LBPC and peaks in particle concentration associated with the process. However, this would discount potentially relevant differences in absolute PNC. For example, the differences in the means of  $PNC_{20-100nm}$  (during process compared to LBPC)

for processes 1B, 2, and 3 were less than one order of magnitude but the absolute differences were in range of tens of thousands of particles  $\text{cm}^{-3}$ .

The excursion guidance criteria values must also account for the particle concentration accuracy of the instruments. Supplemental Information - Table SIII summarises the manufacturer specified instrument accuracy for three instruments. It can be seen from this Table that for the P-Trak data, the peak excursion guidance criteria value will need to be at least 20% higher than the LBPC so as to account for potential instrument inaccuracy.

Another factor the excursion guidance criteria must account for is the difference in response of instruments where the properties of the aerosol being studied differ significantly to that of the calibration particle. The response of the instrument will vary where the properties of the aerosol being studied differ significantly to that of the calibration particle. Real-time particle instruments are calibrated using specific aerosolised substances, for example NaCl, or Arizona road dust. These particles have specific shape, solubility and hygroscopicity [26], and refractive indices [24].

One option is to adopt universal excursion guidance criteria based upon the guidance principles on excursions of atmospheric contaminants within the occupational environment as outlined by both *Safe Work Australia* [1] and the *American Conference of Governmental Industrial Hygienists* [2]. Therefore, a nanotechnology process could be considered to require further assessment if:

- I. Short term exposures/emissions exceed three times the LBPC for more than a total of 30 minutes during a work day; and/or
- II. If a single short term value exceeds five times the LBPC.

A second option is to utilise local excursion guidance criteria. For example, if examination of the real-time particle concentrations for the period before process operation revealed peaks in particle concentration to be typically no greater than twice that of the

LBPC, peak excursion guidance criteria of any single value greater than two times the local particle reference value could be used. A clean-room environment where the air is subjected to high performance filtration would be an example of where local excursion criteria could be utilised.

In cases with low background (e.g., clean-room like air), the critical ratio can be much lower than the ratios recommended above because of the greater control of extraneous particles. In the case where background concentrations are relatively high, the ratio of even three or five may be unacceptable. One approach is to adopt a benchmark particle concentration level for contaminated areas such as that of the BSI [19] and IFA [27] – in this case, if the background concentration is  $> 20000$  particles  $\text{cm}^3$  as measured by CPC, then apply excursion criteria based on a background concentration of  $20000$  particles  $\text{cm}^3$  as measured by a CPC.

In the case of very toxic material the excursion guidance criteria may need to be much lower than permitted for less toxic materials. When regulatory authorities propose exposure standards for nanomaterials, a Peak Limitation value should be assigned and/or specific excursion guidance criteria assigned relative to the 8-hour TWA exposure standard.

Regardless of whether universal or local excursion guidance criteria are chosen, they 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.

To aid discussion on the use of relative difference in LBPC to peak particle concentrations associated with the process of interest, the data in Table II has been arranged as follows. First, the LBPC has been used to assign *local particle reference values* into the following three bands: (a)  $\text{PNC}_{20-1000\text{nm}}$  (b)  $\text{PNC}_{300-3000\text{nm}}$  (c)  $\text{PM}_{2.5}$ . The upper range of  $3000$  nm has been used for the PNC because all aerosol  $\text{PNC} > 3000$  nm were  $1$  particle  $\text{cm}^{-3}$  and therefore negligible in absolute terms. However, in the event that background

PNC and/or nanomaterial aerosol are dominated by particles >3000 nm then a relevant particle reference band could be assigned. Also in such circumstances, a PM<sub>10</sub> rather than, or in addition to the PM<sub>2.5</sub> particle size impactor should be used on the photometer.

Secondly, excursion guidance criteria of “where short term emissions or exposures exceed three times the LBPC for more than a total of 30 minutes per eight-hour working day” and “where a single short term value for emission or exposure exceeds five times the LBPC” have been assigned. These are the triggers for implementing/reviewing control of particle emission.

Thirdly, where particle concentration values exceeded the local particle reference value in accordance with the excursion guidance criteria, the relevant cell within Table II has been shaded. 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.

It can be seen from Table II 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 at the source of emission.

Processes 6A and 6B were also 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<sub>300-3000nm</sub> and PM<sub>2.5</sub> at the emission point for Process 6A was three times the background particle reference value for more than 30 minutes. For Process 6B the PM<sub>2.5</sub> at the emission point was elevated for more than 30 minutes.

It can also be seen from Table II, particle emissions from processes 1A, 1B, 2, and 3 were not strong enough to elevate the particle concentration to greater than three times the local particle reference value for any 30-minute period. However, peak PNC and PM<sub>2.5</sub> concentrations of greater than five times the local particle reference value were 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 in the work area.

In contrast, emissions from processes 4, 6A, and 6B were of sufficient concentration to cause elevation of the particle concentration to greater than three times the local particle reference value for a 30-minute period.

For one data set, peak and mean  $PNC_{20-1000nm}$  emitted from an incidental background source was an order of magnitude greater than that associated with the nanotechnology process. Therefore, universal excursion guidance criteria are limited in their application where sources of background particles are stronger than those from the process of interest. In such circumstances the process of interest can only be assessed and conclusions made regarding the significance of particle emission if these background sources of particles are minimised or isolated. The excursion guidance criteria are not used where a short-term exposure limit has been assigned based upon toxicological or epidemiological data.

The use of a statistical method that would test for the typical variation in measurement values, obtained before and during measurement of the process of interest, could also be utilised in determining the short-term (30 minute) excursion guidance criterion. The statistical method should be valid for time-series data. Klein Entink et al. [28] argue autocorrelation in time-series measurements leads to underestimation of the variance in the data, resulting in a biased test statistic of the t-test, and conclude Autoregressive Integrated Moving Average (ARIMA) models be utilised instead.

A summary of the sampling method to be used in conjunction with the excursion guidance criteria is included in the SII.

## **CONCLUSIONS**

The utility of our study is it evaluated the use excursion guidance criteria as replicable decision criteria in assessing when particle emission was likely to be greater than

background fluctuations in particle concentration and potential error of the instruments. This is critical to exposure control in that it ensures consistent and measurable decisions are made regarding control of particle emission and/or further assessment of particle emission.

Uncertainty exists as to what particle metrics should be used as indicators of potential exposure related health effects and very few health based exposure standards for airborne nanomaterials have been established to date. Although this is a barrier to measurement of particle *exposure*, particle *emission* in terms of number and mass concentration can be characterised with relative ease and certainty at workplaces.

## ACKNOWLEDGEMENTS

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# FIGURES

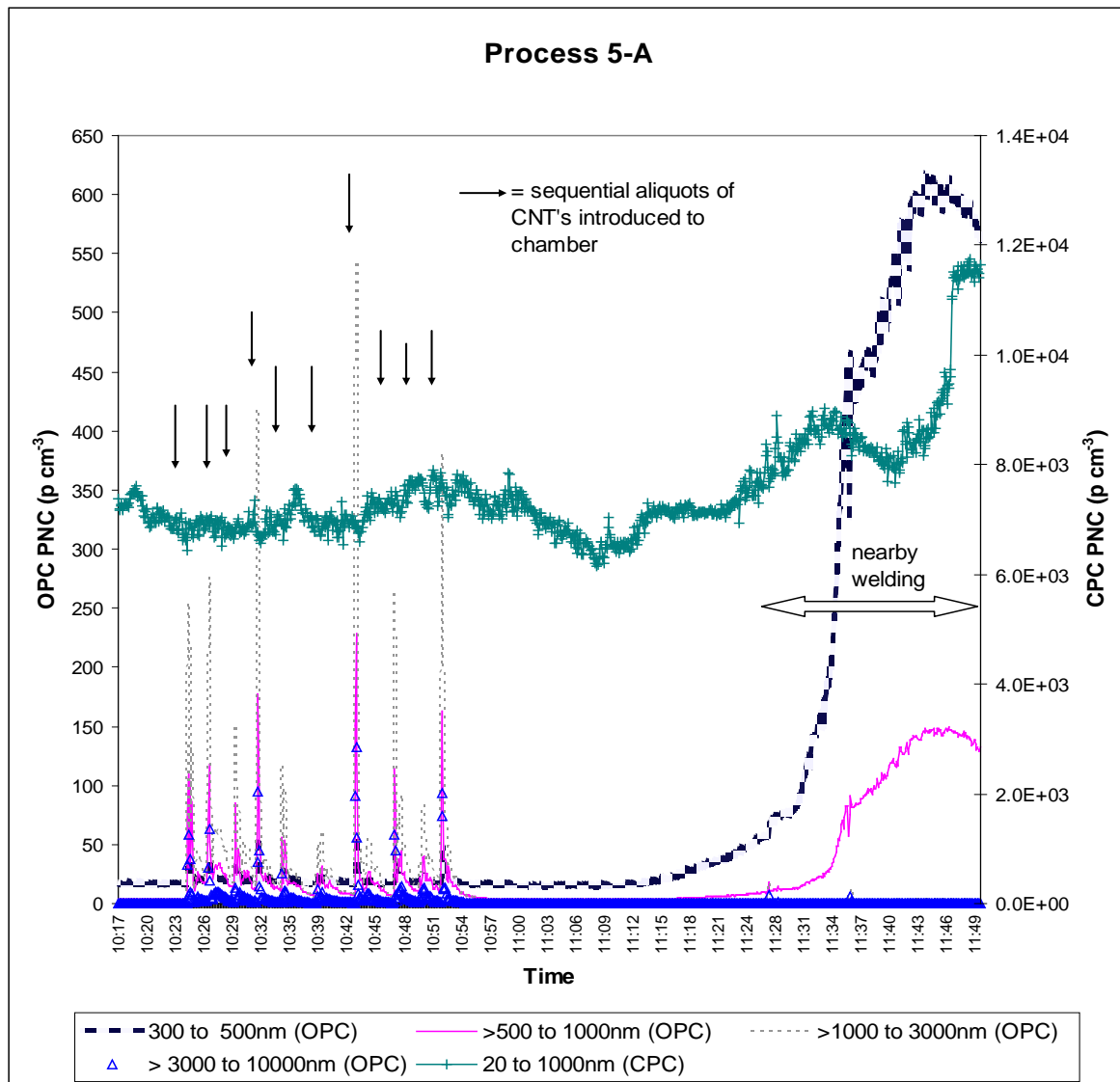


Figure 1(a)

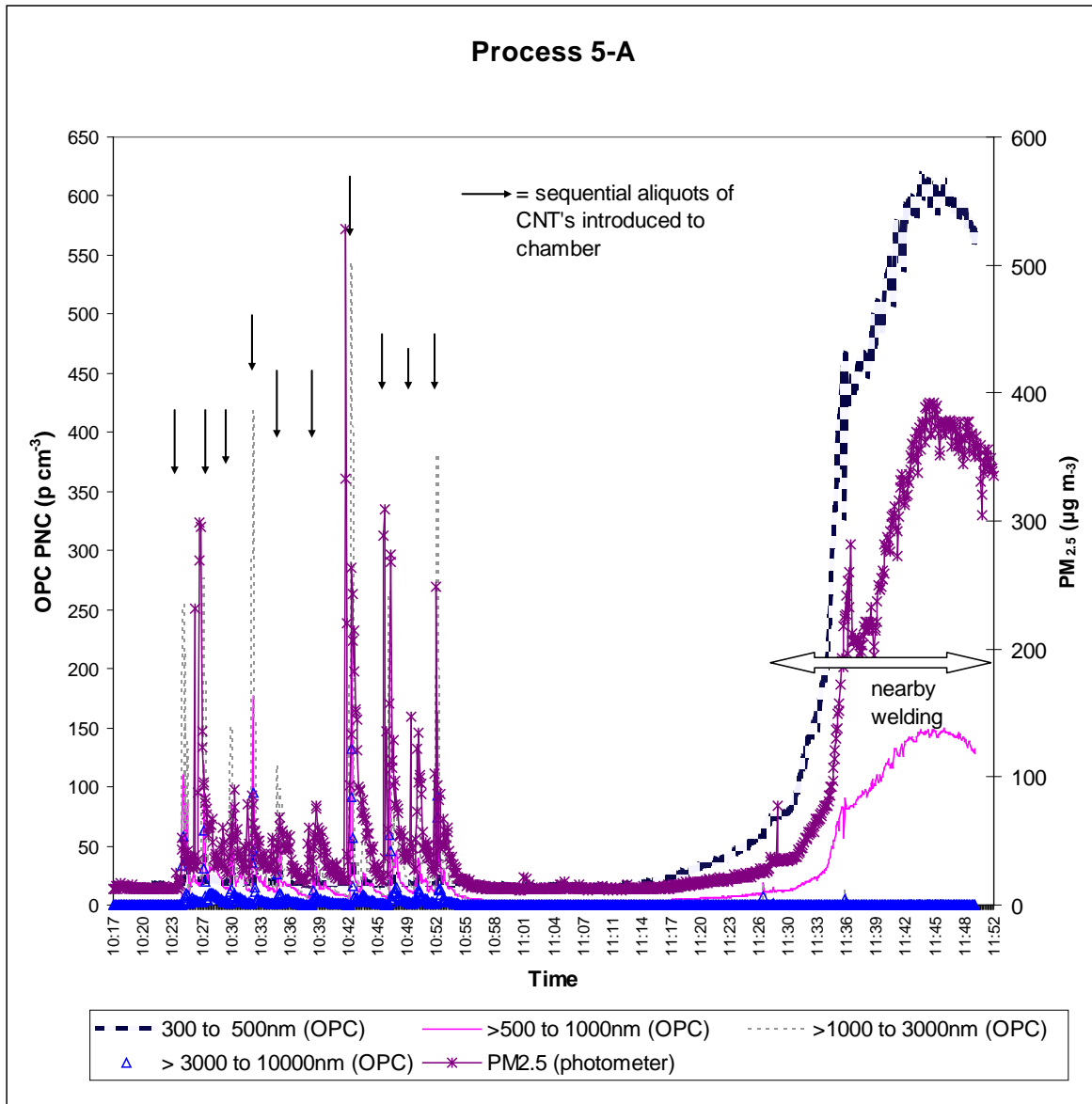


Figure 1(b)

Figure 1 (a) (b): Particle number concentration (PNC) in particle size distribution 300 to 10000nm, with PNC 20 to 1000nm [Figure 1(a)] and  $PM_{2.5}$  concentration [Figure 1(b)] as recorded by co-located optical particle counter (OPC), CPC - P-Trak, and photometer (DustTrak) during and after introduction of solid carbon nanotubes (CNT's) to a chamber.

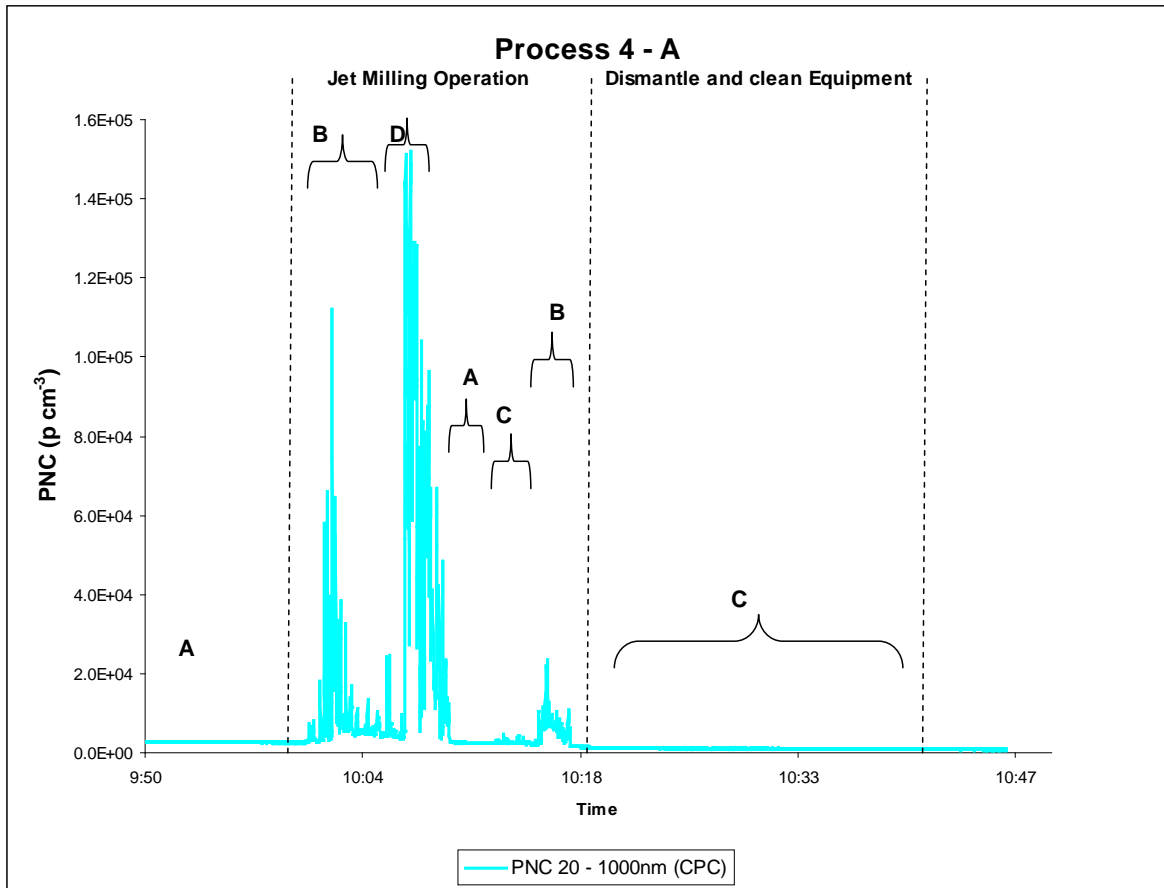


Figure 2(a)

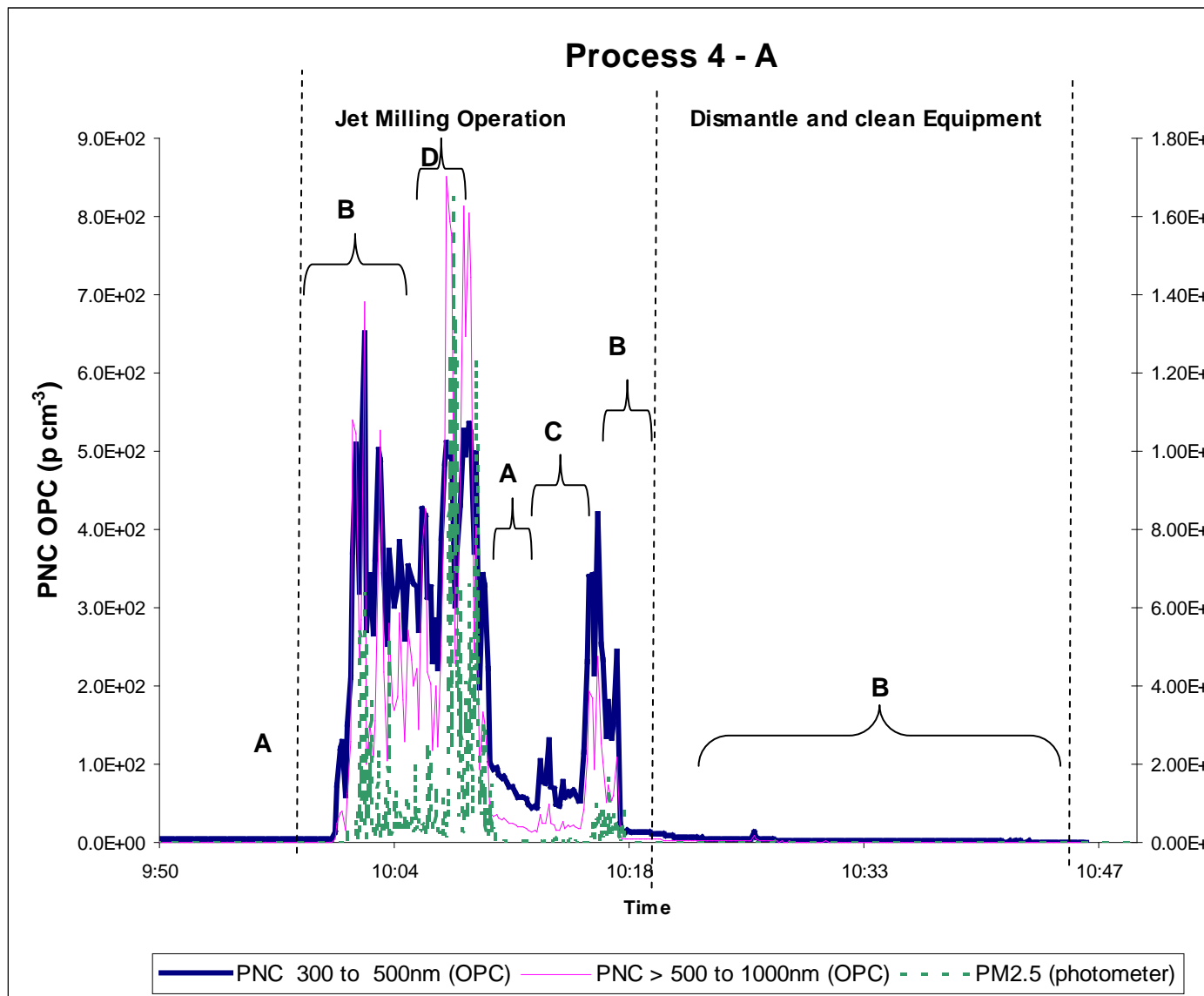


Figure 2(b)

Figure 2 (a) and (b): Particle number concentration (PNC) in particle size distribution 20 nm to 1000nm [Figure 2(a)], plus PNC 300nm to 10000, and PM<sub>2.5</sub> concentration [Figure 2(b)] as recorded by co-located CPC - P-Trak, optical particle counter (OPC), and photometer (DustTrak) during the jet milling of a modified clay product during the first jet milling event. A = background concentration at 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° 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 one p cm<sup>-3</sup>.

## TABLES

**Table I: Summary of peak and mean particle measurement values during operation of the nanotechnology processes relative to the local background particle concentration (LBPC)**

P R O C E S S	PNC <sub>20-1000nm</sub> [particles cm <sup>-3</sup> ]				PNC <sub>300-3000nm</sub> [particles cm <sup>-3</sup> ]				PNC <sub>3000-10000nm</sub> [particles cm <sup>-3</sup> ]				PM <sub>2.5</sub> [μg m <sup>-3</sup> ]			
	CPC P-Trak				OPC				OPC				PHOTOMETER DUSTTRAK			
	During process		Before process		During process		Before process		During process		Before process		During process		Before process	
	M	P	L	P	M	P	L	P	M	P	L	P	M	P	L	P
E	E	B	E	E	E	B	E	E	E	B	E	E	E	B	E	
A	A	P	A	A	A	P	A	A	A	P	A	A	A	P	A	
N	K	C	K	N	K	C	K	N	K	C	K	N	K	C	K	
<b>1A</b>	5.3 x 10 <sup>3</sup>	7.0 x 10 <sup>3</sup>	5.2 x 10 <sup>3</sup>	5.7 x 10 <sup>3</sup>	#	#	#	#	#	#	#	#	9.0	5.0 x 10 <sup>1</sup>	7.0	9.0
<b>1B</b>	3.5 x 10 <sup>4</sup>	1.6 x 10 <sup>5</sup>	1.2 x 10 <sup>4</sup>	1.3 x 10 <sup>4</sup>	#	#	#	#	#	#	#	#	9.0	1.4 x 10 <sup>1</sup>	7.0	1.0 x 10 <sup>1</sup>
<b>2</b>	4.8 x 10 <sup>3</sup>	6.0 x 10 <sup>4</sup>	6.6 x 10 <sup>3</sup>	1.7 x 10 <sup>4</sup>	#	#	#	#	#	#	#	#	8.0	4.0 x 10 <sup>2</sup>	5.0	1.0 x 10 <sup>1</sup>
<b>3</b>	4.0 x 10 <sup>3</sup>	1.1 x 10 <sup>4</sup>	2.7 x 10 <sup>3</sup>	3.2 x 10 <sup>3</sup>	#	#	#	#	#	#	#	#	1.2 x 10 <sup>1</sup>	7.0 x 10 <sup>1</sup>	1.0 x 10 <sup>1</sup>	1.0 x 10 <sup>1</sup>
<b>4<sup>A</sup></b>	1.2 x 10 <sup>4</sup>	1.5 x 10 <sup>5</sup>	5.5 x 10 <sup>2</sup>	5.5 x 10 <sup>2</sup>	4.0 x 10 <sup>2</sup>	8.0 x 10 <sup>2</sup>	1.0	1.0	1.0	2.0	1.0	1.0	4.5 x 10 <sup>2</sup>	1.6 x 10 <sup>4</sup>	1.0	1.0
<b>5A</b>	7.1 x 10 <sup>3</sup>	7.5 x 10 <sup>3</sup>	7.0 x 10 <sup>3</sup>	7.0 x 10 <sup>3</sup>	2.6 x 10 <sup>1</sup>	5.5 x 10 <sup>2</sup>	1.6 x 10 <sup>1</sup>	2.0 x 10 <sup>1</sup>	1.0	1.3 x 10 <sup>2</sup>	1.0	1.0	5.6 x 10 <sup>1</sup>	3.0 x 10 <sup>2</sup>	1.4 x 10 <sup>1</sup>	1.4 x 10 <sup>1</sup>
<b>5B</b>	4.3 x 10 <sup>3</sup>	4.3 x 10 <sup>3</sup>	3.9 x 10 <sup>3</sup>	4.4 x 10 <sup>3</sup>	3.4 x 10 <sup>1</sup>	1.1 x 10 <sup>2</sup>	3.7 x 10 <sup>1</sup>	8.0 x 10 <sup>1</sup>	1.0	4.0	1.0	1.0	3.5 x 10 <sup>1</sup>	1.3 x 10 <sup>2</sup>	2.5 x 10 <sup>1</sup>	3.8 x 10 <sup>1</sup>
<b>6A</b>	8.2 x 10 <sup>3</sup>	5.7 x 10 <sup>4</sup>	7.0 x 10 <sup>3</sup>	1.1 x 10 <sup>4</sup>	8.6 x 10 <sup>1</sup>	5.5 x 10 <sup>2</sup>	3.0	8.0	1.0	1.0	1.0	1.0	4.2 x 10 <sup>2</sup>	1.8 x 10 <sup>4</sup>	7.0	8.0
<b>6B</b>	3.4 x 10 <sup>4</sup>	2.1 x 10 <sup>5</sup>	2.9 x 10 <sup>3</sup>	3.1 x 10 <sup>3</sup>	3.0	4.0	3.0	4.0	1.0	1.0	1.0	1.0	1.9 x 10 <sup>1</sup>	5.5 x 10 <sup>2</sup>	3.0	8.0

Notes: Values for Processes 1A, 1B, 2, 3, and 4 are from grouped data obtained from repeated sampling. # not measured as equipment not available. Δ values reflect jet milling phase only, and do not include cleaning phase. **MEAN** = arithmetic average during process; **PEAK** = highest value measured, **LBPC** = Local Background Particle Concentration (i.e., arithmetic average of background when process not in operation); **PNC** = particle number concentration; **PM** = particle mass; **CPC** = condensation particle counter; **OPC** – optical particle counter

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

	Local particle reference values	Application of excursion criteria using measured particle concentrations relative to local particle reference values		
		Is <i>source emission</i> > 3 times the local particle reference value for more than 30 minutes in 8 hour day?	Is any single <i>source emission</i> peak value > 5 times the local particle reference value?	Is any <i>breathing zone</i> * peak value > 5 times the local particle reference value?
P	a) PNC <sub>20-1000nm</sub> [p cm <sup>-3</sup> ]			
R	b) PNC <sub>300-3000nm</sub> [p cm <sup>-3</sup> ]			
O	c) PM <sub>2.5</sub> [µg m <sup>-3</sup> ]			
C				
E				
S				
S				
1A	a) 5.2 x 10 <sup>3</sup>	no	no	no
	b) #	n/a	n/a	n/a
	c) 6	no	yes = 5.0 x 10 <sup>1</sup> µg m <sup>-3</sup>	no
1B	a) 1.2 x 10 <sup>4</sup>	no	yes = 1.6 x 10 <sup>5</sup> p cm <sup>-3</sup>	no
	b) #	n/a	n/a	n/a
	c) 7	no	no	no
2	a) 6.6 x 10 <sup>3</sup>	no	yes = 6.0 x 10 <sup>4</sup> p cm <sup>-3</sup>	#
	b) #	n/a	n/a	n/a
	c) 4	no	yes = 4.0 x 10 <sup>2</sup> µg m <sup>-3</sup>	no
3	a) 2.7 x 10 <sup>3</sup>	no	yes = 1.1 x 10 <sup>4</sup> p cm <sup>-3</sup>	no
	b) #	n/a	n/a	n/a
	c) 10	no	yes = 7.0 x 10 <sup>1</sup> µg m <sup>-3</sup>	no
4 <sup>Δ</sup>	a) 5.5 x 10 <sup>2</sup>	yes = 1.2 x 10 <sup>4</sup> p cm <sup>-3</sup>	yes = 1.5 x 10 <sup>5</sup> p cm <sup>-3</sup>	no
	b) 1	yes = 4.0 x 10 <sup>2</sup> p cm <sup>-3</sup>	yes = 8.0 x 10 <sup>2</sup> p cm <sup>-3</sup>	yes = 1.0 x 10 <sup>2</sup> p cm <sup>-3</sup>
	c) 1	yes = 4.5 x 10 <sup>2</sup> µg m <sup>-3</sup>	yes = 1.6 x 10 <sup>4</sup> µg m <sup>-3</sup>	yes = 1.7 x 10 <sup>2</sup> µg m <sup>-3</sup>
6A	a) 4.0 x 10 <sup>3</sup>	no	yes = 5.7 x 10 <sup>4</sup>	no
	b) 3	yes = 8.6 x 10 <sup>1</sup> p cm <sup>-3</sup>	yes = 5.5 x 10 <sup>2</sup> p cm <sup>-3</sup>	no
	c) 7	yes = 4.2 x 10 <sup>2</sup> µg m <sup>-3</sup>	yes = 1.8 x 10 <sup>4</sup> µg m <sup>-3</sup>	no
6B	a) 3.1 x 10 <sup>3</sup>	no	yes = 2.1 x 10 <sup>5</sup> p cm <sup>-3</sup>	no
	b) 3	no	no	no
	c) 3	yes = 1.9 x 10 <sup>1</sup> µg m <sup>-3</sup>	yes = 5.5 x 10 <sup>2</sup> µg m <sup>-3</sup>	no

\* - breathing zone measurements are estimates only and were obtained by positioning the instrument aerosol inlet at the breathing zone, and therefore not be regarded as indicative of actual worker exposure

# - no values are able to be calculated because PNC measurements in this particle size range were not conducted

n/a - not applicable because local particle reference values were not calculated as particle measurements were not conducted

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



**TITLE PAGE - SUPPLEMENTAL INFORMATION FILE FOR ONLINE  
ONLY PUBLICATION**

**Title:** Excursion guidance criteria to guide control of peak emission and exposure to airborne engineered particles

**Authorship**

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**Supplemental Information - Table SI: Results of review of selected literature on aerosol measurement methodology**

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<b>Particle metric</b>	<b>Method/instrument</b>	<b>Reference</b>
Particle metric concentration in real-time (approximately 10 nm to several $\mu\text{m}$ )	Condensation particle counter	[1-4]
Particle number Concentration in real-time (approximately 300nm to 20 $\mu\text{m}$ )	Optical particle counter	[3-6]
Particle mass in real-time	Photometer or taper Element Oscillating Microbalance (TEOM)	[7-11]
Particle size distribution in real-time	Scanning Mobility Particle Sizer (SMPS) or Fast Mobility Particle Sizers (FMPS)	[2, 7-9, 11-16]
Off-line chemical, morphological, mass analysis	Electrostatic precipitator or filter membranes for analysis using either electron microscope, phase contrast microscope, elemental and gravimetric techniques	[2, 4-7, 9-11, 13, 17-22]
Surface area in real-time	Diffusion charging using Nanoparticle Surface Area Monitor	[1, 23, 24]
Off-line particle size and morphology	Electron microscope	[2-7, 9, 13, 22, 25]

---

**Supplemental Information - Table SII: Summary of mean particle metrics reflecting the nanotechnology process in operation and the local background particle concentration (LBPC), measured simultaneously at the nanomaterial emission source and 7 m from source for aerosols from 6 nanotechnology processes**

Process	At nanomaterial emission source														Spatial data at 7 m from emission source	
	Mean PNC [particles cm <sup>-3</sup> ] <b>CPC (3781)</b>		Mean PNC [particles cm <sup>-3</sup> ] <b>CPC (P-Trak)</b>		Mean PNC 300 to 3000nm [particles cm <sup>-3</sup> ] <b>OPC</b>		Mean PNC 3000 to 10000nm [particles cm <sup>-3</sup> ] <b>OPC</b>		Mean PM <sub>2.5</sub> [μg m <sup>-3</sup> ] <b>DustTrak</b>		Mean CMD [nm] <b>SMPS</b>		Mean alveolar surface area [μm <sup>2</sup> cm <sup>-3</sup> ] <b>NSAM</b>		Mean PNC [particles cm <sup>-3</sup> ] <b>CPC 3781</b>	
	During	LBPC	During	LBPC	During	LBPC	During	LBPC	During	LBPC	During	LBPC	During	LBPC	During	LBPC
1A	6.4 x 10 <sup>3</sup>	6.3 x 10 <sup>3</sup>	5.3 x 10 <sup>3</sup>	5.2 x 10 <sup>3</sup>	#	#	#	#	9	7	55	54	18	18	7.8 x 10 <sup>3</sup>	7.9 x 10 <sup>3</sup>
1B	2.3 x 10 <sup>4</sup>	1.5 x 10 <sup>4</sup>	#	1.1 x 10 <sup>4</sup>	#	#	#	#	9	7	54	37	1.0 x 10 <sup>2</sup>	31	1.9 x 10 <sup>4</sup>	1.8 x 10 <sup>4</sup>
2	8.5 x 10 <sup>3</sup>	1.0 x 10 <sup>4</sup>	4.8 x 10 <sup>3</sup>	6.6 x 10 <sup>3</sup>	#	#	#	#	8	5	35	31	15	20	1.0 x 10 <sup>4</sup>	1.1 x 10 <sup>4</sup>
3	6.8 x 10 <sup>3</sup>	5.9 x 10 <sup>3</sup>	4.0 x 10 <sup>3</sup>	2.7 x 10 <sup>3</sup>	#	#	#	#	12	10	37	37	18	15	#	#
4 <sup>A</sup>	#	#	1.2 x 10 <sup>4</sup>	5.5 x 10 <sup>2</sup>	4.0 x 10 <sup>2</sup>	< 1	< 1	< 1	4.5 x 10 <sup>2</sup>	1	#	#	#	#	#	#
5A	#	#	7.1 x 10 <sup>3</sup>	7.0 x 10 <sup>3</sup>	26	15	< 1	< 1	56	14	64	60	56	50	9.1 x 10 <sup>3</sup>	8.9 x 10 <sup>3</sup>
5B	#	#	4.3 x 10 <sup>3</sup>	3.9 x 10 <sup>3</sup>	34	37	< 1	< 1	35	25	82	80	32	30	5.4 x 10 <sup>3</sup>	4.3 x 10 <sup>3</sup>
6A	#	#	8.2 x 10 <sup>3</sup>	7.0 x 10 <sup>3</sup>	86	3	< 1	< 1	4.2 x 10 <sup>2</sup>	7	#	#	#	#	#	#
6B	#	#	3.4 x 10 <sup>4</sup>	3.1 x 10 <sup>3</sup>	3	3	< 1	< 1	19	3	#	#	#	#	#	#

Notes: All values are from grouped data obtained from repeated sampling

Instruments/analysis used:

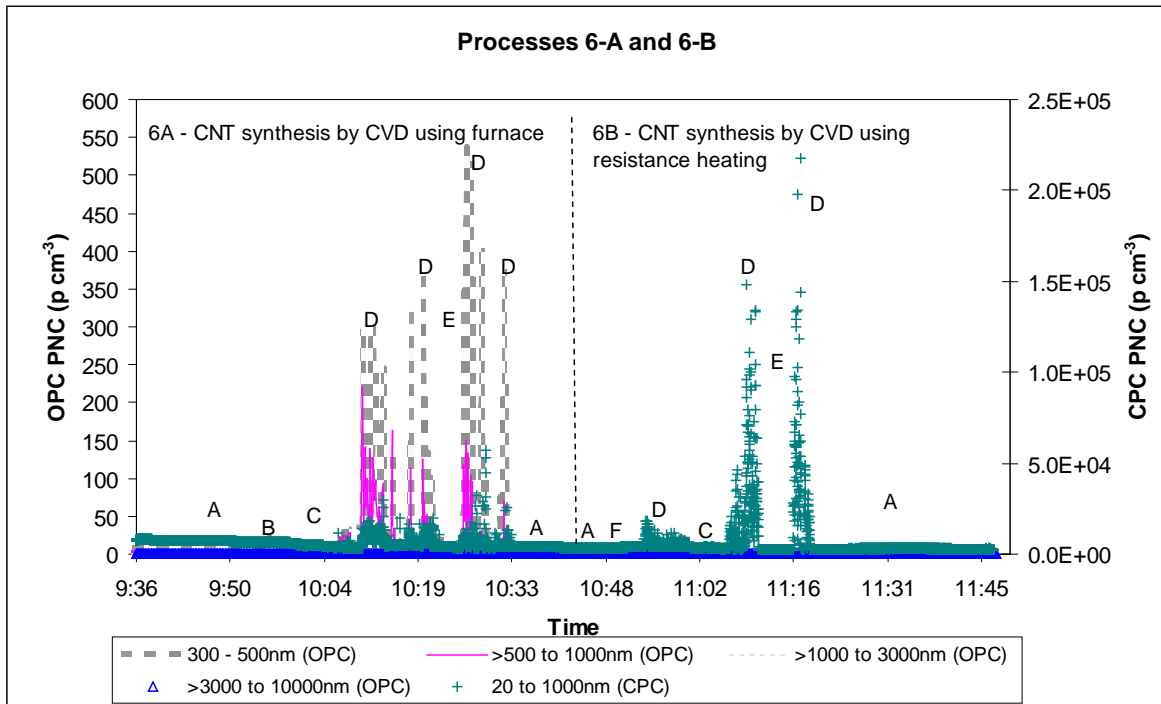
- Process 1A – CPC 3781; CPC P-Trak, DustTrak, scanning mobility particle sizer (SMPS), nanoparticle surface area monitor (NSAM), scanning electron microscope (SEM)
- Process 1B - CPC 3781; DustTrak, SMPS, NSAM
- Process 2 - CPC 3781; P-Trak, CPC 3022, DustTrak, SMPS, NSAM, SEM, TEM. Local extraction ventilation operating during operation of the process
- 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, transmission electron microscope (TEM), Elemental Carbon
- Process 6 - CPC P-Trak; DustTrak, OPC

# not measured as instruments were not available

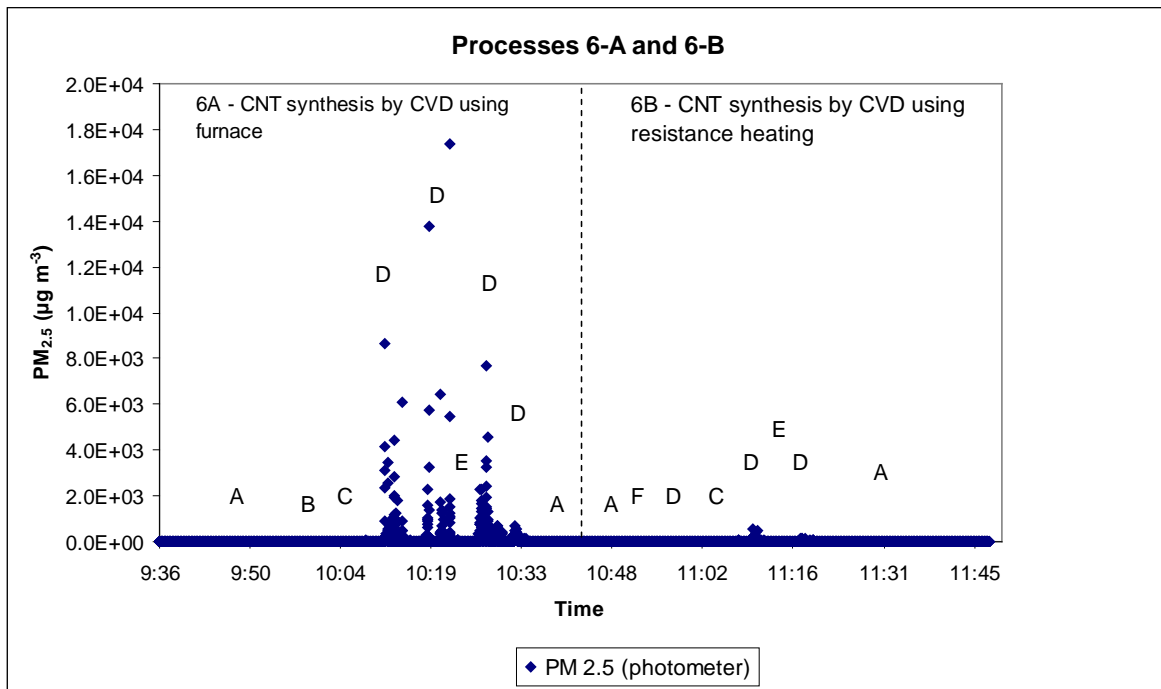
Result is qualitative only because it was noted the filter was overloaded and uneven particulate distribution was observed

$\Delta$  values reflect jet milling phase only, and do not include cleaning phase

The differences in both spatial and temporal absolute PNC recorded by the different CPC's operating simultaneously can be partly explained the differing particle measurement ranges and operating fluids.



Supplemental Information - Figure S1(a)



Supplemental Information - Figure S1(b)

Figure S1 (a) and (b): Particle number concentration in particle size distribution 20 nm to 10000 [Figure S1(a)] and PM<sub>2.5</sub> concentration [Figure S1(b)] as recorded by co-located optical particle counter (OPC), CPC - P-Trak, and photometer (DustTrak) during carbon nanotube synthesis. 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

**Supplemental Information - Table SIII: Manufacturer specified instrument particle concentration accuracy data**

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<b>Instrument</b>	<b>Particle concentration accuracy</b>
TSI Model 8525 P-Trak	$\pm 20\%$ of the reading*
TSI Model 8520 DustTrak	$\pm 0.1\%$ of reading or $\pm 0.001 \text{ mg m}^{-3}$ , whichever is greater
TSI Model 9306 AeroTrak OPC	$\pm 5\%$ <sup>#</sup>

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**Notes:** \* although concentration accuracy is not specified by the manufacturer, a study by Matson et al., [26] 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  $\pm 5\%$  and is a key determinant of accuracy

## Supplemental Information – SI1

In summary, we suggest the use of excursion guidance criteria in accordance with the following method:

- a) 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, and at background points distal to the process, both before and during operation of the process.
  - I. Plot the time-series data.
  - II. Calculate the average of the real-time particle number and mass concentration from grouped data arising from repeated sampling, for the periods before and during operation of the process. Use the average LBPC as the *local particle reference value*.
  - III. Identify the presence of peak particle concentration values for both periods.  
Exclude particle values that are within  $\pm$  of the manufacturer stated accuracy of the instrument, i.e. peak values that are within  $\pm$  of the average of the real-time particle number and mass concentration.
- b) Calculate the ratio of the peak and 30-minute average particle number and mass concentration values for the process operation to that of the *local particle reference value*.
- c) Compare this ratio to either the universal or local *excursion guidance criteria* as a trigger for review of particle controls and/or to conduct further particle emission assessment.

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