

Worker and Environmental Assessment of Potential Unbound Engineered Nanoparticle Releases

Phase III Final Report: Validation of Preliminary Control Band Assignments

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Executive Summary

At the Lawrence Berkeley National Laboratory (LBNL) Environmental Energy Technologies Division (EETD), a multiphase pilot study is being conducted to evaluate the potential for worker exposure and emissions to the outdoor environment of unbound engineered nanoparticles (UNP) and to assess whether there is a need for high-efficiency particulate air (HEPA) exhaust filtration to control emissions to the outdoor environment. The Phase I, II, and III components of the study have been completed on a subset of LBNL laboratories where UNP are used. Phase I study activities involved discussions with researchers and observation of processes involving fumehoods, gloveboxes, countertops, and ablation systems. Phase II study activities involved development of preliminary control bands based on information obtained in Phase I. The Phase III component of this pilot project focused on sampling of research processes to validate, or modify as appropriate, the preliminary control bands assigned in Phase II.

Data collected in Phase III indicate that for some processes, the validated control bands were less stringent than the preliminary control bands; for others, they were unchanged. In all cases, the actual controls used by researchers, during work with UNP, met or exceeded the validated control band. Based on the observations and sampling, research process activities with UNP at LBNL EETD appear to be well planned, reviewed, and controlled. Analytical results indicate low or unmeasurable levels of worker exposure; therefore, the observed work practices and associated controls are deemed effective. Provided that similar approaches applying integrated safety management (ISM) principles are used in other UNP process activities, it can be anticipated that employee exposures to UNP would be similarly controlled. For the nanoscale research tasks evaluated in this project, air sampling indicated negligible emissions of UNP to the outdoor environment, and no regulations or standards require the use of HEPA filtration for the exhaust systems to control emissions to the outdoor environment.

Phase IV of this pilot study will recommend a program of periodic monitoring and assessment for emissions of UNP to the outdoor environment.

1.0

Introduction

At the Lawrence Berkeley National Laboratory (LBNL), there are approximately sixty laboratories where unbound engineered nanoparticles (UNP) are used as part of nanoscale related research activities.¹ To comply with Department of Energy (DOE) Notice N456.1, *The Safe Handling of Unbound Engineered Nanoparticles*, Contractor Requirements Document, Functional Area Requirements for DOE Elements, Section 4, “Exposure Assessment” (DOE 2009), each of these laboratories will need to be evaluated for worker exposures and emissions of UNP to the outdoor environment. To this end, LBNL has retained RJ Lee Group, Inc. (RJLG), to conduct a multiphase pilot study on a subset of LBNL laboratories where UNP are used to evaluate the potential for worker exposure. The study is also intended to evaluate the potential for emissions of UNP to the outdoor environment and assess whether there is a need for additional controls including high-efficiency particulate air (HEPA) exhaust filtration.

The goals of the pilot project are as follows:

- Conduct a worker and environmental exposure assessment for the potential release of UNP.
- Assess the need for additional controls for worker and environmental protection (including the use of HEPA exhaust filtration to protect the environment).
- Establish a periodic worker and environmental monitoring program (air and water) for UNP based on information obtained in the pilot exposure assessment study and guidance provided in the DOE Nanoscale Science Research Centers *Approach to Nanoscale ES&H* document (DOE 2008).

In addition, the pilot project is designed to meet the recommendations of the *Approach to Nanoscale ES&H*, including Attachment 1, Example Industrial Hygiene Sampling Protocol (DOE 2008), and supports LBNL’s commitment to integrated safety management (ISM) by addressing several of the core functions of ISM, including hazard and risk analysis, establishment of controls, and providing analysis and feedback for continuous improvement.

The pilot project is being performed in four phases to review and assess the potential environment, safety and health (ESH) related hazards and existing controls associated with UNP research activities conducted by LBNL’s Environmental Energy Technologies Division (EETD).

Phase I:	Review research process activities and gather data
Phase II:	Develop preliminary control bands
Phase III:	Validate preliminary control bands
Phase IV:	Establish a periodic environmental monitoring and assessment program

¹ As of January 2009. The number of laboratories where UNP is used is not static and has probably increased since January 2009.

The Phase I, II and III components of the study have been completed. Phase I study activities involved discussions with EETD researchers and observation of processes involving fumehoods, gloveboxes, countertops, and ablation systems. Samples of UNP materials used in process activities were obtained from the researchers, and these samples were analyzed using inductively coupled plasma-optical emission spectroscopy (ICP-OES) and/or electron microscopy (EM) to establish morphological and elemental signatures of the various starting UNP materials.

The Phase II study activities involved development of preliminary control bands based on information obtained in Phase I through observation of the research processes, review of existing process controls, characteristics of the starting UNP materials, and review of information related to the UNP materials (e.g., materials safety data sheets). Reports summarizing Phases I and II of the study are available on the LBNL web site (Casuccio et al. 2009a and 2009b).²

The Phase III component of this pilot project was focused on evaluation of worker exposure and emissions to the outdoor environment through sampling of research processes. Data obtained in the Phase III sampling component was used to validate, or modify as appropriate, the preliminary control bands assigned in Phase II.

The following sections of this report summarize the Phase I and II components of the pilot study and provide the results of Phase III activities.

² <http://www.lbl.gov/ehs/> : Worker and Environmental Assessment of Potential Unbound Engineered Nanoparticle Releases, Phase I and II reports.

2.0

Background

Engineered nanoparticles are defined by DOE as “intentionally created . . . particle[s] with one or more dimensions greater than 1 nm and less than 100 nm.” The DOE defines UNP as “engineered nanoparticles that . . . are not contained within a matrix that would be expected to prevent the nanoparticles from being separately mobile and a potential source of exposure.” Additional detail is provided in DOE Notice N456.1 (DOE 2009).

Nanotechnology and the use of UNP is a rapidly developing field. At this time there are no regulatory environmental release limits or worker exposure limits for nanomaterials. Some consensus standards have been issued, but they are still under development by committees such as ASTM Committee E56 on Nanotechnology³ and the ANSI-accredited U.S. Technical Advisory Group to ISO/TC 229.⁴

The DOE Office of Science, in support of ISM, has provided some guidance (DOE 2008) and a policy statement (DOE 2009). The policy specifically states the following:

DOE and its contractors will identify and manage potential health and safety hazards and potential environmental impacts at sites through the use of existing Integrated Safety Management Systems, including Environmental Management Systems. DOE organizations working with nanomaterials will stay abreast of current research and guidance relating to the potential hazards and impacts of nanomaterials, and will ensure that this best current knowledge is reflected in the identification and control of these potential hazards and impacts at their facilities.

This pilot study is an effort to satisfy the DOE policy and to address the uncertainties inherent in a rapidly developing technology field. It is also designed to support the LBNL research organizations by addressing the five ISM core functions. A control banding approach is being used to provide guidance on risk management of UNP (Maynard 2007, Money 2003, NIOSH/CDC 2009, Paik et al. 2009, Schulte et al. 2008, Zalk and Nelson 2008).

In Phase I of the pilot study, work with nanomaterials conducted by the following nine principal investigators in EETD using fumehoods, gloveboxes and countertops was reviewed.

1. John Kerr
2. Thomas Richardson
3. Vincent Battaglia
4. Gao Liu

³ <http://www.astm.org/COMMIT/COMMITTEE/E56.htm>

⁴ http://www.ansi.org/standards_activities/standards_boards_panels/tc229.aspx?menuid=3

5. Robert Kostecki
6. Samuel Mao
7. Rick Russo
8. Don Lucas
9. Andre Anders

After interviews with the principal investigators and research staff, and demonstrations of the research processes, it was determined that research performed in two laboratories under two principal investigators, Gao Liu and Andre Anders, were unlikely sources of occupational exposure or emissions of UNP to the outdoor environment by any release route, and were not considered in subsequent phases of the pilot study.

For research processes selected for further evaluation, samples of the researchers' starting UNP materials were obtained and analyzed to document key particle characteristics such as size, morphology, and chemistry. Information of this nature, noted below in addition to other attributes, was used to estimate potential health/environmental hazards and exposure/release, which were then used to develop the preliminary control bands. The following attributes were used in the development of the preliminary control bands for LBNL processes:

- particle size
- particle morphology
- elemental chemistry
- solubility
- assumed toxicities of starting UNP materials
- amount of material used
- dustiness (or potential for the material to become airborne based on the task/process)
- number of people doing the work
- duration of the operation
- frequency of the operation

A control band matrix was developed in Phase II from information gathered on EETD research activities involving UNP in Phase I and is reproduced below.

		Release/Exposure Probability			
		Unlikely (1)	Low (2)	Likely(3)	Probable (4)
Worker/Environmental Hazard	Very High or Unknown (D)	Control Level III	Control Level III	Control Level IV	Control Level IV
	High (C)	Control Level II	Control Level II	Control Level III	Control Level IV
	Medium (B)	Control Level I	Control Level I	Control Level II	Control Level III
	Low (A)	Control Level I	Control Level I	Control Level I	Control Level II

Figure 2-1 Control Banding Matrix Developed for LBNL UNP Pilot Study

The LBNL preliminary control bands for processes or activities were ranked based on the following:

- I. Minimum control, general area ventilation, work on a bench top.
- II. Work within an approved laboratory ventilation hood required; air cleaning recommended (e.g., HEPA filtration for particulates should be considered for environmental protection).
- III. Containment, such as a glove box, required to prevent loss to the work environment. Particulate effluent from the glove box should be evaluated.
- IV. Review by a specialist required; full containment of the operation and air-cleaning devices (e.g., HEPA filtration for particulates) required on ventilation for environmental protection.

In Phase II, various processes involving seven principal investigators' research projects were assigned to preliminary control bands. The actual controls used were compared to preliminary control bands and three were found to require careful review in Phase III because the assigned control bands suggested that a higher degree of control may be needed. Processes requiring a more detailed review included the use of fumed silica, lithium compounds, and iron disulfide in fumehoods. The preliminary control bands developed in Phase II and actual control levels employed for LBNL research processes evaluated in this pilot study are summarized in Table 2-1.

Additional details related to the Phase I and II components of the study are available in the Phase I and II reports which can be obtained at <http://www.lbl.gov/ehs/>.

Table 2-1 Comparison of Preliminary Control Bands Developed in Phase II and Actual Control Levels

Activity	Preliminary Control Band	Actual Control Level
John Kerr, Building 62, Lab 246		
Fumed silica used in fumehood	Level III	Level II
Fumed silica used in glovebox	Level II	Level III
Carbon black and acetylene black used in glovebox	Level II ^a	Level III
Thomas Richardson, Building 62, Lab 342		
Graphene used in fumehood	Level II ^a	Level II
Gold and silver used in fumehood	Level II	Level II
Carbon black and acetylene black used in glovebox	Level II ^a	Level III
Vincent Battaglia, Building 70, Labs 295/297/299		
Carbon black and acetylene black used in fumehood	Level II ^a	Level II
Lithium compounds and nanosilicon used in fumehood	Level IV ^b	Level II
Carbon black and acetylene black used in glovebox	Level II ^a	Level III
Lithium compounds used in glove box	Level III	Level III
Vincent Battaglia, Building 70, Lab 206		
Brunauer-Emmett-Teller (BET) analysis of carbon black and nanosilicon	Level III	Level III
Robert KostECKI, Building 70, Labs 108/295/297/299		
Lithium iron phosphate used in glovebox	Level III	Level III
Carbon black and acetylene black used in glovebox	Level II ^a	Level III
Graphene thinning performed on countertop	Level I	Level I
Samuel Mao, Building 70, Lab 163		
Fuel cell research used in vacuum chamber	Level III	Level IV
Rick Russo, Building 70, Lab 157		
Laser ablation research used in vacuum chamber	Level III	Level IV
Student research with iron disulfide performed in fumehood	Level IV	Level II
Don Lucas, Building 70, Labs 291/293		
Toxic species detection using nanogold in fumehood	Level II	Level II
Soot generation for combustion research used in combustion chamber	Level I	Level III
Processes Not Evaluated After Phase I^c		
Liu Lab, 70-206: Single-wall carbon nanotubes in storage	Not evaluated	Not evaluated
Anders Lab, 70-274: Solid targets in vacuum chamber	Not evaluated	Not evaluated

^a Originally assigned to control band I; revised to control band II to reflect LBNL requirements^b Originally assigned to control band III; revised to control band IV to account for the nature of the material (dry lithium powder, ultrafine particles)^c For details, refer to Phase I report (Casuccio et al. 2009a)

3.0

Phase III Approach

The control banding approach has gained increasing attention as a management strategy among safety and health practitioners. The control banding strategy groups workplace risks into control bands based on evaluations of hazard and exposure information, and offers a qualitative tool to predict risks and to help define optimum controls. Despite limitations associated with control banding, in the absence of recommended standards, it can be a useful strategy for assessing and controlling occupational hazards as part of a comprehensive safety and health program (NIOSH/CDC 2009). However, it should be realized that specific professional ESH evaluations, such as the industrial hygiene and environmental (source) release sampling performed in Phase III of this project, remain the preferred method for assigning, documenting, and validating controls (Hashimoto 2007). To this end, the sampling and analytical data acquired during the Phase III component of the pilot study was used to validate or modify, as appropriate, the preliminary control bands developed for research processes using fumehoods, gloveboxes, and countertops in Phase II.

Several of the processes that were assigned to preliminary control bands in Phase II were removed from consideration prior to the Phase III sampling program for various reasons.

- The processes involving ablation (Mao, Building 70, Lab 163; and Russo, Building 70, Lab 157) are fully enclosed, do not release UNP during research process operations, and thus were not considered in the Phase III effort.
- The process performed in the fumehood in the Russo laboratory (Building 70, Lab 157), while of interest based on the preliminary control band, has been discontinued.
- The processes performed in the Richardson laboratory (Building 62, Lab 342) fumehood have been discontinued.
- The lithium process previously performed in the Battaglia laboratory (Building 70, Labs 295/297/299) fumehoods has been discontinued.
- The soot combustion process performed in the Lucas laboratory (Building 70, Labs 291/293) was not evaluated further in Phase III because it has minimal potential for release of UNP (the process is fully contained in a gas combustion apparatus that is vented to a combustion hood).
- The process involving Brunauer-Emmett-Teller (BET) analysis of nanopowders (Battaglia, Building 70, Lab 206) was not evaluated in Phase III because the nanomaterials are fully enclosed within a flask for the BET processing. Exposure is not credible under normal work practices and conditions (the only credible scenario for a release from the process is an accidental breaking of the flask). Thus, the current level of control is adequate for this activity based on work practices and controls observed in Phase I. However, preparation and transfer of the nanomaterials into the flask prior to the BET analysis was evaluated in Phase III in Building 70 Lab 218 and Lab 299.

Since the processes conducted in the gloveboxes are similar, only two (Kerr and Battaglia) were planned for further evaluation in Phase III. However, during Phase III the Battaglia glovebox (Battery Fabrication Laboratory) was determined not to be suitable for sampling due to lack of outlets to connect the direct-reading instruments (condensation particle counter [CPC] and optical particle counter [OPC]) to the computer located outside of the glovebox. In addition, there was a concern that the relatively high pressure of the argon atmosphere inside the glovebox could damage the direct-reading instruments. Thus processes using lithium in a glovebox could not be evaluated in Phase III.

A list of processes that were evaluated in Phase II and Phase III from a control banding perspective is provided in Table 3-1. Specific processes selected for further evaluation in Phase III included the following:

1. Fumehoods

- a. Kerr 62-246: fumed silica; dry process (of special interest because the preliminary control band suggested that a greater degree of control was needed)
- b. Battaglia 70-295/297/299: nanosilicon, carbon black; dry process (the nanosilicon process was of special interest because the preliminary control band suggested that a greater degree of control was needed)
- c. Battaglia 70-218: carbon black; dry process (this location was not evaluated in Phase I and II, but the process is similar to that described in the Phase I and II reports for Battaglia 70-295/297/299)
- d. Lucas 70-291/293: gold, wet process

2. Glovebox

- a. Kerr 62-246: fumed silica, carbon black; dry/slurry process

3. Countertop

- a. Kostecki 70-108: graphene; tape transfer

For the fumehoods and countertop processes evaluated in Phase III, samples were obtained at locations representing worker breathing zone, emissions to the outdoor environment (sampling at the source release point), and ambient air within the laboratory (background monitor). For the glovebox samples, only emissions to the outdoor environment (within the glovebox) were evaluated since any potential particulate release is contained within the glovebox enclosure (any leaks in the glovebox would be detected by the pressure monitoring system).

In addition to performing sampling described above, a low-background HEPA-filtered enclosure developed by Rick Kelly (LBNL) was placed over the front of the fumehood at two locations evaluated in Phase III (70-299 and 70-218). The enclosure was designed to minimize the influence of background particles by placing the work area under a slightly positive pressure environment. For these locations, the process was evaluated with and without the enclosure.

The following sections discuss the sampling and analysis methodology and results obtained.

Table 3-1 Summary of EETD Research Evaluated from a Control Banding Perspective

Activity	Phase II	Phase III
John Kerr, Building 62, Lab 246		
Fumed silica used in fumehood	Preliminary control band assigned	Control band revised ^a
Carbon black and acetylene black used in fumehood	Not evaluated; added in Phase III	Control band assigned and validated
Fumed silica used in glovebox	Preliminary control band assigned	Control band validated
Carbon black and acetylene black used in glovebox	Preliminary control band assigned	Control band validated
Thomas Richardson, Building 62, Lab 342		
Carbon black and acetylene black used in glovebox	Preliminary control band assigned	Control band validated (see Kerr Lab)
Vincent Battaglia, Building 70, Labs 295/297/299		
Carbon black and acetylene black used in fumehood	Preliminary control band assigned	Control band validated (see Battaglia Lab 218)
Nanosilicon used in fumehood	Preliminary control band assigned	Control band revised ^a
Carbon black and acetylene black used in glovebox	Preliminary control band assigned	Control band validated (see Kerr Lab)
Vincent Battaglia, Building 70, Lab 218		
Carbon black and acetylene black used in fumehood	Not evaluated; added in Phase III	Control band assigned and validated
Robert Kostecki, Building 70, Lab 295/297/299/108		
Carbon black and acetylene black used in glovebox	Preliminary control band assigned	Control band validated (see Kerr Lab)
Graphene thinning performed on countertop	Preliminary control band assigned	Control band validated
Don Lucas, Building 70, Labs 291/293		
Toxic species detection using nanogold in fumehood	Preliminary control band assigned	Control band validated
Processes Not Evaluated After Phase I		
Liu Lab, 70-206: Single-wall carbon nanotubes in storage	Not evaluated; storage only	
Anders Lab, 70-274: Solid targets in vacuum chamber	Not evaluated; process fully enclosed	
Processes Not Evaluated After Phase II		
Richardson Lab, 62-342: Graphene in fumehood	Preliminary control band assigned	Not evaluated; process discontinued
Richardson Lab, 62-342: Gold in fumehood	Preliminary control band assigned	Not evaluated; process discontinued

Activity	Phase II	Phase III
Richardson Lab, 62-342: Silver in fumehood	Preliminary control band assigned	Not evaluated; process discontinued
Battaglia Lab, 70-295/297/299: Lithium titanate in fumehood	Preliminary control band assigned	Not evaluated; process discontinued
Battaglia Lab, 70-295/297/299: Lithium iron phosphate in fumehood	Preliminary control band assigned	Not evaluated; process discontinued
Battaglia Lab, 70-295/297/299: Lithium titanate in glovebox	Preliminary control band assigned	Not evaluated; glovebox not suitable for sampling
Battaglia Lab, 70-295/297/299: Lithium iron phosphate in glovebox	Preliminary control band assigned	Not evaluated; glovebox not suitable for sampling
Battaglia Lab, 70-206: BET analysis of carbon and nanosilicon in fumehood	Preliminary control band assigned	Not evaluated; process fully enclosed
Kostecki Lab, 70-295/297/299: Lithium iron phosphate in glovebox	Preliminary control band assigned	Not evaluated; glovebox not suitable for sampling
Mao Lab, 70-163: Solid targets in vacuum chamber	Preliminary control band assigned	Not evaluated; process fully enclosed
Russo Lab, 70-157: Solid targets in vacuum chamber	Preliminary control band assigned	Not evaluated; process fully enclosed
Russo Lab, 70-157: Iron sulfide in fumehood	Preliminary control band assigned	Not evaluated; process discontinued
Lucas Lab, 70-291/293: Soot in combustion chamber	Preliminary control band assigned	Not evaluated; process fully enclosed

^a Phase III sampling indicates less stringent controls required

4.0

Sampling and Analysis Methodology

The sampling methodology employed in the Phase III study was based on the protocol provided in Attachment 1 (Example Industrial Hygiene Sampling) of the NSRC *Approach to Nanoscale ES&H, Revision 3a—May 2008* (DOE 2008). This approach recommends use of direct-reading (real-time) particle counters and filtration-based sampling. The sampling was performed by RJLG personnel between April 19, 2010 and April 26, 2010.

Direct-reading particle counters and filtration-based sampling and analysis methods were used to determine particle concentration (particles/cm³ [p/cm³]), total dust (mg/m³) and elemental concentrations (mg/m³). The particle measurements were used to validate, or modify as appropriate, the preliminary control bands developed in Phase II. All sampling was performed by RJLG (John Michael Wilmoth and Gary Casuccio). Linnea Wahl (LBNL) coordinated the sampling activities with the principal investigators. Tim Roberts, Larry McLouth, Max Jakovleski, and Heather Madison (LBNL) provided industrial hygiene support for sampling activities.

Condensation particle counters (TSI Condensation Particle Counter 3007) and OPCs (Grimm SubMicron Aerosol Spectrometer 1.108) were used to provide real-time data. These devices are designed to count particles in the air and they provide data related to particle concentrations (p/cm³). The CPC is designed to measure particles in the size range between 10 nm and approximately 1 μm. The OPC measures particles from 300 nm to 20 μm. Each of these instruments provides only particle count data (these instruments provide no information related to particle chemistry). The CPC and OPC instruments were synchronized such that the data were collected in a simultaneous manner using software developed by Thomas Peters (University of Iowa). The combined use of the CPC and OPC samplers permitted particle concentration data to be reported in the range of 10 nm to 300 nm.

Two sets of particle counters were used in the evaluation of fumehood and countertop processes: one CPC/OPC set was located at the source release point whereas the other CPC/OPC set was located in the laboratory to monitor background conditions. Side-by-side testing was performed with the direct-reading samplers throughout the sampling program to document bias between the samplers. Given that the CPC has a reported accuracy of ± 20% for particle concentration, the side-by-side testing provided a means to document differences in the particle concentration data between the samplers. Side-by-side testing indicated that there was a bias that averaged 10.6%. This value was used to “adjust” the values associated with the laboratory (background) sampler.

The filtration-based air samplers were used to provide additional and more specific information on the particulate matter. The filtration-based samplers were used to simultaneously collect particle matter on polyvinyl chloride (PVC) and polycarbonate (PC) filters at the source release point, the worker breathing zone (worker exposure), and at the laboratory background location for the fumehood and countertop processes. PVC and PC filter cassettes were worn by researchers to collect air samples representative of

the worker's exposure during handling of the UNP while performing research activities. The source sampling was performed by filtering air on PVC and PC filter cassettes directly above the working area and a third sample set was used to collect airborne particulate in the laboratory (removed from the source) to provide a measure of background. The filtration-based samplers were co-located and operated simultaneously with the CPC/OPC particle counters at the source and laboratory background locations.

The PVC samples were collected onto preweighed 37 mm, 0.8 μm pore size filters and were used to determine particulate mass (total dust) via gravimetric analysis following procedures described in National Institute of Occupational Safety and Health (NIOSH) Method 0500 (NIOSH 2003). The PVC filter was also used to determine the elemental concentrations using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) following NIOSH Method 7300 (NIOSH 1994). More information on the gravimetry and ICP analysis can be found in Appendixes A and B.

The PC filters were used for the EM analysis. Air samples were collected onto 25 mm, 0.4 μm pore size substrates. The purpose of the EM analysis was to quantify the airborne concentrations of UNP at the source, worker exposure, and within the laboratory (background). Because UNP can include particles in the nanosize range as well as agglomerates of nanoparticles that can be on the order of micrometers or larger, RJLG developed an analytical methodology that utilized multiple magnifications to maximize the potential for observing UNP in various size ranges. The analysis protocol was in general accordance with published methods (ceramic whiskers in ASTM D-6056 [ASTM 2006a]; airborne asbestos fibers in ASTM D-6281 [ASTM 2006b]), and was based on a combination of transmission electron microscopy (TEM) and high resolution scanning electron microscopy (SEM). The analysis of each sample was segregated into three size fractions ($> 2 \mu\text{m}$, $0.5\text{--}2 \mu\text{m}$, and $< 0.5 \mu\text{m}$), with an applicable magnification for the analysis of each fraction. Particles consistent with the source material identified based on morphology and energy dispersive spectroscopy (EDS) performed for the starting materials obtained in Phase I were counted while monitoring the amount of area analyzed on the sample. The dimensions of each agglomerated structure or individual nanoparticle were recorded and representative images along with elemental spectra were documented. More information on the EM analysis methodology can be found in Appendix C.

One of the complicating factors related to air filtration sampling was that most of the research activities involving use of UNP for the processes evaluated in this study are typically less than a few minutes. In an effort to reduce the analytical uncertainty and to obtain a lower detection limit, the research process was performed over a longer time period (approximately 30 to 70 minutes), which resulted in samples that were collected for 5 to 10 times the normal process time. To further increase the analytical sensitivity, the samples were collected using higher flow rates (approximately 7 L/min) than typically used in industrial hygiene sampling (note that this is a deviation from the recommended flow rates in NIOSH Method 0500 [NIOSH 2003] and NIOSH Method 7300 [NIOSH 1994]). The PVC samples were collected using a Leland Legacy® sampling pump (SKC, Eighty Four, PA). This pump is designed for sample flow rates between 5 and 15 L/min. Tests performed at RJLG prior to the Phase III sampling at LBNL using 37 mm 0.8 μm pore size PVC filters indicated that this pump could sample at the rate of 6.5 L/min for greater than 30 minutes on battery power. A more powerful pump, Quick Take® 30 (SKC, Eighty Four, PA) was

used for the PC filters. Based on tests conducted at RJLG prior to the Phase III sampling at LBNL, this pump was capable of sampling at a rate of 8.4 L/min using 25 mm, 0.4 μm pore size PC filters for at least 30 minutes.

The sampling methodology employed in the Phase III pilot study was similar to that which NIOSH employs as part of the Nanoparticle Emission Assessment Technique (NEAT) program (Methner 2010a and Methner 2010b). In summary, the NEAT employs a combination of direct-reading instruments (CPC and OPC) coupled with filtration-based air sampling with chemical and microscopic analysis. Relatively high flow rates (e.g., 7 L/min) are used to collect the filter samples. The NEAT uses appropriate air sampling filter media that is selected based on the engineered nanomaterial type and the analytical information required, and samples are collected in an “open-face” manner.

Two research processes involving the use of UNP in fumehoods (70-299 and 70-218) were evaluated using a HEPA-filtered enclosure developed by Rick Kelly (LBNL). Particle measurements using the enclosure were performed to explore the potential of using devices of this nature to assist in evaluation of worker exposure and emissions of UNP to the outdoor environment.

The enclosure was connected to a HEPA filter and placed over the front of the fumehood. The HEPA provides filtered air into the enclosure at a rate of approximately 1000 cubic feet per minute (cfm) creating a slightly positive pressure environment in the enclosure and thus minimizing the number of background particles. Figure 4-1 below provides a photograph of the enclosure.



Figure 4-1 Photograph of Enclosure Attached to Fumehood

Similar to measurements in fumehoods evaluated without the enclosure, direct-reading particle counters and filtration-based sampling and analysis methods were used to determine particle concentration (p/cm^3), total dust (mg/m^3), and elemental concentrations (mg/m^3). However, due to space constraints in the enclosure the laboratory background filter samples were collected outside of the enclosure (actual lab background). Measurements inside the enclosure included use of direct-reading instruments in the hood (source) and near the worker, and filtration-based measurements in the hood and near the worker's breathing zone.

The following sections discuss the results obtained from the monitoring of process activities involving the fumehoods (Section 5.0), fumehoods with the Kelly enclosure (Section 6.0), countertop (Section 7.0), and glovebox (Section 8.0).

5.0

Evaluation of Worker Exposure and Emissions to the Outdoor Environment: Processes Involving Fumehoods

In Phase III, five research processes involving the use of UNP in fumehoods were evaluated from the perspective of worker exposure and emissions to the outdoor environment. The processes evaluated included the following principal investigators and laboratory locations: John Kerr, Building 62, Lab 246 (acetylene black and fumed silica); Vincent Battaglia, Building 70, Labs 295/297/299 (nanosilicon); Vincent Battaglia, Building 70, Lab 218 (carbon black); and Don Lucas, Building 70, Labs 291/293 (nanogold).

The following sections summarize the results obtained for the research activities involving fumehoods (results related to the fumehoods tested with the enclosure can be found in Section 6.0).

5.1 John Kerr: Building 62, Lab 246

5.1.1 Research Involving Use of UNP in the Fumehood

The process consists of transferring a portion of acetylene black or fumed silica from the original chemical container and placing it into a glass jar using a spatula. The transferred material is then weighed on a digital, analytical balance. All work is performed in the fumehood. In Phase I, EM analysis of the starting bulk acetylene black material confirmed that the primary particles comprising the agglomerated acetylene black and fumed silica structures were composed of nanoparticles (Casuccio et al. 2009a).

5.1.2 Results for Acetylene Black Process

5.1.2.1 Preliminary Control Band Assignment

Although this process was not demonstrated in Phase I, a preliminary Level I control band is appropriate based on an assumed “medium” (Category B) worker/environmental hazard and a “low” (Category 2) release/exposure probability (refer to Fig. 2-1). The release/exposure probability for acetylene black was determined (without considering any LBNL current controls) based on the nature of the material which is used as a dry powder composed of agglomerations of nanoparticles and used in laboratory quantities (small amounts) for short durations of time (< 5 min; 1–3 times per week).

This process could be assigned to a Level I control band (which indicates only a low level of control is required for this process), but at LBNL it is a requirement to conduct work that could generate engineered nanomaterials in fumehoods, gloveboxes, or other enclosures (LBNL 2010). Therefore the minimum control for this work with UNP would be a functioning laboratory hood (Level II).

Level II controls were noted for this process based on work practices and controls observed during the evaluation of the laboratory in Phase I, which suggests that controls match the risks. To validate the

preliminary control band, the process was monitored for worker exposure and emissions to the outdoor environment of UNP in Phase III.

5.1.2.2 Sampling during the Research Process

Sampling of the acetylene black process was performed on April 19, 2010. All process activity took place in the fumehood. Photographs showing the locations of the source, worker exposure and laboratory background samplers, and work performed during the sampling of the acetylene black process are provided in Appendix D.

5.1.2.3 Comparison of Background, Worker Location, and Process Samples

The results obtained from the direct-reading instruments located in the fumehood indicated that particle concentrations varied from about 4,000 to 7,000 p/cm^3 with an average of 5,163 (standard deviation [s.d.] 818) whereas the laboratory background concentrations varied from about 4,000 to over 11,000 p/cm^3 with an average of 5,605 (s.d. 1628) during the sampling period. A plot illustrating the particle concentrations in the size range of 10–300 nm and the relationship of the hood (source) concentrations to the laboratory background is provided in Fig. 5-1. Note that laboratory background data discussed here and presented in Fig. 5-1 have been adjusted to account for instrument bias (10.6%) observed during the side-by-side instrument testing (see Section 4.0).

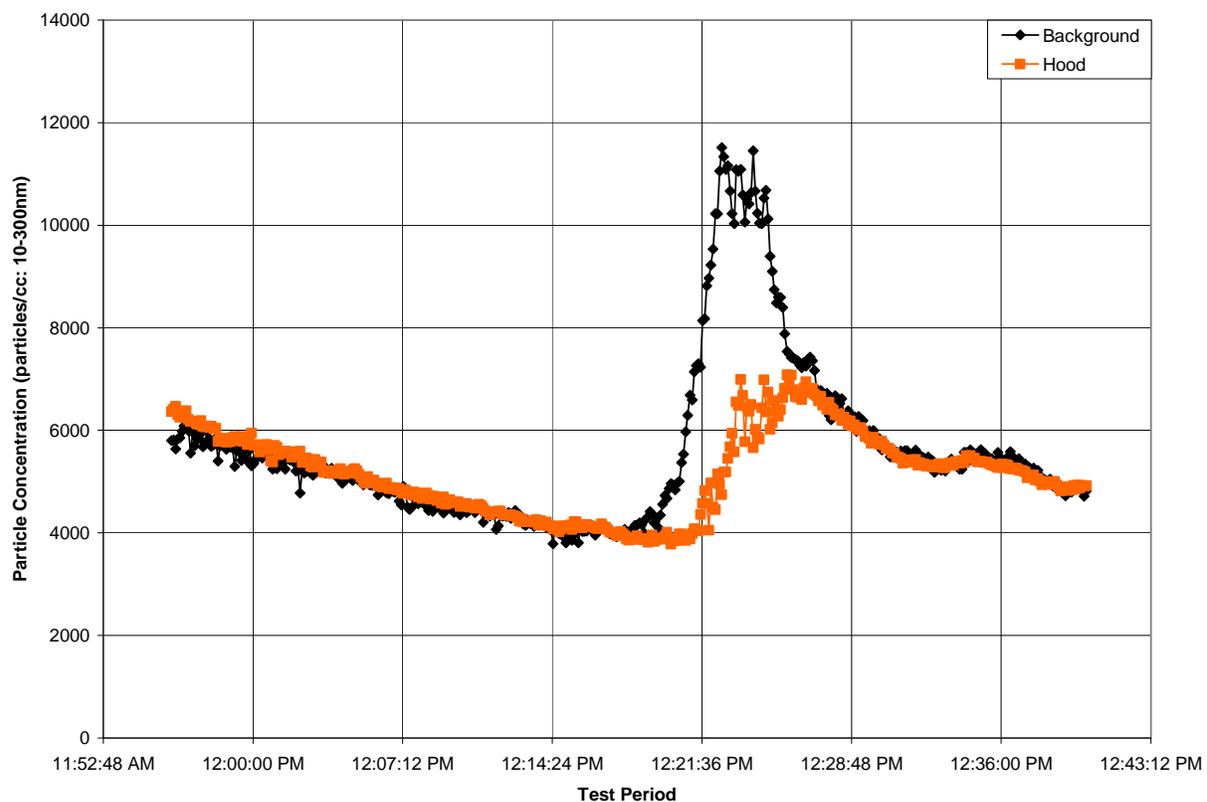


Figure 5-1 Direct-reading Particle Concentration Results for Acetylene Black Process

Review of the data presented in Fig. 5-1 shows that the particle concentrations recorded by both the hood and laboratory background direct-reading instruments tracked closely during the first approximately 25 minutes of testing with a gradual decline in particle concentrations from about 6,000 to 4,000 particles/cm³ during this period. For reasons unknown, the laboratory background sampler concentrations then began to spike, reaching a maximum concentration of 11,512 p/cm³. A few minutes later, it appears that the increased particle concentration in the background air began to affect the particle concentration detected by the source sampler located in the hood; however, the concentration spike observed in the hood increased to only 7,080 p/cm³. The temporal changes in the direct-reading data indicate that particles originating from an unknown source outside of the hood (not related to the acetylene black process) were responsible for the increase in particle concentrations. During the remainder of the test the hood and laboratory background measurements once again tracked closely.

A statistical evaluation (one-tailed t-test with $\alpha = 0.05$) was conducted on paired particle concentration data to determine whether the fumehood (source) concentrations were statistically different from the laboratory background measurements. Results of the t-test indicate that the fumehood concentrations were significantly less than the background measurements (p-value < 0.0001).

Gravimetric analysis of the filtration-based samples collected using an open-face cassette indicates that total dust measurements at the source, worker, and laboratory background locations were below detection limits ($< 5 \times 10^{-2}$ mg); thus the total dust concentration at the worker location based on the volume of air sampled was < 0.265 mg/m³. More information related to the total dust analysis can be found in Appendix A.

The EM analysis, performed on a PC filter collected in an open-face manner, was focused on identifying acetylene black particles. Identification of acetylene black was based on information obtained from the analysis of the starting source material, which indicated that the acetylene black was composed of aciniform structures consisting of rounded and irregularly shaped particles. While the majority of aciniform structures had dimensions on the order of micrometers, the primary particles typically were 30–40 nm (Casuccio et al. 2009a). Although the EM analysis was focused on acetylene black particles, other particles with similar characteristics, including carbon black and soot, could be included in the EM results, so acetylene black particle concentrations may be overestimated by the EM measurements. A summary of the EM results is provided below in Table 5-1. Results indicate that the source sample had the highest concentrations and the worker exposure was similar to or less than background in each size fraction. More information related to the EM analysis can be found in Appendix C.

Table 5-1 Summary of Electron Microscopy Results for Acetylene Black Process

Sample Type	Concentration by Particle Size (particles/cm ³)		
	> 2 μ m	0.5–2 μ m	< 0.5 μ m
Laboratory Background	1×10^{-2}	0.2	675.6
Worker Location	1×10^{-2}	0.3	450.4
Hood (Source) Location	0.2	1.4	1038.2

5.1.2.4 Estimation of Potential Worker Exposure Concentrations

The Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) and the American Conference of Governmental Industrial Hygienists (ACGIH) 8-hour threshold limit value (TLV) for carbon black (assumed to be equivalent to acetylene black) are 3.5 mg/m^3 as a time-weighted average (TWA) for 8 hours per day during a 40-hour work week. As is common with research activities, the research task is performed only a few minutes a day a few times a week; therefore the daily TWA exposures and the weekly dose of UNP are a fraction of the exposure determined while the researcher performs the task. When calculating the 8-hour TWA for UNP, no exposure is attributed to work activities when the researcher is not working with acetylene black (based on interviews with the researchers exposure to acetylene black is not credible during these periods).

The extrapolated 8-hour TWA exposure for total dust was $< 1.8 \times 10^{-2} \text{ mg/m}^3$. The extrapolated 8-hour TWAs for acetylene black based on the EM results are reported as $7 \times 10^{-4} \text{ p/cm}^3$ ($> 2 \text{ }\mu\text{m}$), $2.0 \times 10^{-2} \text{ p/cm}^3$ ($0.5\text{--}2 \text{ }\mu\text{m}$), and 30 p/cm^3 ($< 0.5 \text{ }\mu\text{m}$).

The 8-hour TWA values should be considered conservative since sampling was performed over an extended time period (approximately 6 times the normal research process duration). Sampling time was extended to increase the mass of the collected particulate matter to improve the analytical limits of detection. When researchers' work duration is the normal process time (< 5 minutes), the workday (8 hour) exposure would be approximately 1/6 of those calculated.

5.1.2.5 Estimation of Potential Emissions to the Outdoor Environment

Comparison of direct-reading air concentrations (laboratory background data compared to data obtained at the source in the hood while the researcher was handling acetylene black) show no statistically significant increase in particles that could be emitted to the outdoor environment (see Section 5.1.2.3). This observation is supported by the EM results which indicate that the acetylene black particle concentration at the source location during the handling operation was only a few hundred particles/cm³ above background levels (see Table 5-1).

An approach suggested by Hoover (2010) and applied in the CRC Press handbook edited by Hoover and Maiello (2010) was used to convert the EM results into an estimate of emissions to the outdoor environment. This calculation assumes the following:

- Any acetylene-black-like particles observed in the hood at levels above background concentrations were actually released during the handling operation.
- The density of acetylene black is 1.75 g/cm^3 .
- The particles are spherical in morphology.
- The largest observed particle on the filter sample ($3 \text{ }\mu\text{m}$ diameter) represents the diameter of acetylene black particles identified as greater than $2 \text{ }\mu\text{m}$.
- $2 \text{ }\mu\text{m}$ is a conservative estimate of the diameter of all particles in the size range from 0.5 to $2 \text{ }\mu\text{m}$.
- $0.5 \text{ }\mu\text{m}$ is a conservative estimate of the diameter of all particles less than $0.5 \text{ }\mu\text{m}$.

The total estimated acetylene black available for emission to the outdoor environment can be calculated as the sum of three components, one for each size range identified by EM, as follows:

$$\begin{aligned} & \{(0.19 \text{ particles/cm}^3) \times (10^6 \text{ cm}^3/\text{m}^3) \times (\pi) \times [(3 \text{ }\mu\text{m})^3/6] \times (10^{-12} \text{ cm}^3/\mu\text{m}^3) \times (1.75 \text{ g/cm}^3/\text{particle}) \times (10^3 \text{ mg/g})\} + \\ & \{(1.2 \text{ particles/cm}^3) \times (10^6 \text{ cm}^3/\text{m}^3) \times (\pi) \times [(2 \text{ }\mu\text{m})^3/6] \times (10^{-12} \text{ cm}^3/\mu\text{m}^3) \times (1.75 \text{ g/cm}^3/\text{particle}) \times (10^3 \text{ mg/g})\} + \\ & \{(363 \text{ particles/cm}^3) \times (10^6 \text{ cm}^3/\text{m}^3) \times (\pi) \times [(0.5 \text{ }\mu\text{m})^3/6] \times (10^{-12} \text{ cm}^3/\mu\text{m}^3) \times (1.75 \text{ g/cm}^3/\text{particle}) \times (10^3 \text{ mg/g})\} \end{aligned}$$

The sum of the three components is approximately $5.5 \times 10^{-2} \text{ mg/m}^3$.

Assuming that acetylene black particles were released at this concentration over a 10-minute period as a plume with a cross-sectional area of 0.25 m^2 (0.5 m wide and 0.5 m high) with a linear velocity of 100 ft/min (30.5 m/min), the total mass of the release is estimated to be

$$(5.5 \times 10^{-2} \text{ mg/m}^3) \times (0.25 \text{ m}^2) \times (30.5 \text{ m/min}) \times (10 \text{ min}) = 4.2 \text{ mg}$$

Dispersion of the material to locations beyond the LBNL fence (offsite) was modeled using the EPIcode Gaussian plume model, which has been evaluated by DOE and is included in the DOE safety software central registry (Homann 2003). For a 10-minute release of acetylene black under typical LBNL meteorological conditions, the maximum particle concentration offsite (160 m from a centrally located stack) is conservatively estimated to be approximately $1.8 \times 10^{-6} \text{ mg/m}^3$.

5.1.2.6 Comparison of Potential Offsite Concentration to Environmental Standards

Although no regulations have been established related to the levels of environmental emissions that would necessitate use of HEPA filtration for UNP, it is useful to compare estimated potential offsite concentrations to existing standards and occupational exposure limits (OELs), such as the OSHA PEL established for larger particles, as shown in Table 5-2.

One approach is to compare the estimated maximum offsite concentration of acetylene black to the Environmental Protection Agency's (EPA) 24-hour $\text{PM}_{2.5}$ national ambient air quality standard (NAAQS) of $3.5 \times 10^{-2} \text{ mg/m}^3$. Using this approach, the estimated maximum concentration of acetylene black ($1.8 \times 10^{-6} \text{ mg/m}^3$) would make an insignificant contribution ($5.1 \times 10^{-3} \%$) to the allowable 24-hour $\text{PM}_{2.5}$ standard (see Table 5-2).

A second approach is to scale the current OSHA PEL for acetylene black, 3.5 mg/m^3 (using a "size adjustment" factor to account for the nanoparticle component and a "reduction factor" for public exposure) to estimate a comparative environmental concentration. A size adjustment factor of 6.6×10^{-2} has been described in the European Agency for Safety and Health at Work literature review (EU-OSHA 2009), based on the draft NIOSH report "Evaluation of Health Hazard and Recommendations for Occupational Exposure to Titanium Dioxide" (NIOSH 2005) and the British Standards Institute guide to handling nanomaterials (BSI 2007). A value of 5×10^{-2} can be used as one possible reduction factor for public exposure based on the comparison of the EPA environmental limit of $1 \times 10^{-2} \mu\text{g/m}^3$ for beryllium

compared to the corresponding beryllium OEL of $2 \mu\text{g}/\text{m}^3$ at the time the EPA limit was established. Using the PEL value, size adjustment factor, and public exposure reduction factor, an environmental concentration limit can be calculated as follows:

$$(3.5 \text{ mg}/\text{m}^3) \times (6.6 \times 10^{-2}) \times (5 \times 10^{-2}) = 1.2 \times 10^{-2} \text{ mg}/\text{m}^3$$

The maximum offsite concentration of acetylene black estimated at $1.8 \times 10^{-6} \text{ mg}/\text{m}^3$ represents just 0.02% of the scaled OSHA PEL of $1.2 \times 10^{-2} \text{ mg}/\text{m}^3$ (see Table 5-2).

A third approach involves comparing the estimated maximum offsite concentration of acetylene black to limits for release of acetylene black established by the Bay Area Air Quality Management District (BAAQMD) at 10 pounds/day and 150 pounds/year. Comparison of the estimated maximum offsite concentration to the BAAQMD limits indicates that the emissions to the outdoor environment of acetylene black are a small fraction of the allowable limits (see Table 5-2, where the yearly estimated maximum offsite concentration was based on the process being performed three times a week for 50 weeks a year).

Table 5-2 Comparison of Estimated Maximum Emissions to the Outdoor Environment of Acetylene Black to Various Criteria

Comparison Criterion	Comparison Value	Estimated LBNL Maximum Offsite Concentration	Ratio of LBNL Value to Comparison Value
EPA 24-hr standard for $\text{PM}_{2.5}$	$3.5 \times 10^{-2} \text{ mg}/\text{m}^3$	$1.8 \times 10^{-6} \text{ mg}/\text{m}^3$	5.1×10^{-5}
Scaled environmental concentration value for acetylene black based on a PEL of $3.5 \text{ mg}/\text{m}^3$	$1.2 \times 10^{-2} \text{ mg}/\text{m}^3$	$1.8 \times 10^{-6} \text{ mg}/\text{m}^3$	2×10^{-4}
Airborne acetylene black concentration based on the BAAQMD Level of Significance	10 pounds/day	9×10^{-6} pounds/day	9×10^{-7}
	150 pounds/year	1×10^{-3} pounds/year	7×10^{-6}

5.1.2.7 Summary of Results

Based on the review of the direct-reading and analytical data, the preliminary Level II control band is validated and no additional controls are required for this process. Worker exposure and laboratory background monitoring results demonstrate that the researcher was not exposed to significant airborne UNP during sampling of the acetylene black process (worker exposure was less than laboratory background). Similar exposure results are expected for similar LBNL processes (using similar work practices and similar types and quantities of acetylene black) performed with similar controls.

From an environmental perspective, results obtained in this study indicate that there is a potential for negligible emissions of UNP to the outdoor environment via the ventilation duct. The maximum offsite concentration for this process is estimated to be $1.8 \times 10^{-6} \text{ mg}/\text{m}^3$, which is orders of magnitude lower than applicable standards or a size-scaled PEL. These results indicate that HEPA filtration is not required to control emissions of UNP to the outdoor environment for this and similar research processes.

5.1.3 Results for Fumed Silica Process

5.1.3.1 Preliminary Control Band Assignment

In Phase II, a preliminary Level III control band was assigned to this process based on an assumed “high” (Category C) worker/environmental hazard and a “likely” (Category 3) release/exposure probability (refer to Fig. 2-1). The release/exposure probability for fumed silica was determined (without considering any LBNL current controls) based on the nature of the material which is used as a dry powder and composed of agglomerations of ultra-fine particles which is used in small quantities for a short duration of time (< 5 min; 1–3 times per week).

Level II controls were noted for this process based on work practices and controls observed during the evaluation of the laboratory in Phase I, which suggested that additional process controls are needed based on the preliminary control band. To validate the preliminary control band, the process was monitored for worker exposure and emissions to the outdoor environment of UNP in Phase III.

5.1.3.2 Sampling during the Research Process

Sampling of the fumed silica process was performed on April 19, 2010. All process activity took place in the fumehood. Photos showing the locations of the source, worker exposure and laboratory background samplers, and work performed during the sampling of the fumed silica process are provided in Appendix E.

5.1.3.3 Comparison of Background, Worker Location, and Process Samples

The results obtained from the direct-reading instruments located in the fumehood indicated that particle concentrations varied from about 8,000 to 10,000 p/cm³ with an average of 8,964 (s.d. 491) whereas the laboratory background concentrations varied from about 7,500 to 10,000 p/cm³ with an average of 8,634 (s.d. 508) during the sampling period. A plot illustrating the particle concentrations in the size range of 10–300 nm and the relationship of the hood (source) concentrations to the laboratory background is provided in Fig. 5-2. Note that laboratory background data discussed here and presented in Fig. 5-2 have been adjusted to account for instrument bias (10.6%) observed during the side-by-side instrument testing (see Section 4.0).

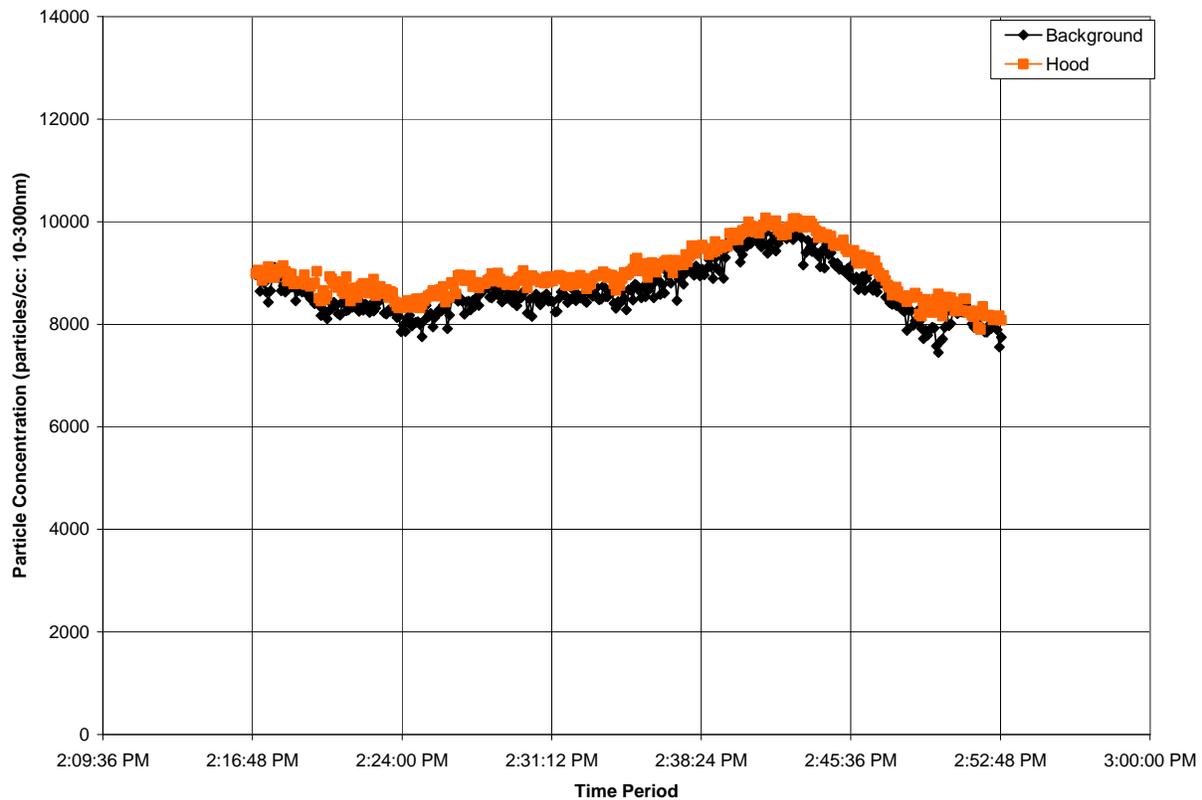


Figure 5-2 Direct-reading Particle Concentration Results for Fumed Silica Process

Review of the data presented in Fig. 5-2 shows that the particle concentrations recorded by both the hood and laboratory background direct-reading instruments tracked closely during the test. A statistical evaluation (one-tailed t-test with $\alpha = 0.05$) was conducted on paired particle concentration data to determine whether the fumehood (source) concentrations were statistically different from the background measurement. Results of the t-test indicate that the fumehood concentrations were significantly greater than the laboratory background (p-value < 0.0001).

Gravimetric analysis of the filtration-based samples collected using an open-face cassette indicates that total dust measurements at the source, worker, and laboratory background locations were below detection limits ($< 5 \times 10^{-2}$ mg); thus the total dust concentration at the worker location based on the volume of sample collected was < 0.273 mg/m³. More information related to the total dust analysis can be found in Appendix A. The ICP-AES results for silicon at the source, worker, and laboratory background locations were below detection limits ($< 2.5 \times 10^{-2}$ mg). The silicon concentration at the worker location based on volume of air sampled was < 0.137 mg/m³. More information related to the ICP-AES analysis can be found in Appendix B.

The EM analysis, performed on a PC filter collected in an open-face manner, was focused on identifying fumed silica particles. The identification was based on information obtained from the analysis of the starting source material, which indicated that the fumed silica was composed of aciniform structures consisting of rounded primary particles. While the majority of aciniform structures had dimensions on the

order of micrometers, the primary particles were typically between 20–30 nm in size (Casuccio et al. 2009a). A summary of the EM results is provided below in Table 5-3. Results indicate that the source sample had the highest concentrations and the worker exposure is similar to or less than laboratory background in each size fraction. More information related to the EM analysis can be found in Appendix C.

Table 5-3 Summary of Electron Microscopy Results for Fumed Silica Process

Sample Type	Concentration by Particle Size (particles/cm ³)		
	> 2 μm	0.5–2 μm	< 0.5 μm
Laboratory Background	< 2 × 10 ⁻³	0.4	155.0
Worker Location	< 2 × 10 ⁻³	0.3	75.4
Hood (Source) Location	0.1	0.6	487.5

5.1.3.4 Estimation of Potential Worker Exposure Concentrations

The OSHA PEL for 100% amorphous silica (calculated as indicated in OSHA 1910.1000 Table Z-3 [80 mg/m³ divided by percent SiO₂]) is 0.8 mg/m³ (8-hour TWA). As is common with research activities, the research task is performed only a few minutes a day a few times a week; therefore the daily TWA exposures and the weekly dose of UNP are a fraction of the exposure determined while the researcher performs the task. When calculating the 8-hour TWA for UNP, no exposure is attributed to work activities when the researcher is not working with fumed silica (based on interviews with the researchers exposure to fumed silica is not credible during these periods).

The extrapolated 8-hour TWA exposure for total dust was < 1.8 × 10⁻² mg/m³. The 8-hour TWA for silicon based on the ICP-AES results was < 9 × 10⁻³ mg/m³. The 8-hour TWAs for fumed silica based on the EM results are reported as 1.3 × 10⁻⁴ p/cm³ (> 2 μm), 2.0 × 10⁻² p/cm³ (0.5–2 μm), and 4.9 p/cm³ (< 0.5 μm).

The 8-hour TWA values should be considered conservative since sampling was performed over an extended time period (approximately 6 times the normal research process duration). Sampling time was extended to increase the mass of the collected particulate matter to improve the analytical limits of detection. When researchers' work duration is the normal process time (< 5 minutes), the workday (8 hour) exposure would be approximately 1/6 of those calculated.

5.1.3.5 Estimation of Potential Emissions to the Outdoor Environment

Comparison of direct-reading air concentrations (laboratory background data compared to data obtained at the source in the hood while the researcher was handling the fumed silica) indicates a potential for a small release of fumed silica on the order of 300 UNP particles/cm³ to the outdoor environment. These results are supported by the EM data which also indicate that the fumed silica particle concentration at the source location during the handling operation was approximately 300 particles/cm³ above background levels (see Table 5-3).

An approach suggested by Hoover (2010) and applied in the CRC Press handbook edited by Hoover and Maiello (2010) was used to convert the EM results into an estimate of emissions to the outdoor environment. This calculation assumes the following:

- Any fumed-silica-like particles observed in the hood at levels above background concentrations were actually released during the handling operation.
- The density of fumed silica is 2.2 g/cm³.
- The particles are spherical in morphology.
- The largest observed particle on the filter sample (10 μm diameter) represents the diameter of fumed silica particles identified as greater than 2 μm.
- 2 μm is a conservative estimate of the diameter of all particles in the size range from 0.5 to 2 μm.
- 0.5 μm is a conservative estimate of the diameter of all particles less than 0.5 μm.

The total estimated fumed silica available for emission to the outdoor environment can be calculated as the sum of three components, one for each size range identified by EM, as follows:

$$\begin{aligned} & \{(0.1 \text{ particles/cm}^3) \times (10^6 \text{ cm}^3/\text{m}^3) \times (\pi) \times [(10 \text{ }\mu\text{m})^3/6] \times (10^{-12} \text{ cm}^3/\mu\text{m}^3) \times (2.2 \text{ g/cm}^3/\text{particle}) \times \\ & (10^3 \text{ mg/g})\} + \\ & \{(0.2 \text{ particles/cm}^3) \times (10^6 \text{ cm}^3/\text{m}^3) \times (\pi) \times [(2 \text{ }\mu\text{m})^3/6] \times (10^{-12} \text{ cm}^3/\mu\text{m}^3) \times (2.2 \text{ g/cm}^3/\text{particle}) \times \\ & (10^3 \text{ mg/g})\} + \\ & \{(332 \text{ particles/cm}^3) \times (10^6 \text{ cm}^3/\text{m}^3) \times (\pi) \times [(0.5 \text{ }\mu\text{m})^3/6] \times (10^{-12} \text{ cm}^3/\mu\text{m}^3) \times (2.2 \text{ g/cm}^3/\text{particle}) \times \\ & (10^3 \text{ mg/g})\} \end{aligned}$$

The sum of the three components is approximately 0.16 mg/m³.

Assuming that fumed silica particles were released at this concentration over a 10-minute period as a plume with a cross-sectional area of 0.25 m² (0.5 m wide and 0.5 m high) with a linear velocity of 100 ft/min (30.5 m/min), the total mass of the release is estimated to be

$$(0.16 \text{ mg/m}^3) \times (0.25 \text{ m}^2) \times (30.5 \text{ m/min}) \times (10 \text{ min}) = 12.2 \text{ mg}$$

Dispersion of the material to locations beyond the LBNL fence (offsite) was modeled using the EPIcode Gaussian plume model, which has been evaluated by DOE and is included in the DOE safety software central registry (Homann 2003). For a 10-minute release of fumed silica under typical LBNL meteorological conditions, the maximum particle concentration offsite (160 m from a centrally located stack) is conservatively estimated to be approximately 5.2×10^{-6} mg/m³.

5.1.3.6 Comparison of Potential Offsite Concentration to Environmental Standards

Although no regulations have been established related to the levels of environmental emissions that would necessitate use of HEPA filtration for UNP, it is useful to compare estimated potential offsite concentrations to existing standards and OELs, such as the OSHA PEL established for larger amorphous silica particles, as shown in Table 5-4.

One approach is to compare the estimated maximum offsite concentration of fumed silica to the EPA's 24-hour PM_{2.5} NAAQS of 3.5×10^{-2} mg/m³. Using this approach, the estimated maximum concentration of fumed silica (5.2×10^{-6} mg/m³) would make an insignificant contribution (1.5×10^{-2} %) to the allowable 24-hour PM_{2.5} standard (see Table 5-4).

A second approach is to scale the current OSHA PEL for amorphous silica, 0.8 mg/m³, using a "size adjustment" factor to account for the nanoparticle component and a "reduction factor" for public exposure to estimate a comparative environmental concentration. A size adjustment factor of 6.6×10^{-2} has been described in the European Agency for Safety and Health at Work literature review (EU-OSHA 2009), based on the draft NIOSH report "Evaluation of Health Hazard and Recommendations for Occupational Exposure to Titanium Dioxide" (NIOSH 2005) and the British Standards Institute guide to handling nanomaterials (BSI 2007). A value of 5×10^{-2} can be used as one possible reduction factor for public exposure based on the comparison of the EPA environmental limit of 1×10^{-2} µg/m³ for beryllium compared to the corresponding beryllium OEL of 2 µg/m³ at the time the EPA limit was established. Using the PEL value, size adjustment factor, and public exposure reduction factor, an environmental concentration limit can be calculated as follows:

$$(0.8 \text{ mg/m}^3) \times (6.6 \times 10^{-2}) \times (5 \times 10^{-2}) = 2.6 \times 10^{-3} \text{ mg/m}^3$$

The maximum offsite concentration of fumed silica estimated at 5.2×10^{-6} mg/m³ represents just 0.2% of the scaled OSHA PEL of 2.6×10^{-3} mg/m³ for amorphous silica (see Table 5-4). This approach suggests that HEPA filtration is not needed for this research process.

A third approach involves comparing the estimated maximum offsite concentration of fumed silica to limits for release of silica established by the Bay Area Air Quality Management District (BAAQMD) at 120 pounds/week. Comparison of the estimated maximum offsite concentration to the BAAQMD limits indicates that the emissions to the outdoor environment of fumed silica are a small fraction of the allowable limits (see Table 5-4, where the yearly estimated maximum offsite concentration was based on the process being performed three times a week for 50 weeks a year).

Table 5-4 Comparison of Estimated Maximum Emissions to the Outdoor Environment of Fumed Silica to Various Criteria

Comparison Criterion	Comparison Value	Estimated LBNL Maximum Offsite Concentration	Ratio of LBNL Value to Comparison Value
EPA 24-hr standard for PM _{2.5}	3.5×10^{-2} mg/m ³	5.2×10^{-6} mg/m ³	1.5×10^{-4}
Scaled environmental concentration value for fumed silica based on an PEL of 0.8 mg/m ³	2.6×10^{-3} mg/m ³	5.2×10^{-6} mg/m ³	2.0×10^{-3}
Airborne silica concentration based on the BAAQMD Level of Significance	120 pounds/year	4.2×10^{-3} /year	3.5×10^{-5}

5.1.3.7 Summary of Results

Based on the review of the direct-reading and analytical data, the preliminary Level III control band is not needed for this process; Level II controls, which are in place for this process, are adequate based on results obtained in this study. Worker exposure and laboratory background monitoring demonstrates that the researcher was not exposed to significant airborne UNP during sampling of the fumed silica process (worker exposure was less than background). Similar exposure results are expected for similar LBNL processes (using similar work practices and similar types and quantities of fumed silica) performed with similar controls.

From an environmental perspective, results obtained in this study indicate that there is a potential for negligible emissions of UNP to the outdoor environment via the ventilation duct. The maximum offsite concentration from this process is estimated to be 5.2×10^{-6} mg/m³, which is orders of magnitude lower than applicable standards or a size-scaled PEL. These results indicate that HEPA filtration is not required to control emissions of UNP to the outdoor environment for this and similar research processes.

5.2 Vincent Battaglia: Building 70, Labs 295/297/299 and 218

5.2.1 Research Involving Nanosilicon and Carbon Black

Two processes involving UNP are performed in the fumehood. One involves weighing dry silicon nanopowder and placing the weighed material on a copper substrate using a metal spatula; the other involves funneling dry powder, such as carbon black or nanosilicon, into a volumetric flask. In Phase I, EM analysis of the starting bulk nanosilicon and carbon black materials confirmed that the primary particles comprising the nanosilicon and carbon black structures were composed of nanoparticles (Casuccio et al. 2009a).

5.2.2 Results for Nanosilicon Process

5.2.2.1 Preliminary Control Band Assignment

In Phase II, a preliminary Level III control band was assigned to this process based on an assumed “unknown” (Category D) worker/environmental hazard and a “low” (Category 2) release/exposure probability (refer to Fig. 2-1). The release/exposure probability for nanosilicon was determined (without considering any LBNL current controls) based on the nature of the material which is used as a dry powder composed of agglomerations of ultra-fine particles and which is used in small quantities for a short duration of time (< 10 min) on an infrequent basis (once per month). Upon additional review, it was determined that although the process is performed infrequently, the release/exposure potential should be considered as “likely” (Category 3) since control banding is a conservative approach to risk assessment. Assuming a “likely” release/exposure probability (Category 3), Level IV controls would be recommended based on the control banding strategy used in this report.

Level II controls were noted for this process based on work practices and controls observed during the evaluation of the laboratory in Phase I, which suggests additional process controls are needed. To validate

the preliminary control band, the process was monitored for worker exposure and emissions to the outdoor environment of UNP in Phase III.

5.2.2.2 Sampling during the Research Process

Sampling of this fumehood process involving nanosilicon powder was performed in Building 70 Laboratory 299 on April 21, 2010. Photographs showing the locations of the source, worker exposure and laboratory background samplers, and work performed during the sampling of the nanosilicon process are provided in Appendix F.

5.2.2.3 Comparison of Background, Worker Location, and Process Samples

The results obtained from the direct-reading instruments located in the fumehood indicated that particle concentrations varied from about 1,600 to 2,300 p/cm³ with an average of 2,024 (s.d. 181) whereas the laboratory background concentrations varied from about 1,800 to 2,600 p/cm³ with an average of 2,229 (s.d. 237) during the sampling period. A plot illustrating the particle concentrations in the size range of 10–300 nm and the relationship of the hood (source) concentrations to the laboratory background is provided in Fig. 5-3. Note that laboratory background data discussed here and presented in Fig. 5-3 have been adjusted to account for instrument bias (10.6%) observed during the side-by-side instrument testing (see Section 4.0).

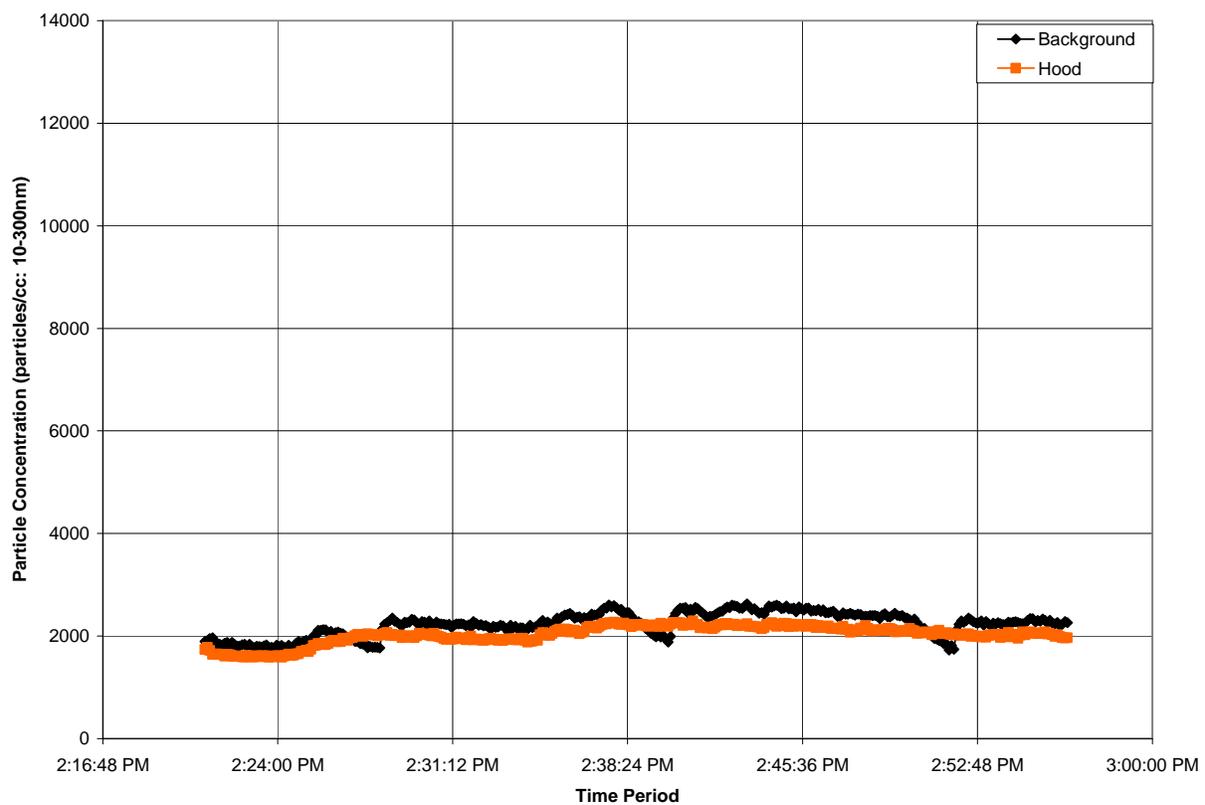


Figure 5-3 Direct-reading Particle Concentration Results for Nanosilicon Process

Review of the data presented in Fig. 5-3 shows that the particle concentrations recorded by both the hood and laboratory background direct-reading instruments tracked closely during the test. An interesting periodic pattern can be observed in the laboratory background data that may be related to the building ventilation system turning on and off. Based on the direct-reading instruments, background particle concentrations were higher throughout most of the test than those measured in the hood.

A statistical evaluation (one-tailed t-test with $\alpha = 0.05$) was conducted on paired particle concentration data to determine whether the fumehood (source) concentrations were statistically different from the laboratory background measurements. Results of the t-test indicate that the fumehood concentrations were significantly less than the background measurements (p-value < 0.0001).

Gravimetric analysis of the filtration-based samples collected using an open-face cassette indicates that total dust measurements at the source, worker, and laboratory background locations were below detection limits ($< 5 \times 10^{-2}$ mg); thus the total dust concentration at the worker location based on the volume of sample collected was < 0.22 mg/m³. More information related to the total dust analysis can be found in Appendix A. The ICP-AES results for silicon at the source, worker, and laboratory background locations were below detection limits ($< 2.5 \times 10^{-2}$ mg). The silicon concentration at the worker location based on volume of air sampled was < 0.11 mg/m³. More information related to the ICP-AES analysis can be found in Appendix B.

The EM analysis, performed on a PC filter collected in an open-face manner, was focused on identifying nanosilicon particles. The identification was based on information obtained from the analysis of the starting source material, which indicated that the nanosilicon particles were composed of aciniform structures consisting of rounded, often spherical primary particles. While the majority of aciniform structures had dimensions on the order of micrometers, the primary particles were typically between 10 and 50 nm (Casuccio et al. 2009a). A summary of the EM results is provided below in Table 5-5. Results indicate that the background sample had the highest concentrations in the < 0.5 μm and $0.5\text{--}2$ μm size fractions. No nanosilicon particles were detected on the worker sample. More information related to the EM analysis can be found in Appendix C.

Table 5-5 Summary of Electron Microscopy Results for Nanosilicon Process

Sample Type	Concentration by Particle Size (particles/cm ³)		
	> 2 μm	0.5–2 μm	< 0.5 μm
Laboratory Background	1×10^{-3}	4×10^{-2}	123.0
Worker Location	$< 2 \times 10^{-3}$	$< 4 \times 10^{-2}$	< 65.8
Hood (Source) Location	1×10^{-3}	$< 4 \times 10^{-2}$	< 62.3

5.2.2.4 Estimation of Potential Worker Exposure Concentrations

There are no ACGIH or OSHA values for nanosilicon powder. The ACGIH TLV for silicon is 10 mg/m³. The OSHA PEL for silicon is 10 mg/m³ (total dust) and 5 mg/m³ (respirable fraction). As is common with

research activities, the research task is performed only a few minutes a day, once a month; therefore the daily TWA exposures and the weekly dose of UNP are a fraction of the exposure determined while the researcher performs the task. When calculating the 8-hour TWA for UNP, no exposure is attributed to work activities when the researcher is not working with nanosilicon (based on interviews with the researchers exposure to nanosilicon is not credible during these periods).

The extrapolated 8-hour TWA exposure for total dust was $< 1.7 \times 10^{-2} \text{ mg/m}^3$. The 8-hour TWA for silicon based on the ICP-AES results was $< 8 \times 10^{-3} \text{ mg/m}^3$. The 8-hour TWAs for nanosilicon based on the EM results are reported as $< 1.5 \times 10^{-4} \text{ p/cm}^3$ ($> 2 \text{ }\mu\text{m}$), $< 3.0 \times 10^{-3} \text{ p/cm}^3$ ($0.5\text{--}2 \text{ }\mu\text{m}$), and $< 4.9 \text{ p/cm}^3$ ($< 0.5 \text{ }\mu\text{m}$).

The 8-hour TWA values should be considered conservative since sampling was performed over an extended time period (approximately 3 times the normal research process duration). Sampling time was extended to increase the mass of the collected particulate matter to improve the limits of detection. When researchers' work duration is the normal process time (< 10 minutes), the workday (8 hour) exposure would be approximately 1/3 of those calculated.

5.2.2.5 Estimation of Potential Emissions to the Outdoor Environment

No emissions to the outdoor environment of nanosilicon are indicated when the direct-reading and EM data are compared to the laboratory background data. Since no UNP emissions were measured at the source, there is no impact of UNP on the outdoor environment.

5.2.2.6 Summary of Results

Based on the review of the direct-reading and analytical data, the preliminary Level IV control band is not needed for this process. Level II controls, which are in place for this process, are adequate based on results obtained in this study. Worker exposure and laboratory background monitoring demonstrates that the researcher was not exposed to significant airborne UNP during sampling of the nanosilicon process (worker exposure was less than background). Similar exposure results are expected for similar processes (using similar work practices and similar types and quantities of nanosilicon) performed with similar controls.

From an environmental perspective, since no UNP emissions were measured at the source or in the fumehood HEPA filtration is not required to control emissions of UNP to the outdoor environment for this and similar research processes.

5.2.3 Results for Carbon Black Process

5.2.3.1 Preliminary Control Band Assignment

Although this process was not demonstrated in this location in Phase I, a preliminary Level I control band is appropriate for this type of process assumed "medium" (Category B) worker/environmental hazard and a "low" (Category 2) release/exposure probability (refer to Fig. 2-1). The release/exposure probability for carbon black was determined (without considering any LBNL current controls) based on the nature of the

material which is used as a dry powder and composed of agglomerations of nanoparticles and used in small amounts for short durations of time (< 5 min; 2 times per week).

This process could be assigned to a Level I control band (which indicates only a low level of control is required for this process), but at LBNL it is a requirement to conduct work that could generate engineered nanomaterials in fumehoods, gloveboxes, or other enclosures (LBNL 2010). Therefore the minimum control for this work with nanomaterials would be a functioning laboratory hood (Level II).

Level II controls were noted for this process based on work practices and controls observed during the evaluation of the laboratory in Phase I, which suggests that the controls match the risks. To validate the preliminary control band, the process was monitored for worker exposure and emissions to the outdoor environment of UNP in Phase III.

5.2.3.2 Sampling during the Research Process

Sampling of the carbon black process was performed in the fumehood in Building 70 Laboratory 218 on April 22, 2010. All process activity took place in the fumehood. Photographs showing the locations of the source, worker exposure and laboratory background samplers, and work performed during the sampling of the carbon black process are provided in Appendix G.

5.2.3.3 Comparison of Background, Worker Location, and Process Samples

The results obtained from the direct-reading instruments located in the fumehood indicated that particle concentrations varied from about 2,200 to 3,100 p/cm³ with an average of 2,703 (s.d. 253) whereas the laboratory background concentrations varied from about 2,100 to over 3,300 p/cm³ with an average of 2,766 (s.d. 286) during the sampling period. A plot illustrating the particle concentrations in the size range of 10–300 nm and the relationship of the hood (source) concentrations to the laboratory background is provided in Fig. 5-4. Note that laboratory background data discussed here and presented in Fig. 5-4 have been adjusted to account for instrument bias (10.6%) observed during the side-by-side instrument testing (see Section 4.0).

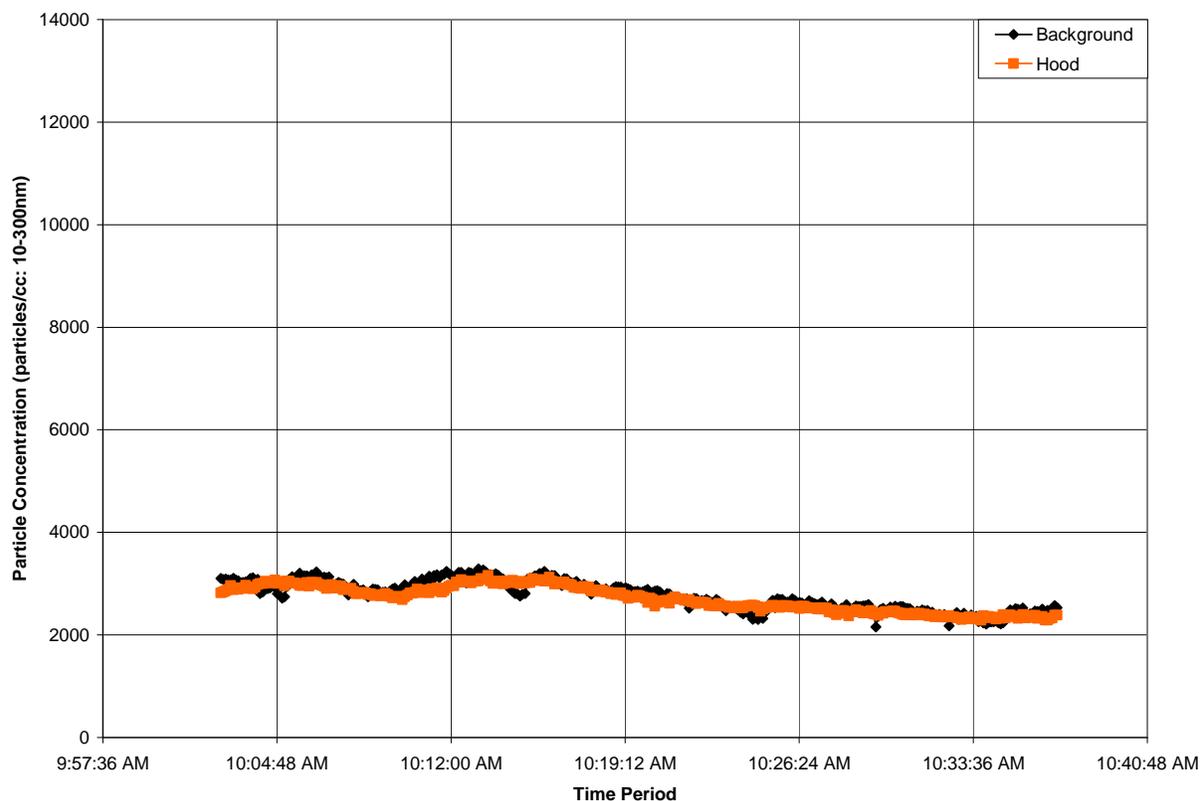


Figure 5-4 Direct-reading Particle Concentration Results for Carbon Black Process

Review of the data presented in Fig. 5-4 shows that the particle concentrations recorded by both the hood and laboratory background direct-reading instruments tracked closely during the entire test. Similar to the test on nanosilicon powder conducted in Building 70 Lab 299 (see Fig. 5-3), an interesting periodic pattern can be observed in the laboratory background data that may be related to the building ventilation system turning on and off.

A statistical evaluation (one-tailed t-test with $\alpha = 0.05$) was conducted on paired particle concentration data to determine whether the fumehood (source) concentrations were statistically different from the laboratory background measurements. Results of the t-test indicate that the fumehood concentrations were significantly less than the background measurements (p-value < 0.0001).

Gravimetric analysis of the filtration-based samples collected in a close-face manner (based on recommendations from LBNL Industrial Hygiene Group staff) indicates that the total dust measurements at the source, worker, and laboratory background locations were below detection limits ($< 5 \times 10^{-2}$ mg); thus the total dust concentration at the worker location based on volume of air sampled was < 0.234 mg/m³. More information related to the total dust analysis can be found in Appendix A.

The EM analysis, performed on a PC filter collected in an open-face manner, was focused on identifying carbon black particles. Identification of carbon black was based on information obtained from the analysis of the starting source material, which indicated that the carbon black was composed of aciniform

structures consisting of rounded and irregularly shaped particles. While the majority of aciniform structures had dimensions on the order of micrometers, the primary particles typically were 30–40 nm (Casuccio et al. 2009a). Although the EM analysis was focused on particles that had characteristics of carbon black, particles with similar characteristics, including acetylene black and soot, could be included in the EM results, so the carbon black particle concentrations may be overestimated by the EM measurements. A summary of the EM results is provided below in Table 5-6. Results were similar for each sample in each size fraction. More information related to the EM analysis can be found in Appendix C.

Table 5-6 Summary of Electron Microscopy Results for Carbon Black Process

Sample Type	Concentration by Particle Size (particles/cm ³)		
	> 2 μm	0.5–2 μm	< 0.5 μm
Laboratory Background	3 × 10 ⁻³	0.4	320.6
Worker Location	3 × 10 ⁻³	0.5	480.4
Hood (Source) Location	2 × 10 ⁻³	0.2	473.7

5.2.3.4 Estimation of Potential Worker Exposure Concentrations

The OSHA PEL and the ACGIH 8-hour TLV for carbon black are 3.5 mg/m³ as a TWA for 8 hours per day during a 40-hour work week. As is common with research activities, the research task is performed only minutes a day, twice a week; therefore the daily TWA exposures and the weekly dose of UNP are a fraction of the exposure determined while the researcher performs the task. When calculating the 8-hour TWA, no exposure is attributed to work activities when the researcher is not working with carbon black (based on interviews with researchers exposure to carbon black is not credible during these periods).

The extrapolated 8-hour TWA exposure for total dust was < 1.7 × 10⁻² mg/m³. The 8-hour TWAs for the worker sample for carbon black based on the EM results are reported as 2.2 × 10⁻⁴ p/cm³ (> 2 μm), 3.6 × 10⁻² p/cm³ (0.5–2 μm), and 35 p/cm³ (< 0.5 μm).

The 8-hour TWA values should be considered conservative since sampling was performed over an extended time period (approximately 6 times the normal research process duration). Sampling time was extended to increase the mass of the collected particulate matter to improve the limits of detection. When researchers' work duration is the normal process time (< 5 minutes), the workday (8 hour) exposure would be approximately 1/6 of those calculated.

5.2.3.5 Estimation of Potential Emissions to the Outdoor Environment

Comparison of direct-reading air concentrations (laboratory background data compared to data obtained at the source in the hood while the researcher was handling carbon black) show no statistically significant increase in particles that could be emitted to the outdoor environment (see Section 5.2.3.3). This observation is supported by the EM results which indicate that the carbon black particle concentration at

the source location during the handling operation was only a few hundred particles/cm³ above background levels (see Table 5-6).

An approach suggested by Hoover (2010) and applied in the CRC Press handbook edited by Hoover and Maiello (2010) was used to convert the EM results into an estimate of emissions to the outdoor environment. This calculation assumes the following:

- Any carbon-black-like particles observed in the hood at levels above background concentrations were actually released during the handling operation.
- The density of carbon black is 1.75 g/cm³.
- The particles are spherical in morphology.
- The largest observed particle on the filter sample (3 μm diameter) represents the diameter of carbon black particles identified as greater than 2 μm.
- 2 μm is a conservative estimate of the diameter of all particles in the size range from 0.5 to 2 μm.
- 0.5 μm is a conservative estimate of the diameter of all particles less than 0.5 μm.

The total estimated carbon black available for emission to the outdoor environment can be calculated as the sum of three components, one for each size range identified by EM, as follows. Note that for two size ranges (> 2 μm and 0.5–2 μm) the estimated concentration is zero, since the laboratory background measurement was greater than the hood (source) location measurement. The calculation is thus reduced to a single equation.

$$(153 \text{ particles/cm}^3) \times (10^6 \text{ cm}^3/\text{m}^3) \times (\pi) \times [(0.5 \text{ } \mu\text{m})^3/6] \times (10^{-12} \text{ cm}^3/\mu\text{m}^3) \times (1.75 \text{ g/cm}^3/\text{particle}) \times (10^3 \text{ mg/g}) = 1.8 \times 10^{-2} \text{ mg/m}^3.$$

Assuming that carbon black particles were released at this concentration over a 10-minute period as a plume with a cross-sectional area of 0.25 m² (0.5 m wide and 0.5 m high) with a linear velocity of 100 ft/min (30.5 m/min), the total mass of the release is estimated to be

$$(1.8 \times 10^{-2} \text{ mg/m}^3) \times (0.25 \text{ m}^2) \times (30.5 \text{ m/min}) \times (10 \text{ min}) = 1.4 \text{ mg}$$

Dispersion of the material to locations beyond the LBNL fence (offsite) was modeled using the EPIcode Gaussian plume model, which has been evaluated by DOE and is included in the DOE safety software central registry (Homann 2003). For a 10-minute release of carbon black under typical LBNL meteorological conditions, the maximum particle concentration offsite (160 m from a centrally located stack) is conservatively estimated to be approximately $6.0 \times 10^{-7} \text{ mg/m}^3$.

5.2.3.6 Comparison of Potential Offsite Concentration to Environmental Standards

Although no regulations have been established related to the levels of environmental emissions that would necessitate use of HEPA filtration for UNP, it is useful to compare estimated potential offsite concentrations to existing standards and OELs, such as the OSHA PEL established for larger particles, as shown in Table 5-7.

One approach is to compare the estimated maximum offsite concentration of carbon black to the EPA's 24-hour PM_{2.5} NAAQS of 3.5×10^{-2} mg/m³. Using this approach, the estimated maximum concentration of carbon black (6.0×10^{-7} mg/m³) would make an insignificant contribution (1.7×10^{-3} %) to the allowable 24-hour PM_{2.5} standard (see Table 5-7).

A second approach is to scale the current OSHA PEL for carbon black, 3.5 mg/m³ (using a “size adjustment” factor to account for the nanoparticle component and a “reduction factor” for public exposure) to estimate a comparative environmental concentration. A size adjustment factor of 6.6×10^{-2} has been described in the European Agency for Safety and Health at Work literature review (EU-OSHA 2009), based on the draft NIOSH report “Evaluation of Health Hazard and Recommendations for Occupational Exposure to Titanium Dioxide” (NIOSH 2005) and the British Standards Institute guide to handling nanomaterials (BSI 2007). A value of 5×10^{-2} can be used as one possible reduction factor for public exposure based on the comparison of the EPA environmental limit of 1×10^{-2} µg/m³ for beryllium compared to the corresponding beryllium OEL of 2 µg/m³ at the time the EPA limit was established. Using the PEL value, size adjustment factor, and public exposure reduction factor, an environmental concentration limit can be calculated as follows:

$$(3.5 \text{ mg/m}^3) \times (6.6 \times 10^{-2}) \times (5 \times 10^{-2}) = 1.2 \times 10^{-2} \text{ mg/m}^3$$

The maximum offsite concentration of carbon black estimated at 6.0×10^{-7} mg/m³ represents just 5×10^{-3} % of the scaled OSHA PEL of 1.2×10^{-2} mg/m³ (see Table 5-7).

A third approach involves comparing the estimated maximum offsite concentration of carbon black to limits for release of carbon black established by the Bay Area Air Quality Management District (BAAQMD) at 10 pounds/day and 150 pounds/year. Comparison of the estimated maximum offsite concentration to the BAAQMD limits indicates that the emissions to the outdoor environment of carbon black are a small fraction of the allowable limits (see Table 5-7, where the yearly estimated maximum offsite concentration was based on the process being performed two times a week for 50 weeks a year).

Table 5-7 Comparison of Estimated Maximum Emissions to the Outdoor Environment of Carbon Black to Various Criteria

Comparison Criterion	Comparison Value	Estimated LBNL Maximum Offsite Concentration	Ratio of LBNL Value to Comparison Value
EPA 24-hr standard for PM _{2.5}	3.5×10^{-2} mg/m ³	6.0×10^{-7} mg/m ³	1.7×10^{-5}
Scaled environmental concentration value for carbon black based on a PEL of 3.5 mg/m ³	1.2×10^{-2} mg/m ³	6.0×10^{-7} mg/m ³	5.0×10^{-5}
Airborne carbon black concentration based on the BAAQMD Level of Significance	10 pounds/day	3.1×10^{-6} pounds/day	3.1×10^{-7}
	150 pounds/year	4.6×10^{-4} pounds/year	3.1×10^{-6}

5.2.3.7 Summary of Results

Based on the review of the direct-reading and analytical data, the preliminary Level II control band is validated for this process. Worker exposure and laboratory background monitoring demonstrates that the researcher was not exposed to significant airborne UNP during sampling of the carbon black process. Similar exposure results are expected for similar processes (using similar work practices and similar types and quantities of carbon black) performed with similar controls.

From an environmental perspective, results indicate that there is a potential for negligible emissions of UNP to the outdoor environment via the ventilation duct. The maximum offsite concentration for this process is estimated at 6.0×10^{-7} mg/m³, which is orders of magnitude lower than applicable standards or a size-scaled PEL. These results indicate that HEPA filtration is not required to control emissions of UNP to the outdoor environment for this and similar research processes.

5.3 Don Lucas: Building 70, Labs 291/293

5.3.1 Research Involving Detection of Toxic Species Using Nanogold Particles

Gold nanorods and nanospheres are applied to a substrate and evaluated for their efficiency as an enhanced method for detection of mercury gas. Milligram quantities of input materials (gold rods and spheres) are obtained in an aqueous solution and manipulated within a fumehood. Sonication of the aqueous solution is performed on a countertop. In Phase I, EM analysis confirmed that the nanogold particles were composed of particles with dimensions less than 100 nm (Casuccio et al. 2009a)

5.3.2 Results for Nanogold Process

5.3.2.1 Preliminary Control Band Assignment

In Phase II, a preliminary Level II control band was assigned to this process based on an assumed “high” (Category C) worker/environmental hazard and a “low” (Category 2) release/exposure probability (refer to Fig. 2-1). The release/exposure probability was determined (without considering any LBNL current controls) based on the nature of the material which is contained in an aqueous solution and is used in small quantities for a short time duration (< 10–15 min; 1–5 times per week).

Level II controls were noted for this process based on work practices and controls observed during the evaluation of the laboratory in Phase I, which suggests that the controls match the risk. To validate the preliminary control band, the process was monitored for worker exposure and emissions to the outdoor environment of UNP in Phase III.

5.3.2.2 Sampling during the Research Process

Sampling of the nanogold process was performed on April 23, 2010. Process activity took place in the fumehood and on the countertop (centrifuge). Photographs showing the locations of the source, worker exposure and laboratory background samplers, and work performed during the sampling of the gold nanoparticle process are provided in Appendix H.

5.3.2.3 Comparison of Background, Worker Location, and Process Samples

The results obtained from the direct-reading instruments located in the fumehood indicated that particle concentrations varied from about 4,300 to 7,200 p/cm³ with an average of 5663 (s.d. 804) whereas the laboratory background concentrations varied from about 3,700 to 7,800 p/cm³ with an average of 5,927 (s.d. 926) during the sampling period. A plot illustrating the particle concentrations in the size range of 10–300 nm and the relationship of the hood (source) concentrations to the laboratory background is provided in Fig. 5-5. Note that laboratory background data discussed here and presented in Fig. 5-5 have been adjusted to account for instrument bias (10.6%) observed during the side-by-side instrument testing (see Section 4.0).

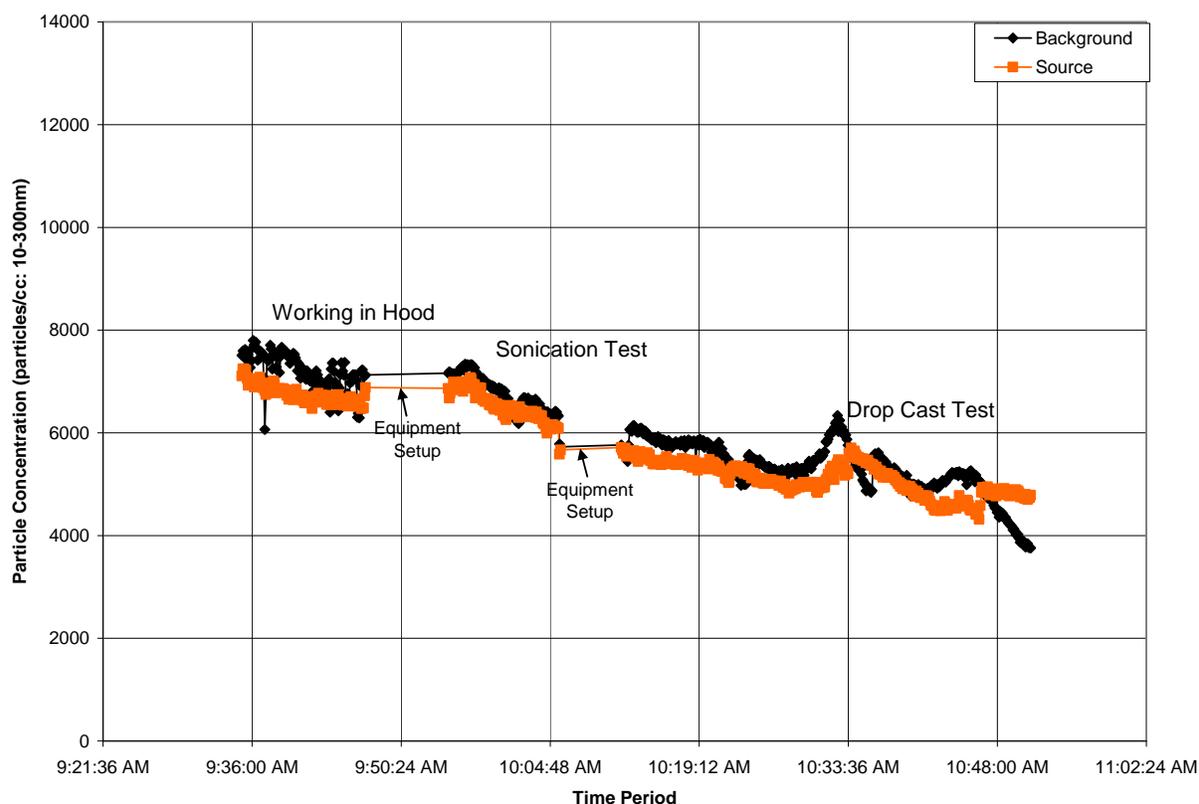


Figure 5-5 Direct-reading Particle Concentration Results for Gold Nanoparticle Process

Review of the data presented in Fig. 5-5 shows that the particle concentrations recorded by both the hood and laboratory background direct-reading instruments tracked closely during the entire test, with the background sampler generally recording slightly higher concentrations than the hood monitor.

A statistical evaluation (one-tailed t-test with $\alpha = 0.05$) was conducted on paired particle concentration data to determine whether the fumehood (source) concentrations were statistically different from the laboratory background measurements. Results of the t-test indicate that the fumehood concentrations were significantly less than the background measurements (p-value < 0.0001).

Gravimetric analysis of the filtration-based samples collected in a close-face manner (based on recommendations from LBNL Industrial Hygiene Group staff) indicates that total dust measurements at the source, worker, and laboratory background locations were below detection limits ($< 5 \times 10^{-2}$ mg); thus the total dust concentration at the worker location based on volume of air sampled was < 0.11 mg/m³. More information related to the total dust analysis can be found in Appendix A. The ICP-AES results for gold at the source, worker, and laboratory background locations were below detection limits ($< 2.5 \times 10^{-4}$ mg). The gold concentration at the worker location based on volume of air sampled was $< 5.5 \times 10^{-4}$ mg/m³. More information related to the ICP-AES analysis can be found in Appendix B.

The EM analysis, performed on a PC filter collected in an open-face manner, was focused on identifying nanogold particles. Identification of nanogold particles was based on information obtained from the analysis of the starting source material, which indicated that the particles were composed of rod-shaped particles with dimensions approximately 20 nm in diameter and approximately 50 nm in length, and rounded and spherical particles that were approximately 40–50 nm in diameter (Casuccio et al. 2009a). A summary of the EM results is provided below in Table 5-8. No nanogold particles were detected in any size fraction. More information related to the EM analysis can be found in Appendix C.

Table 5-8 Summary of Electron Microscopy Results for Gold Nanoparticle Process

Sample Type	Concentration by Particle Size (particles/cm ³)		
	> 2 μ m	0.5–2 μ m	< 0.5 μ m
Laboratory Background	$< 1 \times 10^{-3}$	$< 2 \times 10^{-2}$	< 31.6
Worker Location	$< 1 \times 10^{-3}$	$< 2 \times 10^{-2}$	< 35.0
Hood (Source) Location	$< 1 \times 10^{-3}$	$< 2 \times 10^{-2}$	< 33.2

5.3.2.4 Estimation of Potential Worker Exposure Concentrations

There are no OSHA PEL or American Institute of Chemical Engineers (AIChE) values for nanogold or gold. Using silver as a conservative surrogate, the ACGIH TLV is 0.1 mg/m³ (TWA), and the OSHA PEL is 1×10^{-2} mg/m³ (TWA). As is common with research activities, the research task is performed only 10 to 15 minutes a day, a few times per week; therefore the daily TWA exposures and the weekly dose of UNP are a fraction of the exposure determined while the researcher performs the task. When calculating the 8-hour TWA for UNP, no exposure is attributed to work activities when researchers are not working with nanogold particles (based on interviews with the researchers exposure to nanogold is not credible during these periods).

The extrapolated 8-hour TWA exposure for total dust was $< 1.7 \times 10^{-2}$ mg/m³. The 8-hour TWA for gold based on the ICP-AES results was $< 8.3 \times 10^{-5}$ mg/m³. The 8-hour TWAs for nanogold particles based on the EM results are reported as $< 1.5 \times 10^{-4}$ p/cm³ (> 2 μ m), $< 3.0 \times 10^{-3}$ p/cm³ (0.5–2 μ m), and < 4.81 p/cm³ (< 0.5 μ m).

The 8-hour TWA values should be considered conservative since sampling was performed over an extended time period (approximately 4–6 times the normal research process duration). Sampling time was extended to increase the mass of the collected particulate matter to improve the analytical limits of detection. When researchers' work duration is the normal process time, the workday (8 hour) exposure would be approximately 1/4 to 1/6 of those calculated.

5.3.2.5 Estimation of Potential Emissions to the Outdoor Environment

No emissions to the outdoor environment of nanogold are indicated when the direct-reading and EM data are compared to laboratory background data. Since no UNP emissions were measured at the source, there is no impact of UNP on the outdoor environment.

5.3.2.6 Summary of Results

Based on the review of the direct-reading and analytical data, the preliminary Level II control band is validated for this process. Worker exposure and laboratory background monitoring demonstrates that the researcher was not exposed to significant airborne UNP during sampling of the nanogold process. Similar exposure results are expected for similar processes (using similar work practices and similar types and quantities of nanogold) performed with similar controls.

From an environmental perspective, since no UNP emissions were measured at the source HEPA filtration is not required to control emissions of UNP to the outdoor environment for this and similar processes.

6.0

Evaluation of Worker Exposure and Emissions to the Outdoor Environment: Processes Involving Fumehoods Tested with the Kelly Enclosure

Two research processes involving the use of UNP in fumehoods discussed in Section 5.0 were evaluated using a low-background HEPA-filtered enclosure developed by Rick Kelly (LBNL). Results are discussed below. Note that laboratory background filter samples were collected outside of the enclosure (as discussed in Section 4.0).

6.1 Vincent Battaglia: Building 70, Labs 299 and 218

6.1.1 Results for Nanosilicon Process Performed in Enclosure

6.1.1.1 Sampling during the Research Process

Testing of this process was performed in a fumehood in Building 70 Laboratory 299. Sampling of the process involving nanosilicon powder in the enclosure was performed on April 21, 2010 (testing of this process without the enclosure was performed on April 19, 2010; see Section 5.2.2). All process activity took place in the fumehood within the enclosure. Photographs showing the locations of the source, worker exposure and laboratory background samplers, and work performed during the sampling of the nanosilicon process are provided in Appendix I.

6.1.1.2 Comparison of Background, Worker Location, and Process Samples

The results obtained from the direct-reading instruments located in the fumehood indicated that particle concentrations varied from about 4 to 348 p/cm³ with an average of 73 (s.d. 42) whereas the enclosure background concentrations varied from about 27 to 248 p/cm³ with an average of 116 (s.d. 40) during the sampling period. A plot illustrating the particle concentrations in the size range of 10–300 nm and the relationship of the hood (source) concentrations to the laboratory background is provided in Fig. 6-1. Note that laboratory background data discussed here and presented in Fig. 6-1 have been adjusted to account for instrument bias (10.6%) observed during the side-by-side instrument testing (see Section 4.0).

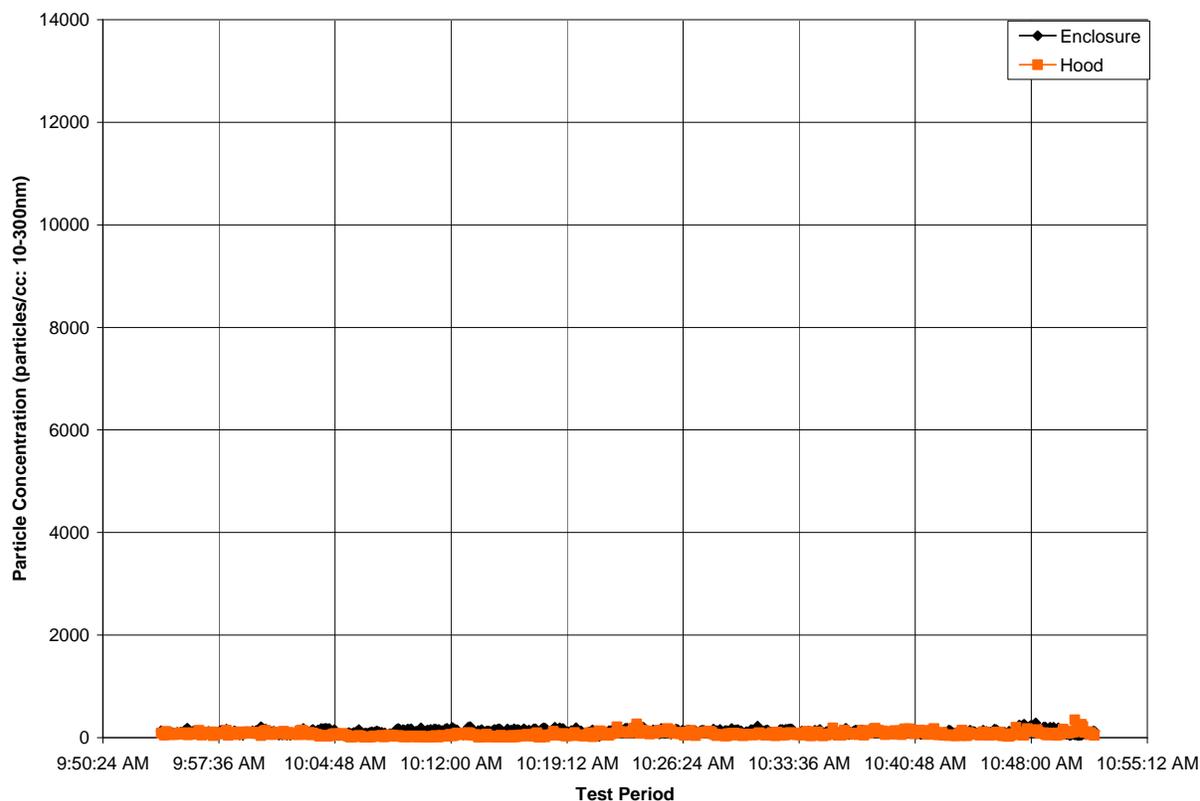


Figure 6-1 Direct-reading Particle Concentration Results for Nanosilicon Process in Enclosure

Review of the data presented in Fig. 6-1 shows that the particle concentrations recorded by both the hood and laboratory background direct-reading instruments tracked closely during the duration of the test and the values for both the hood and the enclosure were at extremely low particle concentrations. A statistical evaluation (one-tailed t-test with $\alpha = 0.05$) was conducted on paired particle concentration data to determine whether the fumehood (source) concentrations were statistically different from the laboratory background measurements. Results of the t-test indicate that the fumehood concentrations were significantly less than the background measurements (p-value < 0.0001).

Gravimetric analysis of the filtration-based samples collected using an open-face cassette indicates that total dust measurements in the hood (source), worker, and laboratory background locations were below detection limits ($< 5 \times 10^{-2}$ mg); thus the total dust concentration for the worker sample based on volume of sample collected was < 0.139 mg/m³. More information related to the total dust analysis can be found in Appendix A. The ICP-AES results for silicon at the source, worker, and laboratory background locations were below detection limits ($< 2.5 \times 10^{-2}$ mg). The silicon concentration for the worker sample based on volume of air sampled was $< 7 \times 10^{-2}$ mg/m³. More information related to the ICP-AES analysis can be found in Appendix B.

The EM analysis, performed on a PC filter collected in an open-face manner, was focused on identifying nanosilicon particles. A summary of the EM results is provided below in Table 6-1. Results indicate that the laboratory background sample (outside of the enclosure) had the highest concentrations in the

< 0.5 μm and 0.5–2 μm size fractions. More information related to the EM analysis can be found in Appendix C.

Table 6-1 Summary of Electron Microscopy Results for Nanosilicon Process in Enclosure

Sample Type	Concentration by Particle Size (particles/cm ³)		
	> 2 μm	0.5–2 μm	< 0.5 μm
Background (outside enclosure)	1×10^{-3}	0.1	114.6
Worker Exposure (in enclosure)	1×10^{-3}	5×10^{-2}	< 41.4
Source (in enclosure)	1×10^{-3}	4×10^{-2}	38.7

6.1.1.3 Estimation of Potential Worker Exposure Concentrations

The extrapolated 8-hour TWA for total dust was $< 1.4 \times 10^{-2} \text{ mg/m}^3$. The extrapolated 8-hour TWA for silicon based on the ICP-AES results was $< 8 \times 10^{-3} \text{ mg/m}^3$. The extrapolated 8-hour TWAs for fumed silica based on the EM results are reported as $< 1.2 \times 10^{-4} \text{ p/cm}^3$ (> 2 μm), $< 6 \times 10^{-3} \text{ p/cm}^3$ (0.5–2 μm), and $< 5.0 \text{ p/cm}^3$ (< 0.5 μm).

The 8-hour TWA values should be considered conservative since sampling was performed over an extended time period (at least 10 times the normal research process duration). Sampling time was extended to increase the mass of collected particulate matter to improve the limits of detection. When researchers' work duration is the normal process time, the workday (8 hour) exposure would be < 10% of those calculated.

6.1.1.4 Estimation of Potential Emissions to the Outdoor Environment

No emissions to the outdoor environment of nanosilicon are indicated when the direct-reading data and the EM results are compared to the laboratory background data. Since there were no UNP emissions to the outdoor environment for this process (source release concentrations were less than background), there is no impact of UNP on the outdoor environment.

6.1.1.5 Summary of Results

Worker exposure and laboratory background monitoring demonstrates that the researcher was not exposed to significant airborne UNP during sampling of the nanosilicon process in the enclosure. Similar exposure results are expected for similar processes performed in the enclosure (using similar work practices, types and quantities of nanosilicon) performed with similar controls.

From an environmental perspective, since no UNP emissions were measured at the source HEPA filtration is not required to control emissions of UNP to the outdoor environment for this and similar research processes.

The enclosure, while reducing the background concentrations substantially, did not result in any different conclusions related to worker exposure or emissions to the outdoor environment for this process (see Section 5.2.2).

6.1.2 Results for Carbon Black Process Performed in Enclosure

6.1.2.1 Sampling during the Research Process

Testing of this process was performed in a fumehood in Building 70 Laboratory 218. Sampling of the carbon black process in the enclosure was performed on April 22, 2010 (testing of this process without the enclosure was performed on April 19, 2010; see Section 5.2.3). All process activity took place in the fumehood within the enclosure. Photos showing the locations of the source, worker exposure and laboratory background samplers, and work performed during the sampling of the carbon black process are provided in Appendix J.

6.1.2.2 Comparison of Background, Worker Location, and Process Samples

The results obtained from the direct-reading instruments located in the fumehood indicated that particle concentrations varied from about 15 to 826 p/cm³ with an average of 123 (s.d. 107) whereas the laboratory background concentrations varied from about 2 to over 385 p/cm³ with an average of 27 (s.d. 32) during the sampling period. A plot illustrating the particle concentrations in the size range of 10–300 nm and the relationship of the hood (source) concentrations to the laboratory background is provided in Fig. 6-2. Note that laboratory background data discussed here and presented in Fig. 6-2 have been adjusted to account for instrument bias (10.6%) observed during the side-by-side instrument testing (see Section 4.0).

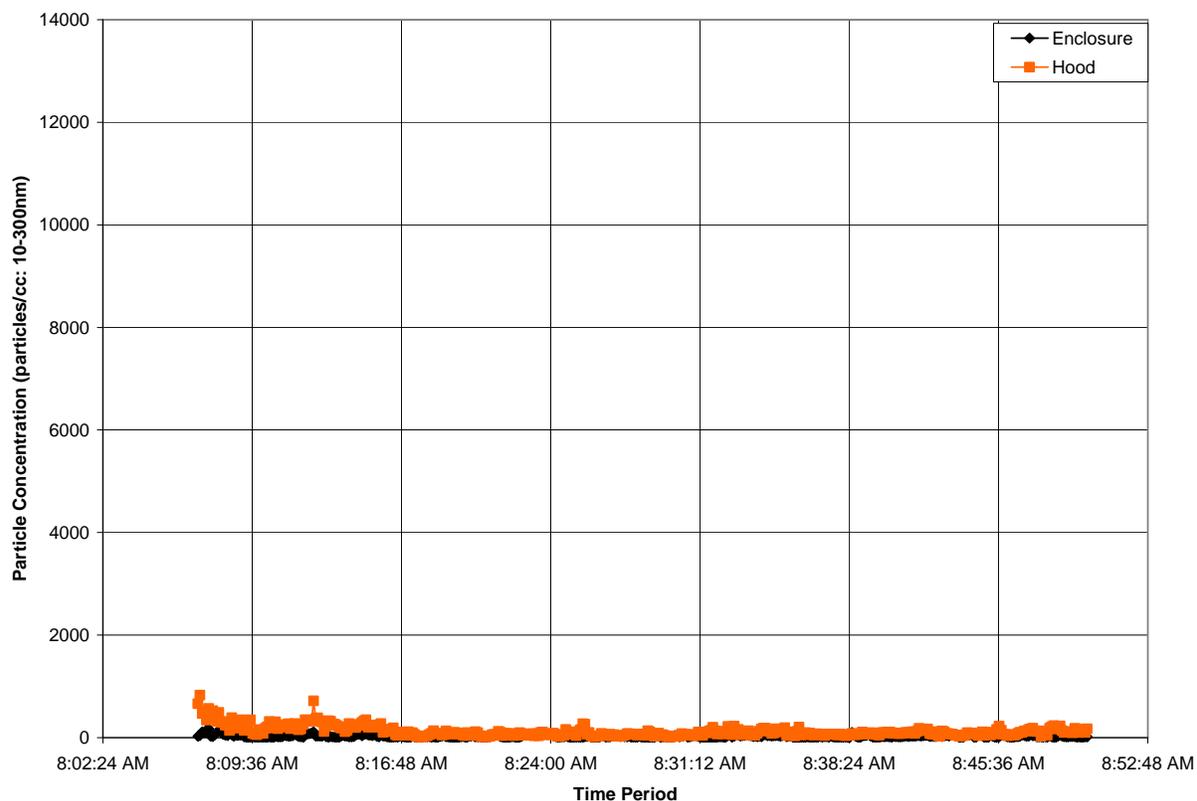


Figure 6-2 Direct-reading Particle Concentration Results for Carbon Black Process in Enclosure

Review of the data presented in Fig. 6-2 shows that the particle concentrations recorded by both the hood and laboratory direct-reading instruments tracked closely during the duration of the test and the values for both the hood and the enclosure were at extremely low particle concentrations. A statistical evaluation (one-tailed t-test with $\alpha = 0.05$) was conducted on paired particle concentration data to determine whether the fumehood (source) concentrations were statistically different from the background measurements. Results of the t-test indicate that the fumehood concentrations were significantly greater than the laboratory background measurements (p -value < 0.0001).

Gravimetric analysis of the filtration-based samples collected in a close-face manner (based on recommendations from LBNL Industrial Hygiene Group staff) indicate that total dust measurements at the source, worker, and laboratory background locations were below detection limits ($< 5 \times 10^{-2}$ mg); thus the total dust concentration for the worker sample based on volume of air sampled was < 0.242 mg/m³. More information related to the total dust analysis can be found in Appendix A.

The EM analysis performed on a PC filter collected in an open-face manner was focused on identifying carbon black particles. Although the EM analysis was focused on carbon black, other particles with similar characteristics, including acetylene black and soot, could be included in the EM results so the carbon black particle concentrations may be overestimated by the EM measurements. A summary of the EM results is provided below in Table 6-2. Results indicate that the source sample had the highest

concentrations and the worker exposure was similar to or less than background in each size fraction. More information related to the EM analysis can be found in Appendix C.

Table 6-2 Summary of Electron Microscopy Results for Carbon Black Process in Enclosure

Sample Type	Concentration by Particle Size (particles/cm ³)		
	> 2 μm	0.5–2 μm	< 0.5 μm
Background (outside enclosure)	< 1 × 10 ⁻³	4 × 10 ⁻²	249.9
Worker Exposure (in enclosure)	< 2 × 10 ⁻³	< 4 × 10 ⁻²	133.5
Source (in enclosure)	4 × 10 ⁻²	0.4	600.7

6.1.2.3 Estimation of Potential Worker Exposure Concentrations

The extrapolated 8-hour TWA for total dust was < 1.78 × 10⁻² mg/m³. The extrapolated 8-hour TWAs for carbon black based on the EM results are reported as 1.5 × 10⁻⁴ p/cm³ (> 2 μm), < 3 × 10⁻³ p/cm³ (0.5–2 μm), and 9.8 p/cm³ (< 0.5 μm).

The 8-hour TWA values should be considered conservative since sampling was performed over an extended time period (approximately 6 times the normal research process duration). Sampling time was extended to increase the mass of the collected particulate matter to improve the analytical limits of detection. When researchers' work duration is the normal process time, the workday (8 hour) exposure would be < 1/6 of those calculated.

6.1.2.4 Estimation of Potential Emissions to the Outdoor Environment

Comparison of direct-reading air concentrations (laboratory background data compared to data obtained at the source in the hood while the researcher was handling carbon black) indicate a potential small release of carbon black to the outdoor environment. This observation is supported by the EM results which indicate that the carbon black particle concentration at the source location during the handling operation was only a few hundred particles/cm³ above background levels (see Table 6-2).

An approach suggested by Hoover (2010) and applied in the CRC Press handbook edited by Hoover and Maiello (2010) was used to convert the EM results into an estimate of emissions to the outdoor environment. This calculation assumes the following:

- Any carbon-black-like particles observed in the hood at levels above background concentrations were actually released during the handling operation.
- The density of carbon black is 1.75 g/cm³.
- The particles are spherical in morphology.
- The largest observed particle on the filter sample (3 μm diameter) represents the diameter of carbon black particles identified as greater than 2 μm.
- 2 μm is a conservative estimate of the diameter of all particles in the size range from 0.5 to 2 μm.

- 0.5 μm is a conservative estimate of the diameter of all particles less than 0.5 μm .

The total estimated carbon black available for emission to the outdoor environment can be calculated as the sum of three components, one for each size range identified by EM, as follows:

$$\begin{aligned} & \{(4 \times 10^{-2} \text{ particles/cm}^3) \times (10^6 \text{ cm}^3/\text{m}^3) \times (\pi) \times [(3 \mu\text{m})^3/6] \times (10^{-12} \text{ cm}^3/\mu\text{m}^3) \times (1.75 \text{ g/cm}^3/\text{particle}) \\ & \times (10^3 \text{ mg/g})\} + \\ & \{(0.4 \text{ particles/cm}^3) \times (10^6 \text{ cm}^3/\text{m}^3) \times (\pi) \times [(2 \mu\text{m})^3/6] \times (10^{-12} \text{ cm}^3/\mu\text{m}^3) \times (1.75 \text{ g/cm}^3/\text{particle}) \times \\ & (10^3 \text{ mg/g})\} + \\ & \{(351 \text{ particles/cm}^3) \times (10^6 \text{ cm}^3/\text{m}^3) \times (\pi) \times [(0.5 \mu\text{m})^3/6] \times (10^{-12} \text{ cm}^3/\mu\text{m}^3) \times (1.75 \text{ g/cm}^3/\text{particle}) \times \\ & (10^3 \text{ mg/g})\} \end{aligned}$$

The sum of the three components is approximately $4.4 \times 10^{-2} \text{ mg/m}^3$.

Assuming that carbon black particles were released at this concentration over a 10-minute period as a plume with a cross-sectional area of 0.25 m^2 (0.5 m wide and 0.5 m high) with a linear velocity of 100 ft/min (30.5 m/min), the total mass of the release is estimated to be

$$(4.4 \times 10^{-2} \text{ mg/m}^3) \times (0.25 \text{ m}^2) \times (30.5 \text{ m/min}) \times (10 \text{ min}) = 3.4 \text{ mg}$$

Dispersion of the material to locations beyond the LBNL fence (offsite) was modeled using the EPIcode Gaussian plume model, which has been evaluated by DOE and is included in the DOE safety software central registry (Homann 2003). For a 10-minute release of carbon black under typical LBNL meteorological conditions, the maximum particle concentration offsite (160 m from a centrally located stack) is conservatively estimated to be approximately $1.5 \times 10^{-6} \text{ mg/m}^3$. The estimated impact of the carbon black on the environment is similar to the evaluation of this process performed without the enclosure (see Section 5.2.3); that is, the maximum offsite concentration is orders of magnitude lower than applicable standards or a size-scaled PEL.

6.1.2.5 Summary of Results

Worker exposure and laboratory background monitoring demonstrates that the researcher was not exposed to significant airborne UNP during sampling of the carbon black process in the enclosure. Similar exposure results are expected for similar processes performed in the enclosure (using similar work practices and similar types and quantities of carbon black) performed with similar controls.

From an environmental perspective, results obtained in this study indicate that there is a potential for negligible emissions of UNP to the outdoor environment via the ventilation duct. The maximum offsite concentration for this process is estimated at $1.5 \times 10^{-6} \text{ mg/m}^3$, which is orders of magnitude lower than applicable standards or a size-scaled PEL. These results indicate that HEPA filtration is not required to control emissions of UNP to the outdoor environment for this and similar research processes.

The enclosure, while reducing the background concentrations substantially, did not result in any different conclusions related to worker exposure or emissions to the outdoor environment for this process (see Section 5.2.3).

7.0

Evaluation of Worker Exposure and Emissions to the Outdoor Environment: Process Involving Countertop

In Phase III, one research process involving the use of UNP on a countertop was evaluated from the perspective of worker exposure as well as potential emissions to the outdoor environment. The process evaluated involved the following principal investigator and laboratory location: Robert Kostecki, Building 70, Laboratory 108.

7.1 Robert Kostecki: Building 70, Lab 108

7.1.1 Research Involving Graphene

This process involves the “thinning” of graphene, using adhesive tape to delaminate layers of graphene to a single-layer flat sheet of carbon until layers of approximately 0.3 nm are obtained. In Phase I, EM analysis indicated that layers of the graphene can be nanometers in thickness, but the other dimensions are typically in the micrometer-to-millimeter size range.

7.1.2 Results for Graphene Process

7.1.2.1 Preliminary Control Band Assignment

In Phase II, a preliminary Level I control band was assigned to the graphene process based on an assumed “low” worker/environmental hazard (Category A) and classified as an “unlikely” (Category 1) release/exposure probability (refer to Fig. 2-1). The release/exposure probability was determined (without considering any LBNL current controls) based on the nature of the material which is solid and is used in small quantities for a short time duration (< 5–10 min; 2 times per month). Further, because the process involves removing layers of the graphene using tape, it was assumed that most of the material removed in the thinning process would adhere to the tape.

Level I controls were noted for this process during the evaluation of the laboratory in Phase I, thus based on the preliminary control band assignment, controls appear to be commensurate with the degree of risk. To validate the preliminary control band, the process was monitored for worker exposure and the potential for emissions to the outdoor environment of UNP in Phase III.

7.1.2.2 Sampling during the Research Process

Sampling of the graphene process was performed on April 26, 2010. All process activity took place on the countertop. Photographs showing the locations of the source, worker exposure and laboratory background samplers, and work performed during the sampling of the gold nanoparticle process are provided in Appendix K.

7.1.2.3 Comparison of Background, Worker Location, and Process Samples

The results obtained from the direct-reading instruments located at the source indicated that particle concentrations varied from about 9,000 to 9,800 p/cm³ with an average of 9,401 (s.d. 129) whereas the laboratory background concentrations varied from about 8,100 to over 9,800 p/cm³ with an average of 9,300 (s.d. 265) during the sampling period. A plot illustrating the particle concentrations in the size range of 10–300 nm and the relationship of the hood (source) concentrations to the laboratory background is provided in Fig. 7-1. Note that laboratory background data discussed here and presented in Fig. 7-1 have been adjusted to account for instrument bias (10.6%) observed during the side-by-side instrument testing (see Section 4.0).

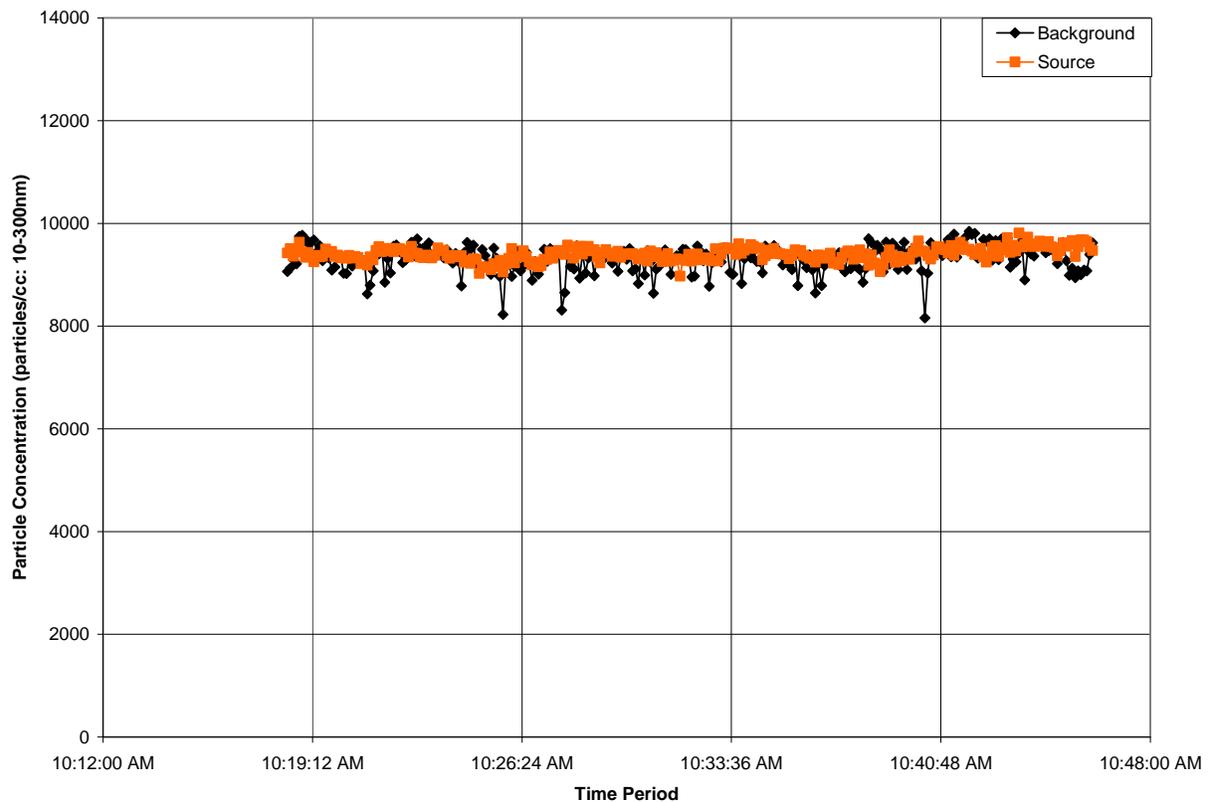


Figure 7-1 Particle Concentration Results for Graphene Process

Review of the data presented in Fig. 7-1 shows that the particle concentrations recorded by both the hood and laboratory background direct-reading instruments tracked closely during the entire test. A statistical evaluation (one-tailed t-test with $\alpha = 0.05$) was conducted on paired particle concentration data to determine whether the countertop (source) concentrations were statistically different from the laboratory background measurements. Results of the t-test indicate that the countertop concentrations were significantly greater than background measurements (p-value < 0.0001).

Gravimetric analysis of the filtration-based samples collected in a close-face manner (based on recommendations from LBNL Industrial Hygiene Group staff) indicate that total dust measurements at the source, worker, and laboratory background locations were below detection limits ($< 5 \times 10^{-2}$ mg); thus the total dust concentration based on volume of air sampled was < 0.288 mg/m³. More information related to the total dust analysis can be found in Appendix A.

The EM analysis, performed on a PC filter collected in an open-face manner, was focused on the identification of graphene particles. Identification of the graphene particles was based on information obtained from the analysis of the starting source material, which indicated that the particles were composed of thin platelets that tended to be agglomerated (Casuccio et al. 2009a). A summary of the EM results is provided below in Table 7-1. More information related to the EM analysis can be found in Appendix C.

Table 7-1 Summary of Electron Microscopy Results for Graphene Process

Sample Type	Concentration by Particle Size (particles/cm ³)		
	> 2 μ m	0.5–2 μ m	< 0.5 μ m
Laboratory Background	$< 2 \times 10^{-3}$	$< 5 \times 10^{-2}$	< 79.1
Worker Location	$< 2 \times 10^{-3}$	$< 5 \times 10^{-2}$	< 84.6
Hood (Source) Location	4×10^{-3}	$< 5 \times 10^{-2}$	< 82.3

7.1.2.4 Estimation of Potential Worker Exposure Concentrations

While graphene toxicity has not been studied from a health effects perspective, the material is chemically similar to carbon black and graphite which have low toxicity. The OSHA PEL and the ACGIH TLV for carbon black is 3.5 mg/m³ as a TWA for 8 hours per day during a 40-hour work week; for graphite, the ACGIH 8-hour TLV is 2.5 mg/m³ and the OSHA 8-hour TWA PEL is 2.5 mg/m³.

The 8-hour TWA for total dust was $< 1.6 \times 10^{-2}$ mg/m³. The 8-hour TWAs for graphene particles based on the EM results are reported as $< 1.2 \times 10^{-4}$ p/cm³ ($> 2 \mu$ m), $< 3 \times 10^{-3}$ p/cm³ (0.5–2 μ m), and < 4.9 p/cm³ ($< 0.5 \mu$ m).

The 8-hour TWA values should be considered conservative since sampling was performed over an extended time period (approximately 3 times the normal research process duration). Sampling time was extended to increase the mass of the collected particulate matter to improve the limits of detection. When researchers' work duration is the normal process time, the workday (8 hour) exposure would be $< 1/3$ of those calculated.

7.1.2.5 Estimation of Potential Emissions to the Outdoor Environment

Only two large potential graphene particles ($> 10 \mu$ m) were detected during the EM analysis. These particles were determined not to be representative of UNP based on their size. From an environmental perspective, the direct-reading and EM data do not indicate any emission of graphene UNP particles.

7.1.2.6 Summary of Results

Worker exposure and source monitoring results demonstrate that the researcher was not exposed to significant airborne UNP during sampling of the graphene process, and the preliminary Level I control band is validated for this process. Similar exposure results are expected for similar processes (using similar work practices and similar types and quantities of graphene) performed with similar controls.

From an environmental perspective, since no UNP particles were generated during the graphene process, HEPA filtration is not required to control emissions of UNP to the outdoor environment for this and similar processes.

8.0

Evaluation of Worker Exposure and Emissions to the Outdoor Environment: Process Involving Glovebox

The glovebox tested in Phase III is used for processes involving UNP for research conducted by principal investigator Kerr (Building 62 Laboratory 246). It should be noted that the glovebox is under positive pressure in a helium atmosphere during normal operations. For testing purposes, the pressure in the glovebox was reduced to minimize potential for damage of the sampling equipment. Because the glovebox in the Battaglia lab (Building 70 Laboratory 299) was not suitable for sampling (see Section 3.0), the Battaglia lab's processes using lithium in a glovebox could not be evaluated in Phase III.

8.1 John Kerr: Building 62, Lab 246

8.1.1 Research Involving Fumed Silica and Carbon (Acetylene) Black in Glovebox

This research process involves manipulation of dry nanomaterials (silica, metals, and carbon black) in milligram to gram quantities. For the glovebox samples, only emissions to the outdoor environment (from within the glovebox) were evaluated since any potential particulate release is contained within the glovebox enclosure.

8.1.1.1 Preliminary Control Band Assignment

In Phase II, a preliminary Level I control band was assigned to this process based on the use of carbon (acetylene) black, but the control band increases to Level II for work with the most hazardous material, fumed silica, which was assumed to have a "high" (Category C) worker/environmental hazard and a "low" (Category 2) release/exposure probability (refer to Fig. 2-1). For both materials, the release/exposure probability was determined (without considering any LBNL current controls) to be low because the materials (fumed silica and carbon black) are used in laboratory quantities, and the researcher is working in an enclosed, inert environment.

Level III controls were noted for this process based on work practices and controls observed during the evaluation of the laboratory in Phase I. The observed control level for this process exceeded the degree of risk based on the preliminary control band. In Phase III, the process was monitored for release of UNP within the glovebox (no worker exposure since any potential particulate release is contained within the glovebox enclosure).

8.1.1.2 Sampling during the Research Process

Sampling of the glovebox process was performed on April 20 and 23, 2010. All process activity took place within the glovebox. Photographs showing the activities related to the process involving the glovebox tests performed on April 20 and April 23 are provided in Appendix L and Appendix M.

The results obtained from the direct-reading instruments located inside the glovebox during the April 20 test indicated that particle concentrations varied from about 3 to 21,401 p/cm³ with an average of 862 (s.d. 2259). The time period from 10:27 to about 11:10 reflects particle concentrations in the glovebox when no activities were being performed, and indicates that particle concentrations were near zero. At approximately 11:10, process activity began with the opening of the passthrough door containing the fumed silica and carbon black which would be used during process operations. A spike in particle concentration to approximately 21,000 p/cm³ was noted at this time. From that time on, the particle concentrations gradually decreased while research activities were conducted with the fumed silica and carbon black materials. A second spike was noted at approximately 11:18 with particle concentrations increasing to about 9,000, however, this spike did not correlate with any process activities. The average particle concentration from 11:10 to the end of the test was 2,286 (s.d. 3224).

A plot illustrating the particle concentrations in the size range of 10–300 nm is provided in Fig. 8-1.

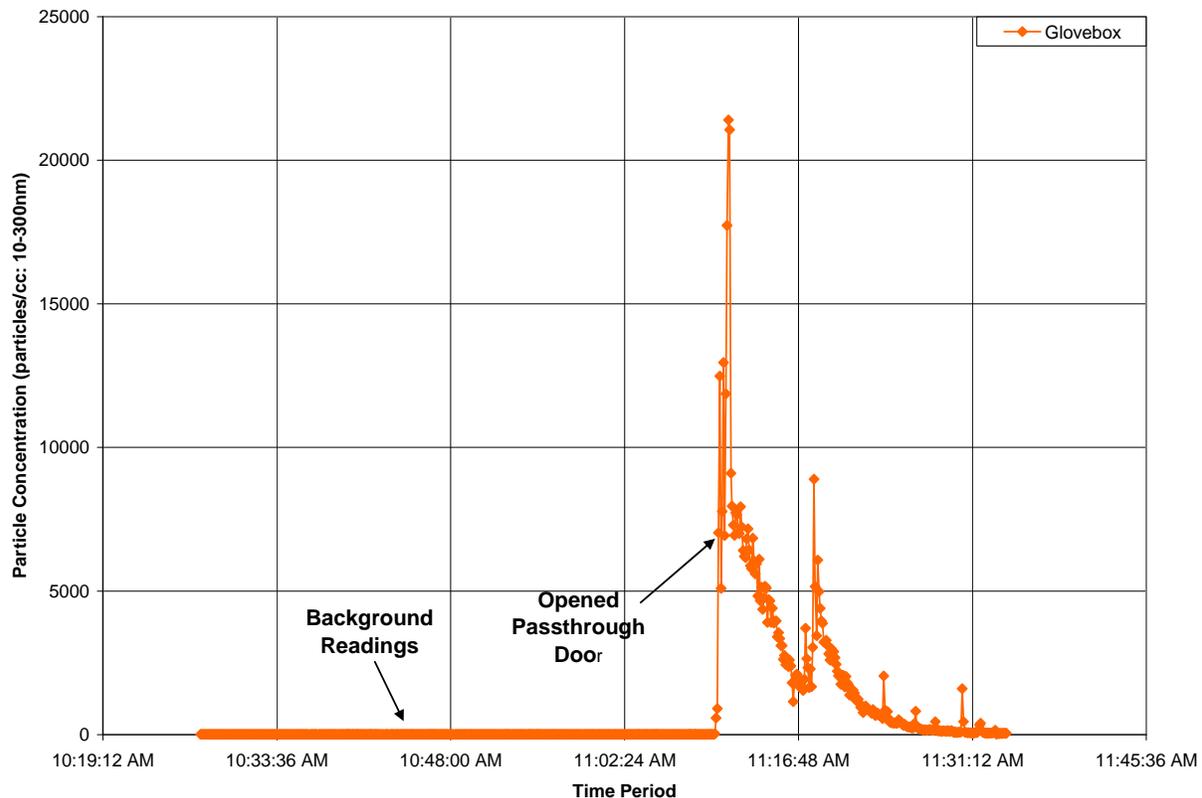


Figure 8-1 Particle Concentration Results for Glovebox Process on April 20, 2010

In an effort to learn more about this process and to provide more insight on the interpretation of the data, the glovebox was sampled again on April 23, 2010. In addition to the use of the direct-reading instruments, samples were also collected on PC filters in the glovebox and in the laboratory (background) using filtration-based methods.

For this test, more attention was paid to researcher activities, and processing with fumed silica and carbon black was performed over different time periods. The results obtained from the direct-reading instruments indicated that particle concentrations associated with carbon black varied from about 10 to 40 p/cm³ with an average of 23 (s.d. 6). Particle concentrations associated with fumed silica varied from about 15 to 40 p/cm³ with an average of 22 (s.d. 5). Particle concentrations remained low until the passthrough door was opened, at which time the particle concentrations spiked to over 18,000. A plot illustrating the particle concentrations in the size range of 10–300 nm is provided in Fig. 8-2.

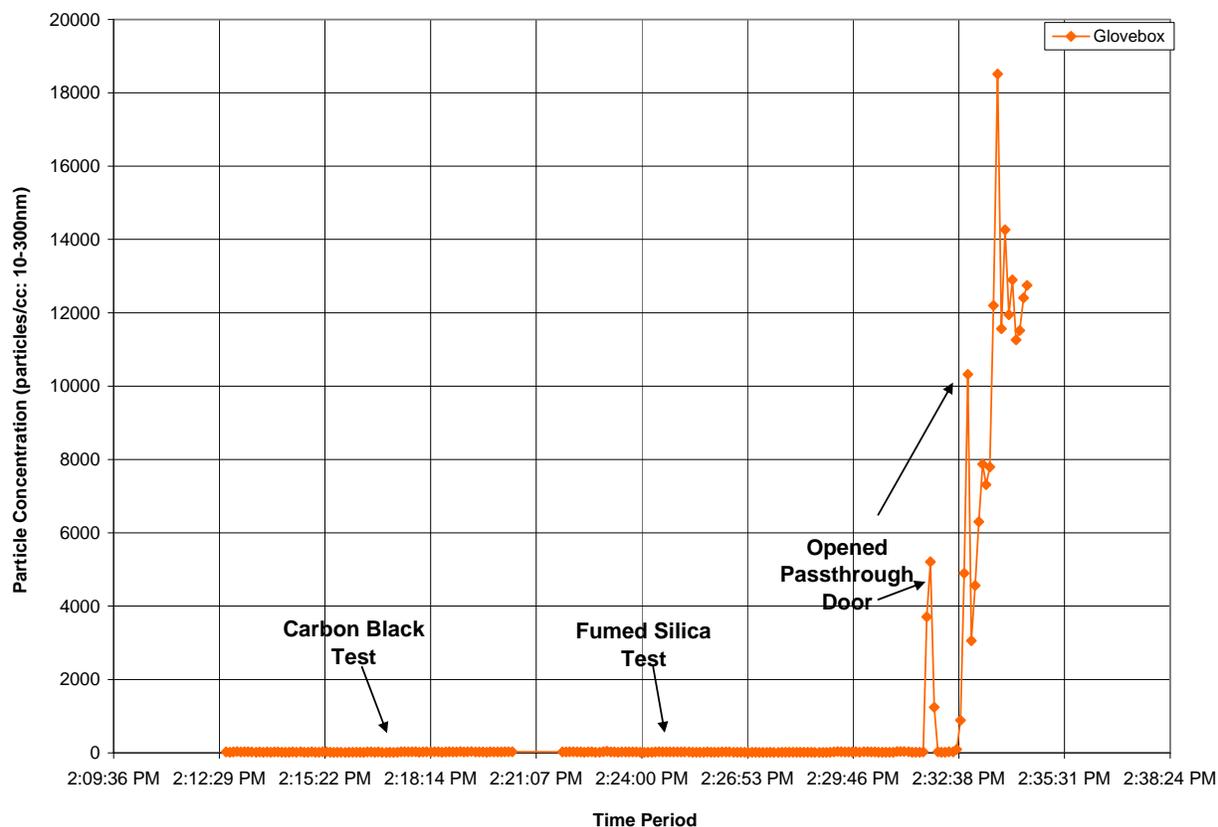


Figure 8-2 Particle Concentration Results for Glovebox Process on April 23, 2010

Review of the data presented in Fig. 8-2 shows that there was no increase in particle concentrations when the researcher was working with the carbon black and fumed silica materials. However, as was observed in the April 20th test, a spike in particle concentrations was observed when the passthrough door was opened. The passthrough door was then opened and closed several times and each time the particle concentrations increased.

EM analysis of the filter collected in the glovebox showed various particle types including carbon species, silicon, and metals; however, particle concentrations are not provided because sample volume was not obtained due to difficulties in working with the equipment in the glovebox.

It should be noted that the measurements are subject to some bias because sampling was performed in a helium environment. Since air is 7.2 times more dense than helium at 68°F and 1 atm, sampling would

have to be performed at a flow rate approximately 7 times faster in a helium environment to achieve the same total volume as compared to sampling in air. The CPC showed a “pump blocked” message during sampling in the glovebox indicating that the instrument was having difficulty pulling the sample at the flow rate required. Based on personal communication with TSI technical support representative, the CPC measurements are qualified as the readings are suspected to have some unknown bias.

8.1.1.3 Summary of Results

Based on sampling performed on April 20, 2010, no emissions to the outdoor environment of fumed silica or carbon black are indicated by the direct-reading data collected while the researcher was working with the materials. A spike in particle concentration was observed when the passthrough door was opened; however, the source of the spike was not determined (the EM results were inconclusive). As noted, there is uncertainty in the interpretation of the result when sampling in a helium atmosphere. However, because the research with nanomaterials performed in the glovebox is similar to that performed in fumehoods (see Section 5) from the perspective of materials used (e.g., processing activities and duration), negligible emissions to the outdoor environment are expected. Therefore, HEPA filtration is not required to control emissions of UNP to the outdoor environment for this and similar processes.

In summary, the controls exceed the risk for this process and for other similar processes performed with similar materials in other gloveboxes considered in this pilot study (Battaglia, Kostecki, and Richardson laboratories).

9.0

Conclusions

The purpose of the Phase III component of the LBNL pilot study was to evaluate worker exposure and emissions to the outdoor environment of UNP and to validate or modify, as appropriate, the preliminary control bands developed in Phase II based on results of the sampling campaign.

As noted previously, the Phase III evaluation was based on data from samples collected while the research process was performed over a longer period (approximately 30 to 70 minutes) than is typical (less than a few minutes). In addition, the samples were collected using higher flow rates (approximately 7 L/min) than typically used in industrial hygiene sampling. The extension of sampling time and flow rates was done to increase the ability to detect and quantify low airborne levels of UNP. In spite of these conservative conditions, the results of this study indicate the following:

- None of the processes evaluated in EETD result in significant emissions to the outdoor environment, so HEPA filtration is not required.
- The low-background enclosure was effective in reducing background particulates.
- None of the researchers involved in the study were exposed to significant levels of airborne UNP during the evaluation of the processes and workers are adequately protected by existing controls and work practices.
- Similar exposure results are expected for similar processes performed with similar controls.
- The preliminary control bands for many of the processes were conservative.
- Similar control bands can be used for similar processes with similar controls.
- Controls for all processes evaluated meet or exceed the controls suggested by the validated control band.

For some processes, the validated control bands were less stringent than the preliminary control bands; for others, they were unchanged. In all cases, the actual control level met or exceeded the validated control band. A comparison of the preliminary, actual, and validated control bands for processes evaluated in this study are provided in Table 9-1.

Based on the observations and sampling, research process activities with UNP at LBNL EETD appear to be well planned, reviewed, and controlled. Analytical results indicate low or unmeasurable levels of worker exposure; therefore the observed work practices and associated controls are deemed effective. Provided that similar approaches applying ISM principles are used in other UNP process activities, it can be anticipated that employee exposures to UNP would be similarly controlled.

For the nanoscale research tasks evaluated in this project, no regulations or standards require the use of HEPA filtration for the exhaust systems to control emissions to the outdoor environment. The air

sampling indicated negligible emissions of UNP to the outdoor environment from the research processes evaluated. However, the evaluation of need for HEPA filtration of nanoscale research to control emissions to the outdoor environment remains a component of the research review process and ISM when new research or where significant modifications of existing research is planned.

The information developed in this project can be strengthened statistically by additional sampling of these or similar processes. Such sampling will be the subject of Phase IV of this pilot study, which will recommend a program of periodic monitoring and assessment of emissions of UNP to the outdoor environment.

Table 9-1 Comparison of Preliminary, Actual, and Validated Control Bands for Evaluated Processes

Activity	Phase II		Phase III
	Preliminary Control Band	Actual Control Level	Validated Control Band
John Kerr, Building 62, Lab 246			
Fumed silica used in fumehood	III	II	II
Carbon black and acetylene black used in fumehood	II	II	II
Fumed silica used in glovebox	II	III	II
Carbon black and acetylene black used in glovebox	II ^a	III	II
Thomas Richardson, Building 62, Lab 342			
Carbon black and acetylene black used in glovebox	II ^a	III	II
Vincent Battaglia, Building 70, Labs 295/297/299			
Carbon black and acetylene black used in fumehood	II ^a	II	II
Silicon used in fumehood	III	II	II
Carbon black and acetylene black used in glovebox	II ^a	III	II
Vincent Battaglia, Building 70, Lab 218			
Carbon black and acetylene black used in fumehood	II ^a	II	II
Robert Kostecki, Building 70, Lab 295/297/299/108			
Carbon black and acetylene black used in glovebox	II ^a	III	II
Graphene used on countertop	I	I	I
Don Lucas, Building 70, Labs 291/293			
Toxic species detection using nanogold in fumehood	II	II	II

^a Originally assigned to Control Band I; revised to Control Band II to reflect LBNL requirements

10.0

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Appendix A

Gravimetric Results



RJ Lee Group, Inc.
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August 27, 2010

Ms. Linnea Wahl
Pilot Study Project Manager
Ernest Orlando Lawrence Berkeley National Laboratory
Berkeley, CA 94720

Re: Gravimetric Results of UNP Phase III Study

Dear Linnea:

This report summarizes the gravimetric results for Phase III of the Worker and Environmental Assessment of Potential Unbound Engineered Nanoparticle (UNP) Releases pilot study.

Eight research laboratory processes involving the use of six nanoparticle materials described in Table 1 were evaluated at the Lawrence Berkeley National Laboratory (LBNL) Environmental Energy Technologies Division (EETD). For each process, air samples were collected during routine laboratory procedures representative of source release point, the worker breathing zone (worker exposure), and laboratory background concentrations. The samples were analyzed to determine the total dust loading on the filter, following the NIOSH 0500 method¹.

Table 1. UNP Process Evaluation

LBNL Laboratory	Nanoparticle Material
Bldg 62 Lab 246	Acetylene Black
Bldg 62 Lab 246	Fumed Si
Bldg 70 Lab 299	Nano Si ²
Bldg 70 Lab 299	Nano Si
Bldg 70 Lab 218	Carbon Black ²
Bldg 70 Lab 218	Carbon Black
Bldg 70 Lab 291	Nano Au
Bldg 70 Lab 108	Graphene

Sample Collection

Air samples were collected onto pre-weighed 37 millimeter (mm), 0.8 micrometer (μm) pore size polyvinyl chloride (PVC) filters by RJLG personnel between April 18, 2010 and April 22, 2010 (these filters were also used for the inductively coupled plasma atomic emission spectrometry (ICP-AES) analysis). The source, worker exposure, and laboratory background samples were simultaneously collected for each process. Personnel samples were collected in the breathing zone of the researcher while performing routine research process procedures. The source release

¹ NIOSH Manual of Analytical Methods, "Particles Not Otherwise Regulated, Total", Method 0500, Issue 2, August 15, 1994.

² Sampling performed in the Rick Kelly enclosure.

Ernst Orlando Lawrence Berkeley National Laboratory
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Page 2 of 3

samples were collected by filtering air directly above the work area. The background samples were collected in an area of the laboratory removed from the processing operations.

Sample Preparation

The samples were prepared for gravimetric analysis by removing the end caps on the pre-weighed cassette and placing the cassette into a desiccator. The desiccator was maintained at 25% ±10% relative humidity and the cassette was left in the desiccator for a minimum of 8 hours.

Analytical Methods

Once the sample has been desiccated, the cassette is taken to the Mettler Toledo UMT2 Microbalance to be post weighed. Following NIOSH 0500, the cassette is then cut at the taped seam to remove the filter. The filter is removed and placed on a static strip to remove any static. The filter is then carefully placed on the microbalance pan and the weight is recorded to the nearest 0.001 milligrams (mg). The pre-weight for this cassette is subtracted from the post weight to determine the dust loading on the filter. A dust concentration is then determined by taking the dust mass in mg divided by the air volume in Liters (L) and multiplying by 1000 for a final result in mg/m³. The results of the gravimetric analysis are attached at the end of this report.

These results are submitted pursuant to RJ Lee Group's current terms and conditions of sale, including the company's standard warranty and limitation of liability provisions. No responsibility or liability is assumed for the manner in which the results are used or interpreted.

Should you have any questions regarding this information, please do not hesitate to contact us.

Sincerely,



Rich Kautz
Project Supervisor

cc: G. Casuccio (RJLG)

Ernst Orlando Lawrence Berkeley National Laboratory
RJ Lee Group Project No. GSG905991
August 27, 2010
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LABORATORY REPORT

Lawrence Berkeley National Laboratory
1 Cyclotron Road Mail Stop 85B0198
Berkeley, CA 94720
ATTENTION: Linnea Wahl
TELEPHONE: 510 - 486 - 7623

REPORT DATE June 4, 2010
SAMPLES RECEIVED May 3, 2010
RJ LEE GROUP JOB NO. GSG905991
SUBCONTRACT NO. 6879922

ANALYSIS: Total Dust on Air Filters
METHODS: Gravimetry, NIOSH 0500

Detection Limit: 0.050 mg Total Dust

Sample Identification				Air	Net Dust	Dust	Sampling	
Field I.D.	LBNL Laboratory	Nanoparticle Material	Location	Volume (liters)	Mass (mg)	Concentration (mg/m ³)	Date	Filter Type
176278	Bldg 62 Lab 246	Acetylene Black	Worker Exposure	188.8	< 0.050	< 0.265	04/19/10	0.8 mm PVC
176272	Bldg 62 Lab 246	Acetylene Black	Source	204.8	< 0.050	< 0.244	04/19/10	0.8 mm PVC
176271	Bldg 62 Lab 246	Acetylene Black	Background	201.6	< 0.050	< 0.248	04/19/10	0.8 mm PVC
176275	Bldg 62 Lab 246	Fumed Si	Worker Exposure	182.9	< 0.050	< 0.273	04/19/10	0.8 mm PVC
176276	Bldg 62 Lab 246	Fumed Si	Source	198.4	< 0.050	< 0.252	04/19/10	0.8 mm PVC
176277	Bldg 62 Lab 246	Fumed Si	Background	192.2	< 0.050	< 0.260	04/19/10	0.8 mm PVC
176273	Bldg 70 Lab 299	Nano Si	Background (Outside Enclosure)	365.4	< 0.050	< 0.137	04/21/10	0.8 mm PVC
176282	Bldg 70 Lab 299	Nano Si	Worker Exposure (In Enclosure)	359.6	< 0.050	< 0.139	04/21/10	0.8 mm PVC
176280	Bldg 70 Lab 299	Nano Si	Source (In Enclosure)	371.2	< 0.050	< 0.135	04/21/10	0.8 mm PVC
176283	Bldg 70 Lab 299	Nano Si	Background	230.4	< 0.050	< 0.217	04/21/10	0.8 mm PVC
176274	Bldg 70 Lab 299	Nano Si	Worker Exposure	226.8	< 0.050	< 0.220	04/21/10	0.8 mm PVC
176295	Bldg 70 Lab 299	Nano Si	Source	234.	< 0.050	< 0.214	04/21/10	0.8 mm PVC
176285	Bldg 70 Lab 218	Carbon Black	Background (Outside Enclosure)	224.	< 0.050	< 0.223	04/22/10	0.8 mm PVC
176286	Bldg 70 Lab 218	Carbon Black	Worker Exposure (In Enclosure)	207.	< 0.050	< 0.242	04/22/10	0.8 mm PVC
176294	Bldg 70 Lab 218	Carbon Black	Source (In Enclosure)	220.5	< 0.050	< 0.227	04/22/10	0.8 mm PVC
176284	Bldg 70 Lab 218	Carbon Black	Background	224.	< 0.050	< 0.223	04/22/10	0.8 mm PVC
176288	Bldg 70 Lab 218	Carbon Black	Worker Exposure	213.5	< 0.050	< 0.234	04/22/10	0.8 mm PVC
176289	Bldg 70 Lab 218	Carbon Black	Source	206.5	< 0.050	< 0.242	04/22/10	0.8 mm PVC
176293	Bldg 70 Lab 291	Au Nanorods	Background	474.5	< 0.050	< 0.105	04/23/10	0.8 mm PVC
176287	Bldg 70 Lab 291	Au Nanorods	Source	452.6	< 0.050	< 0.110	04/23/10	0.8 mm PVC
176300	Bldg 70 Lab 291	Au Nanorods	Worker Exposure	452.6	< 0.050	< 0.110	04/23/10	0.8 mm PVC
176290	Bldg 70 Lab 108	Graphene	Background	173.6	< 0.050	< 0.288	04/26/10	0.8 mm PVC
176292	Bldg 70 Lab 108	Graphene	Worker Exposure	173.6	< 0.050	< 0.288	04/26/10	0.8 mm PVC
176299	Bldg 70 Lab 108	Graphene	Source	184.8	< 0.050	< 0.271	04/26/10	0.8 mm PVC
176281	Field Blank			N/A	< 0.050	N/A	N/A	0.8 mm PVC
176296	Field Blank			N/A	< 0.050	N/A	N/A	0.8 mm PVC
176297	Field Blank			N/A	< 0.050	N/A	N/A	0.8 mm PVC
176351	Field Blank			N/A	< 0.050	N/A	N/A	0.8 mm PVC

N/A Not Applicable


Richard A. Kautz Project Supervisor 06/04/10 Date

These results are submitted pursuant to RJ Lee Group's current terms and conditions of sale, including the company's standard warranty and limitation of liability provisions. No responsibility or liability is assumed for the manner in which the results are used or interpreted. Unless notified in writing to return the samples covered by this report, RJ Lee Group will store the samples for a period of thirty (30) days before discarding. A shipping and handling fee will be assessed for the return of any samples. This laboratory operates in accord with ISO 17025 guidelines, and holds limited scopes of accreditation under AIHA Lab ID 100364, NY ELAP Lab Code 101208-0, EPA Lab Code PA00162, CA ELAP Certificate 1970, PA DEP Lab ID 02-00396, VA DCLS Lab ID 00297, and LA DEQ Agency Interest 94775. This report may not be used to claim product endorsement by any laboratory accrediting agency.

Appendix B

Inductively Coupled Plasma-Atomic Emission Spectrometry Results



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August 27, 2010

Ms. Linnea Wahl
Pilot Study Project Manager
Ernest Orlando Lawrence Berkeley National Laboratory
Berkeley, CA 94720

Re: Inductively Coupled Plasma Atomic Emission Spectrometry Results of UNP Phase III Study

Dear Linnea:

This report summarizes the inductively coupled plasma atomic emission spectrometry (ICP-AES) results for Phase III of the Worker and Environmental Assessment of Potential Unbound Engineered Nanoparticle (UNP) Releases pilot study.

Four research laboratory processes involving the use of two nanoparticle materials described in Table 1 were evaluated at the Lawrence Berkeley National Laboratory (LBNL) Environmental Energy Technologies Division (EETD). For each process, air samples were collected during routine laboratory procedures representative of source release point, the worker breathing zone (worker exposure), and laboratory background concentrations. The samples were analyzed to determine the concentration of the UNP using ICP-AES, following the NIOSH 7300 method¹.

Table 1. UNP Experiments

LBNL Laboratory	Nanoparticle Material
Bldg 62 Lab 246	Fumed Si
Bldg 70 Lab 299	Nano Si ²
Bldg 70 Lab 299	Nano Si
Bldg 70 Lab 291	Nano Au

Sample Collection

Air samples were collected onto pre-weighed 37 millimeter (mm), 0.8 micrometer (μm) pore size polyvinyl chloride (PVC) filters by RJLG personnel between April 18, 2010 and April 22, 2010 (these filters were also used for the gravimetry analysis). The source, worker exposure, and laboratory background samples were simultaneously collected for each process. Personnel samples were collected in the breathing zone of the researcher while performing routine research

¹ NIOSH Manual of Analytical Methods, "Elements by ICP", Method 7300, Issue 3, March 15, 2003.

² Sampling performed in the Rick Kelly enclosure.

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RJ Lee Group Project No. GSG905991
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process procedures. The source release samples were collected by filtering air directly above the work area. The background samples were collected in an area of the laboratory removed from the processing operations.

Sample Preparation

The cassettes were opened and the filters were carefully transferred into beakers using tweezers. Approximately 2 milliliters (mL) of nitric acid was mixed with a few drops of hydrofluoric acid and added to all of the beakers. The beakers were covered with watch glasses and heated for 30 minutes on a hotplate at 140°C until 0.5 mL of acid remained. The samples were then diluted to a final volume of 25 mL with double dionized water. For the samples that were analyzed for gold, 2 mL of aqua regia was mixed with the nitric acid, instead of hydrofluoric acid.

Analytical Methods

The digested samples were analyzed in a Varian 730ES ICP-AES following NIOSH Method 7300. Results are attached to the end of this report.

These results are submitted pursuant to RJ Lee Group's current terms and conditions of sale, including the company's standard warranty and limitation of liability provisions. No responsibility or liability is assumed for the manner in which the results are used or interpreted.

Should you have any questions regarding this information, please do not hesitate to contact us.

Sincerely,



Lykourgos Iordanidis, Ph.D.
Manager, Chemistry

cc: G. Casuccio (RJLG)



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DRAFT LABORATORY REPORT

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Berkeley, CA 94720Attn: Linnea Wahl
Phone: 510-486-7623
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Email: lewahl@lbl.govRJ Lee Group Job No.: GSG905991
RJ Lee Group Chemistry Job No.: IN11052010P004
Samples Received: May 11, 2010
Report Date: July 9, 2010
Client Project: N/A
Purchase Order No.: N/AMatrix: Air and Emissions
Prep/Analysis: NIOSH 7300 / NIOSH 7300-PA
NIOSH 7300 / NIOSH 7300 mod-PA

Client Sample ID Location	Sampling Date	Sample Volume (L)	Analyte	Sample Concentration (mg/filter)	Minimum Reporting Limit (mg/filter)	Sample Concentration mg/m ³	Minimum Reporting Limit (mg/m ³)	Analysis Date	Q
176275 Bldg 62 Lab 246 Worker Exposure	04/19/2010	182.9 L	Silicon	<0.0250	0.0250	<0.137	0.137	05/21/2010	BLD
176276 Bldg 62 Lab 246 Source	04/19/2010	198.4 L	Silicon	<0.0250	0.0250	<0.126	0.126	05/21/2010	BLD
176277 Bldg 62 Lab 246 Background	04/19/2010	192.2 L	Silicon	<0.0250	0.0250	<0.130	0.130	05/21/2010	BLD
176273 Bldg 70 Lab 299 Background (Outside Enclosure)	04/21/2010	355.4 L	Silicon	<0.0250	0.0250	<0.0703	0.0703	05/21/2010	BLD
176282 Bldg 70 Lab 299 Worker Exposure (In Enclosure)	04/21/2010	359.6 L	Silicon	<0.0250	0.0250	<0.0695	0.0695	05/21/2010	BLD
176280 Bldg 70 Lab 299 Source (In Enclosure)	04/21/2010	371.2 L	Silicon	<0.0250	0.0250	<0.0673	0.0673	05/21/2010	BLD
176283 Bldg 70 Lab 299 Background	04/21/2010	230.4 L	Silicon	<0.0250	0.0250	<0.109	0.109	05/21/2010	BLD
176274 Bldg 70 Lab 299 Worker Exposure	04/21/2010	226.8 L	Silicon	<0.0250	0.0250	<0.110	0.110	05/21/2010	BLD
176295 Bldg 70 Lab 299 Source	04/21/2010	234 L	Silicon	<0.0250	0.0250	<0.107	0.107	05/21/2010	BLD
176293 Bldg 70 Lab 291 Background	04/23/2010	474.5 L	Gold	<0.000250	0.000250	<0.000527	0.000527	05/20/2010	
176287 Bldg 70 Lab 291 Source	04/23/2010	452.6 L	Gold	<0.000250	0.000250	<0.000552	0.000552	05/20/2010	
176300 Bldg 70 Lab 291 Worker Exposure	04/23/2010	452.6 L	Gold	<0.000250	0.000250	<0.000552	0.000552	05/20/2010	

Philip Grindle
Laboratory Supervisor



RJ Lee Group, Inc.
350 Hochberg Road, Monroeville, PA 15146
Tel: (724)325-1776 | Fax: (724)733-1799

DRAFT LABORATORY REPORT

Lawrence Berkeley Lab
Environment, Health & Safety, 85B-0109
1 Cyclotron Road Mail Stop 85B0198
Berkeley, CA 94720

Attn: Linnea Wahl
Phone: 510-486-7623
Fax: 510-486-6603
Email: lewahl@lbl.gov

RJ Lee Group Job No.: GSG905991
RJ Lee Group Chemistry Job No.: IN11052010P004
Samples Received: May 11, 2010
Report Date: July 9, 2010
Client Project: N/A
Purchase Order No.: N/A
Matrix: Air and Emissions
Prep/Analysis: NIOSH 7300 / NIOSH 7300-PA
NIOSH 7300 / NIOSH 7300 mod-PA

Client Sample ID Location	Sampling Date	Sample Volume (L)	Analyte	Sample Concentration (mg/filter)	Minimum Reporting Limit (mg/filter)	Sample Concentration mg/m ³	Minimum Reporting Limit (mg/m ³)	Analysis Date	Q
------------------------------	------------------	-------------------	---------	--	---	--	--	------------------	---

Analyst Comments:

Report Qualifiers (Q):

H = Holding times for preparation or analysis exceeded

E = Value above highest calibration standard

J = Value below lowest calibration standard but above MDL (Method Detection Limit)

L = LCS (Laboratory Control Standard)/SRM (Standard Reference Material) recovery
outside accepted recovery limits

B = Analyte detected in the associated Method Blank

S = Spike Recovery outside accepted limits

R = RPD (relative percent difference) outside accepted limits

D = RL (reporting limit verification) outside accepted limits

These results are submitted pursuant to RJ Lee Group's current terms and conditions of sale, including the company's standard warranty and limitation of liability provisions. No responsibility or liability is assumed for the manner in which the results are used or interpreted. Unless notified in writing to return the samples covered by this report, RJ Lee Group will store the samples for a period of thirty (30) days before discarding. A shipping and handling fee will be assessed for the return of any samples.

This laboratory operates in accord with ISO 17025:2005 guidelines, and holds a limited scope of accreditation under AIHA Lab ID 100364, NY ELAP Lab Code 10884, EPA Lab Code PA00162, CA ELAP Certificate 1970, PA DEP Lab ID 02-00396, VA DCLS Lab ID 00297, and LA DEQ Agency Interest 94775. This report may not be used to claim product endorsement by any laboratory accrediting agency. The results contained in this report relate only to the items tested or to the sample(s) as received by the laboratory. Any reproduction of this document must be in full for the report to be valid.

Quality Control data is available upon request. Results have not been blank corrected unless otherwise noted. Samples were received in good condition unless otherwise noted.

Philip Grindle
Laboratory Supervisor

Appendix C

Electron Microscopy Results



RJ LeeGroup, Inc.
350 Hochberg Road, Monroeville, PA 15146
Tel: (724) 325-1776 | Fax: (724) 733-1799

August 27, 2010

Ms. Linnea Wahl
Pilot Study Project Manager
Ernest Orlando Lawrence Berkeley National Laboratory
Berkeley, CA 94720

Re: Electron Microscopy Results of UNP Phase III Study

Dear Linnea:

This report summarizes the electron microscopy results for Phase III of the Worker and Environmental Assessment of Potential Unbound Engineered Nanoparticle (UNP) Releases pilot study.

Eight research laboratory processes involving the use of six nanoparticle materials described in Table 1 were evaluated at the Lawrence Berkeley National Laboratory (LBNL) Environmental Energy Technologies Division (EETD). For each process, air samples were collected during routine laboratory procedures representative of source release point, the worker breathing zone (worker exposure), and laboratory background contributions. The samples were analyzed to quantify the airborne concentrations of source materials using an electron microscopy protocol developed by RJ Lee Group, Inc. (RJLG), based, in part, on the ASTM D-6056¹ for ceramic whiskers and ASTM D-6281² for airborne asbestos fibers.

Table 1. UNP Experiments

LBNL Laboratory	Nanoparticle Material
Bldg 62 Lab 246	Acetylene Black
Bldg 62 Lab 246	Fumed Si
Bldg 70 Lab 299	Nano Si ³
Bldg 70 Lab 299	Nano Si
Bldg 70 Lab 218	Carbon Black ³
Bldg 70 Lab 218	Carbon Black
Bldg 70 Lab 291	Au Nanorods
Bldg 70 Lab 108	Graphene

¹ ASTM (1996), Standard Test Method for Determining Concentration of Airborne Single-Crystal Ceramic Whiskers in the Workplace Environment by Transmission Electron Microscopy, ASTM International, Method D-6056, December 10, 1996.

² ASTM (2006), Standard Test Method for Airborne Asbestos Concentration in Ambient and Indoor Atmospheres as Determined by Transmission Electron Microscopy Direct Transfer (TEM), ASTM International, Method D-6281, April 1, 2006.

³ Sampling performed in the Rick Kelly enclosure.

Ernst Orlando Lawrence Berkeley National Laboratory
RJ Lee Group Project No. GSG90599
August 27, 2010
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Sample Collection

Air samples were collected onto 25 millimeter (mm), 0.2 micrometer (μm) pore size polycarbonate (PC) filters by RJLG personnel between April 18, 2010 and April 22, 2010. The source, worker exposure, and laboratory background samples were simultaneously collected for each experiment. Personnel samples were collected in the breathing zone of the researcher while performing routine research process procedures. The source release samples were collected by filtering air directly above the work area. The background samples were collected in an area of the laboratory removed from the processing operations.

Sample Preparation

The PC filter air samples were prepared for electron microscopy analysis using a direct transfer technique. The direct transfer procedure, such as that described by Burdette and Rood⁴, involved coating the filter with evaporated carbon, then dissolving the PC substrate using chloroform. The intact carbon film containing the collected airborne particulate was deposited on a copper 200 mesh locater grid typically used for analysis of air samples by transmission electron microscopy (TEM).

Analytical Methods

TEM and scanning electron microscopy (SEM) methods were combined in the analysis of the source, worker exposure, and laboratory background samples. The SEM instrumentation used in the analyses was a Hitachi S-5500 ultra-high resolution field emission scanning electron microscope (FESEM) with scanning transmission (STEM) capabilities. The FESEM analyses were performed at an accelerating voltage of 30 kV. The TEM instrumentation used in the analyses of the samples was a JOEL 1200II and the analyses were performed at an accelerating voltage of 120 kV. Compositional information was obtained on both the FESEM and the TEM through collection and processing of characteristic X-rays using energy dispersive X-ray spectroscopy (EDS).

Determination of the particle concentrations often requires that a sample be analyzed using multiple magnifications to maximize the area coverage and the potential for observing structures. The analysis of each sample was segregated into three size fractions, with an applicable magnification for the analysis of each fraction. Particles consistent with the source material, identified based on morphology and EDS, were counted while monitoring the amount of area analyzed on the sample. The dimensions of each agglomerated structure or individual nanoparticle were recorded and representative images along with elemental spectra were documented.

The first component of the FESEM analysis involved surveying 100 grid openings at a magnification of 1300x. This low magnification scan was performed to document agglomerated nanoparticles of interest measuring greater than $\sim 2 \mu\text{m}$ in average diameter. The second magnification involves scanning four grid openings at 20,000X in order to count and measure agglomerated source particles between ~ 0.5 and $2 \mu\text{m}$. Finally, source particles measuring

⁴ G. J. Burdett and A. P. Rood, Environ. Sci. Technol., 17, 643, 1983.

Ernst Orlando Lawrence Berkeley National Laboratory
RJ Lee Group Project No. GSG90599
August 27, 2010
Page 3 of 4

between 3 and 500 nanometers (nm) were counted and measured in 20 randomly selected fields at a magnification of 100,000x.

Table 2 is attached at the end of the report and presents the results of the source particle concentrations for each of the eight experiments. Source particle concentrations for each of the three size fractions were calculated separately. Overall, particle concentrations of the source material were highest at the source, and background source particle concentrations were usually higher than worker exposure levels.

These results are submitted pursuant to RJ Lee Group's current terms and conditions of sale, including the company's standard warranty and limitation of liability provisions. No responsibility or liability is assumed for the manner in which the results are used or interpreted.

Should you have any questions regarding this information, please do not hesitate to contact us.

Sincerely,



Kristin L. Bunker, Ph.D.
Senior Scientist

cc: G. Casuccio (RJLG)

Ernst Orlando Lawrence Berkeley National Laboratory
 RJ Lee Group Project No. GSG90599
 August 27, 2010
 Page 4 of 4

Table 2. Electron Microscopy Results



350 Hochberg Road Monroeville, PA 15146
 Voice 724/325-1776 Fax 724/733-1799

LABORATORY REPORT

Lawrence Berkeley National Laboratory
 1 Cyclotron Road Mail Stop 85B0198
 Berkeley, CA 94720
 ATTENTION: Linnea Wahl
 TELEPHONE: 510 - 486 - 7623

REPORT DATE **June 18, 2010**
 SAMPLES RECEIVED **May 3, 2010**
 RJ LEE GROUP NO. **GSG905991**
 SUBCONTRACT NO. **6879922**

ANALYSIS: Particle Concentration Measurements
 METHODS: Electron Microscopy

Field ID	LBNL Laboratory	Nanoparticle Material	Location	Sampling Date	Air Volume (L)	Particle Counts			Concentration (Particles/cc)		
						>2 µm	0.5-2 µm	<500 nm	>2 µm	0.5-2 µm	<500 nm
						1300x	20000x	100000x	1300x	20000x	100000x
5284217	Bldg 62 Lab 246	Acetylene Black	Worker Exposure	4/19/10	227.2	5	6	6	0.01	0.3	450.4
5284218	Bldg 62 Lab 246	Acetylene Black	Source	4/19/10	246.4	54	34	15	0.2	1.4	1038.2
5284219	Bldg 62 Lab 246	Acetylene Black	Background	4/19/10	227.2	5	5	9	0.01	0.2	675.6
5284220	Bldg 62 Lab 246	Fumed Si	Worker Exposure	4/19/10	226.3	0	7	1	< 0.002	0.3	75.4
5284221	Bldg 62 Lab 246	Fumed Si	Source	4/19/10	244.9	88	16	7	0.1	0.6	487.5
5284222	Bldg 62 Lab 246	Fumed Si	Background	4/19/10	220.1	0	8	2	< 0.002	0.4	155.0
5284224	Bldg 70 Lab 299	Nano Si	Worker Exposure (In Enclosure)	4/21/10	411.8	1	2	0	0.001	0.05	< 41.4
5284225	Bldg 70 Lab 299	Nano Si	Source (In Enclosure)	4/21/10	440.8	1	2	1	0.001	0.04	38.7
5284223	Bldg 70 Lab 299	Nano Si	Background (Outside Enclosure)	4/21/10	446.6	1	3	3	0.001	0.1	114.6
5284227	Bldg 70 Lab 299	Nano Si	Worker Exposure	4/21/10	259.2	0	0	0	< 0.002	< 0.04	< 65.8
5284228	Bldg 70 Lab 299	Nano Si	Source	4/21/10	273.6	1	0	0	0.001	< 0.04	< 62.3
5284226	Bldg 70 Lab 299	Nano Si	Background	4/21/10	277.2	1	1	2	0.001	0.04	123.0
5284230	Bldg 70 Lab 218	Carbon Black	Worker Exposure (In Enclosure)	4/22/10	255.5	0	0	2	< 0.002	< 0.04	133.5
5284231	Bldg 70 Lab 218	Carbon Black	Source (In Enclosure)	4/22/10	255.5	24	10	9	0.04	0.4	600.7
5284229	Bldg 70 Lab 218	Carbon Black	Background (Outside Enclosure)	4/22/10	273.0	0	1	4	< 0.001	0.04	249.9
5284233	Bldg 70 Lab 218	Carbon Black	Worker Exposure	4/22/10	248.5	2	12	7	0.003	0.5	480.4
5284234	Bldg 70 Lab 218	Carbon Black	Source	4/22/10	252.0	1	6	7	0.002	0.2	473.7
5284232	Bldg 70 Lab 218	Carbon Black	Background	4/22/10	266.0	2	10	5	0.003	0.4	320.6
5284233-R	Bldg 70 Lab 218	Carbon Black	Worker Exposure - Reprep	4/22/10	248.5	0	19	9	< 0.002	0.8	617.7
5284234-R	Bldg 70 Lab 218	Carbon Black	Source - Reprep	4/22/10	252.0	2	17	8	0.003	0.7	541.4
5284232-R	Bldg 70 Lab 218	Carbon Black	Background - Reprep	4/22/10	266.0	0	15	5	< 0.001	0.6	320.6
5282581	Bldg 70 Lab 291	Nano Au	Worker Exposure	4/23/10	540.2	0	0	0	< 0.001	< 0.02	< 31.6
5282582	Bldg 70 Lab 291	Nano Au	Source	4/23/10	487.5	0	0	0	< 0.001	< 0.02	< 35.0
5282580	Bldg 70 Lab 291	Nano Au	Background	4/23/10	513.5	0	0	0	< 0.001	< 0.02	< 33.2
5284236	Bldg 70 Lab 108	Graphene	Worker Exposure	4/26/10	201.6	0	0	0	< 0.002	< 0.05	< 84.6
5284237	Bldg 70 Lab 108	Graphene	Source	4/26/10	207.2	2	0	0	0.004	< 0.05	< 82.3
5284235	Bldg 70 Lab 108	Graphene	Background	4/26/10	215.6	0	0	0	< 0.002	< 0.05	< 79.1

Appendix D

Photos of UNP Research Process: Acetylene Black in Fumehood,
John Kerr's Lab, 62-246



Fig. 1. Mike Wilmoth (RJLG) begins setting up the sampling pumps.



Fig. 2. Setup of fumehood and background samplers.



Fig. 3. Work area inside of fumehood (note location of direct-reading sampling tubes and filter cassettes).

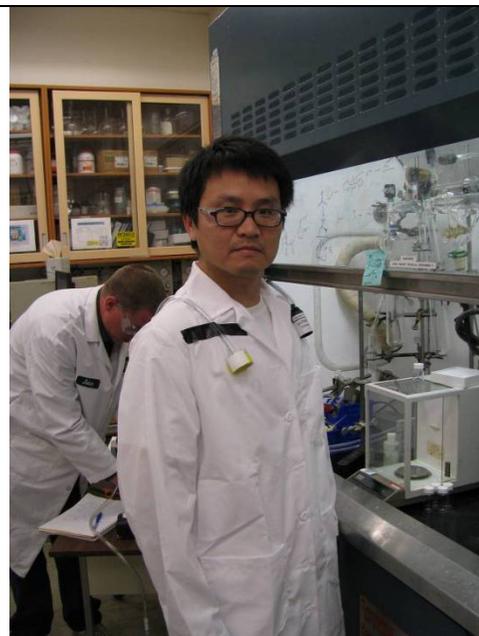


Fig. 4. Researcher prepares to work with acetylene black wearing personal samplers on the left and right shoulders in his breathing zone.



Fig. 5. Researcher performing work with acetylene black.



Fig. 6. Researcher transferring acetylene black between containers (note the location of samplers in relation to the work area).



Fig. 7. Work gloves soiled with acetylene black at the completion of the research process activities.

Appendix E

Photos of UNP Research Process: Fumed Silica in
Fumehood, John Kerr's Lab, 62-246

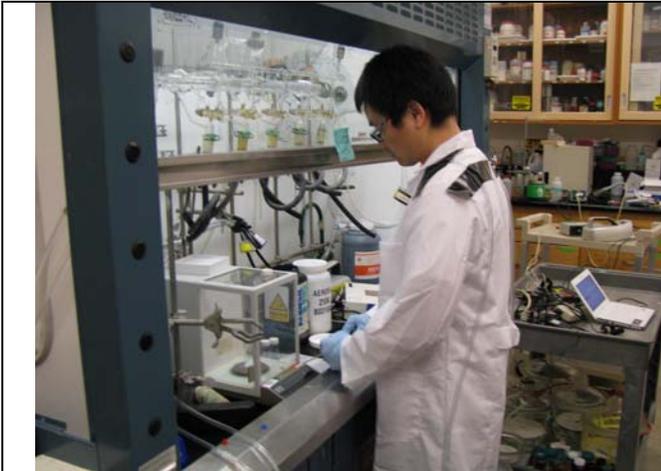


Fig. 1. Researcher begins working with fumed silica in the hood.



Fig. 2. Researcher transferring fumed silica from large to small container.



Fig. 3. Air samples are being collected above the work area of researcher.

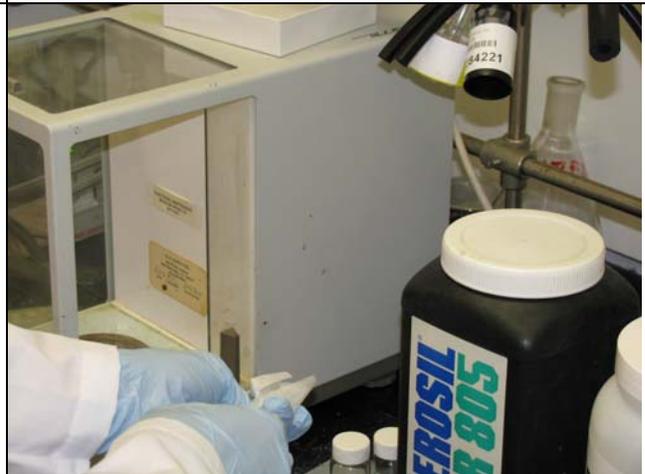


Fig. 4. Close-up of material being used. Researcher cleans off equipment in hood at completion of transfer process.

Appendix F

Photos of UNP Research Process: Nanosilicon in Fumehood,
Vincent Battaglia's Lab, 70-299



Fig. 1. Mike Wilmoth (RJLG) places personal samplers on researcher.



Fig. 2. Gary Casuccio (RJLG) observes the work being performed in the fumehood.

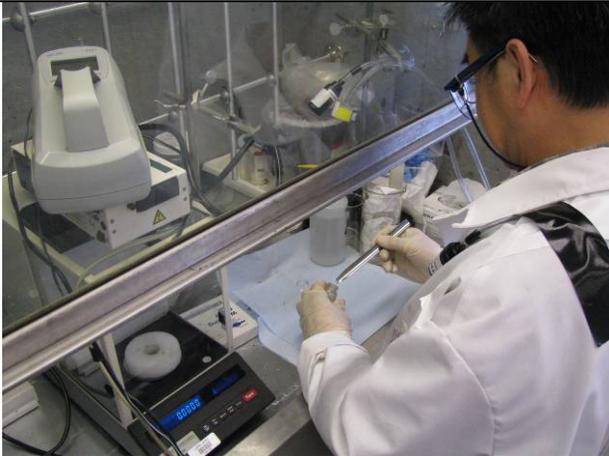


Fig. 3. Nanosilicon powder being transferred to small container.



Fig. 4. Close-up of transfer process.



Fig. 5. Photo of location of direct-reading samplers in relation to work area.

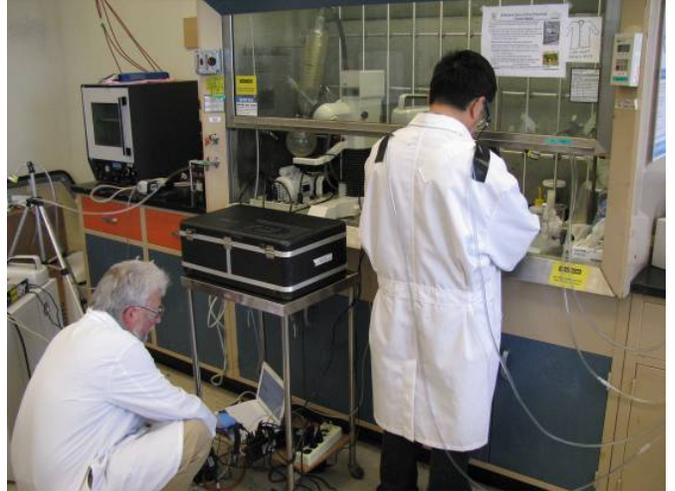


Fig. 6. Gary Casuccio (RJLG) reviews direct-reading data during the test.



Fig. 7. Work location in relation to background samplers (back left of image).



Fig. 8. Researcher transfers nanosilicon into the glass vial in preparation for the BET analysis.



Fig. 9. Researcher cleans up work station concluding the process activities.

Appendix G

Photos of UNP Research Process: Carbon Black in Fumehood,
Vincent Battaglia's Lab, 70-218



Fig. 1. Photo showing location of fumehood and lab background samplers.

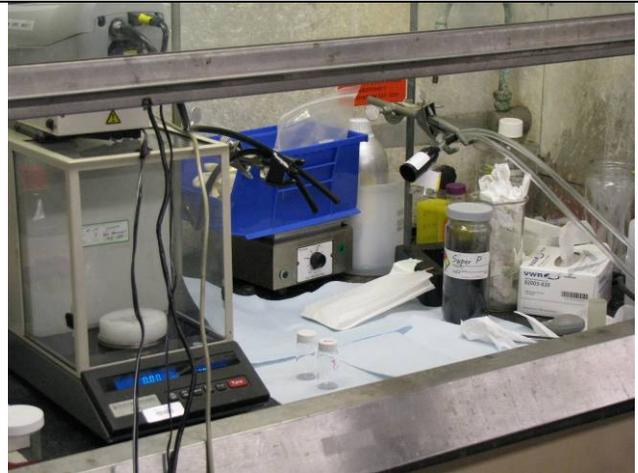


Fig. 2. Sampling location inside of fumehood.

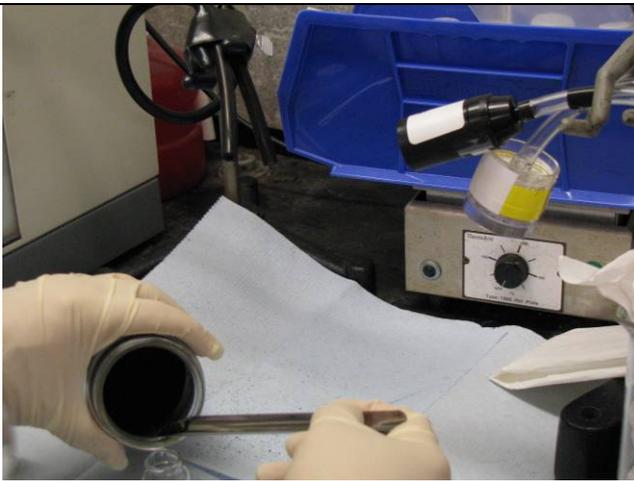


Fig. 3. Researcher transferring carbon black between containers.

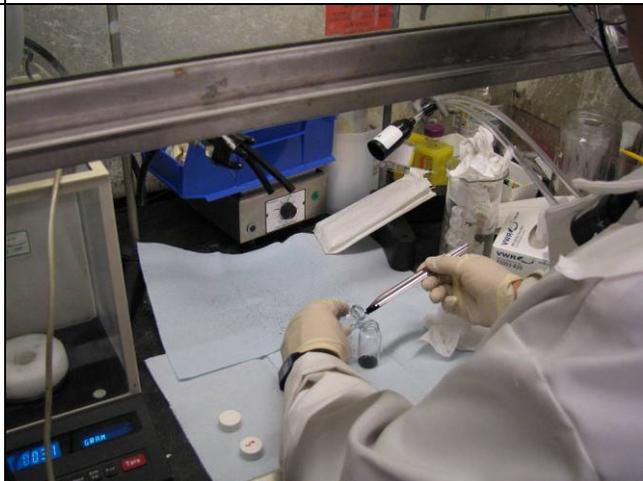


Fig. 4. Photo showing sample locations in relation to work area.



Fig. 5. Carbon black being transferred near the inlet of the samplers.



Fig. 6. Researcher transfers carbon black into glass vial in preparation for BET analysis.



Fig. 7. Researcher cleans equipment inside of the hood.

Appendix H

Photos of UNP Research Process: Nanogold in Fumehood and
Countertop, Don Lucas's Lab, 70-291/293



Fig. 1. Photo showing location of fumehood and lab background samplers.



Fig. 2. Researcher transferring nanogold aqueous solution via pipette from one container to another.



Fig. 3. Close-up of pipette tip and sampling containers.



Fig. 4. Researcher working at fumehood.



Fig. 5. Researcher sonicating sample containers on countertop.



Fig. 6. Close-up of sonication.



Fig. 7. Researcher places 4 drops of nanogold aqueous solution onto glass dish.



Fig. 8. Location of samplers inside fumehood.

Appendix I

Photos of UNP Research Process: Nanosilicon in Fumehood
Enclosure, Vincent Battaglia's Lab, 70-299



Fig. 1. Mike Wilmoth (RJLG) collects direct-reading background data inside the enclosure.



Fig. 2. Gary Casuccio (RJLG) collects direct-reading background data outside the enclosure.



Fig. 3. Close-up of CPC reading in the enclosure (191 p/cm³) shows that the enclosure is effectively filtering the ambient air.

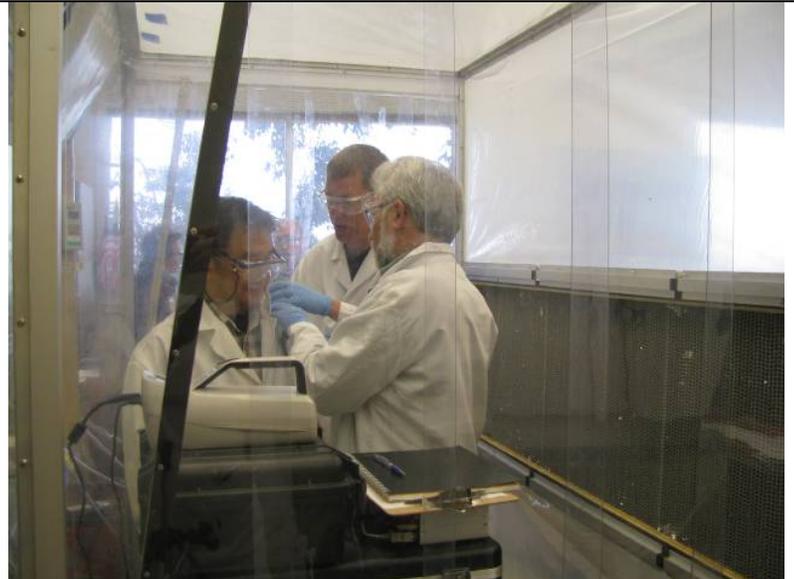


Fig. 4. Gary Casuccio and Mike Wilmoth (both RJLG) place personal samplers over each shoulder of researcher.

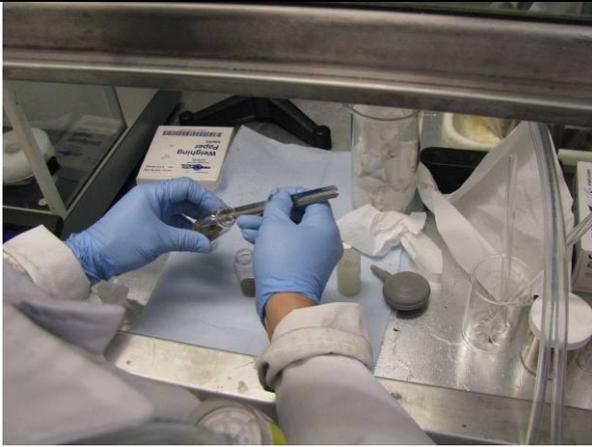


Fig. 5. Researcher transfers nanosilicon from large container to small container.

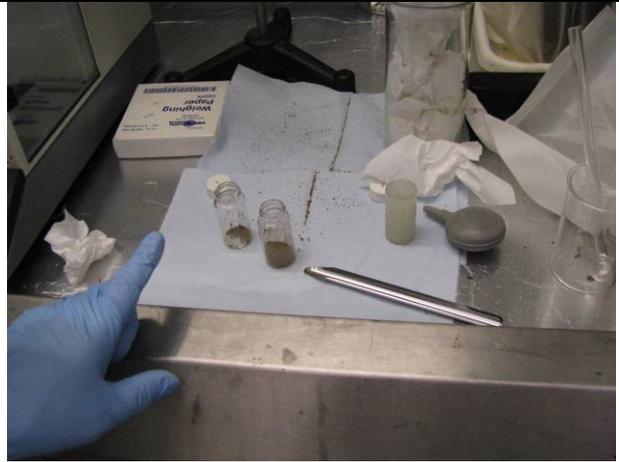


Fig. 6. Photo showing nanosilicon that spilled onto the paper towel during transfer process activities.

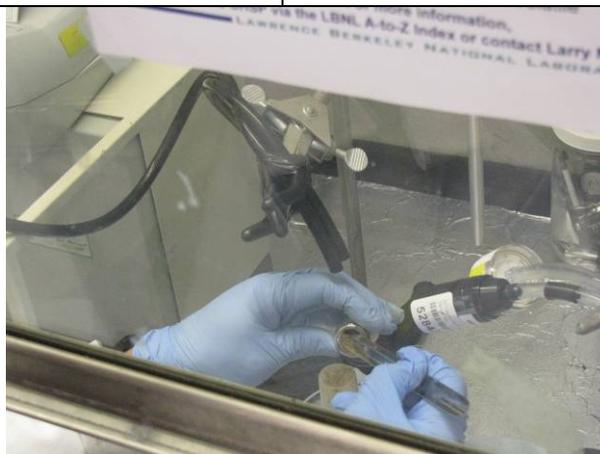


Fig. 7. Transferring nanosilicon into glass vial in preparation for BET analysis.

Appendix J

Photos of UNP Research Process: Carbon Black in Fumehood
Enclosure, Vincent Battaglia's Lab, 70-218



Fig. 1. Sampling locations in fumehood and enclosure.



Fig. 2. Work area with samplers inside fumehood.



Fig. 3. Researcher begins working inside enclosure.



Fig. 4. Researcher transfers carbon black from a large bag to a small container.

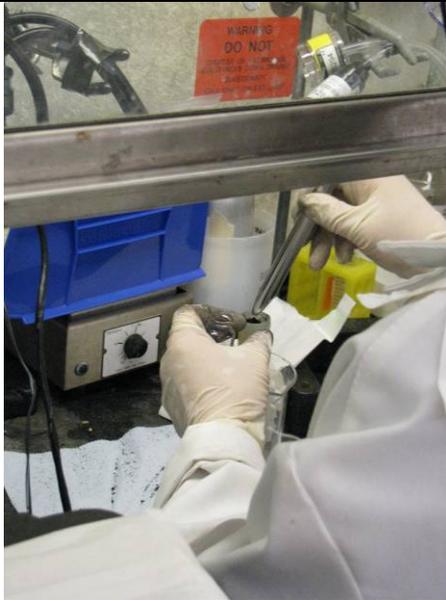


Fig. 5. Researcher transfers carbon black into the glass vial in preparation of the BET analysis.



Fig. 6. Close-up of carbon black being transferred.



Fig. 7. Photo showing carbon black that spilled onto the paper towel during transfer process activities.



Fig. 8. The researcher cleans off equipment at completion of research process activities.



Fig. 9. Rick Kelly and Gilbert Torres (both LBNL) dismantle the enclosure.

Appendix K

Photos of UNP Research Process: Graphene on Countertop,
Robert Kostecki's Lab, 70-108



Fig. 1. Researcher preparing workstation on countertop.



Fig. 2. Location of samplers above the work area.



Fig. 3. Location of background samplers in relation to countertop.



Fig. 4. Preparation of graphene sample on two overlapping layers of tape.

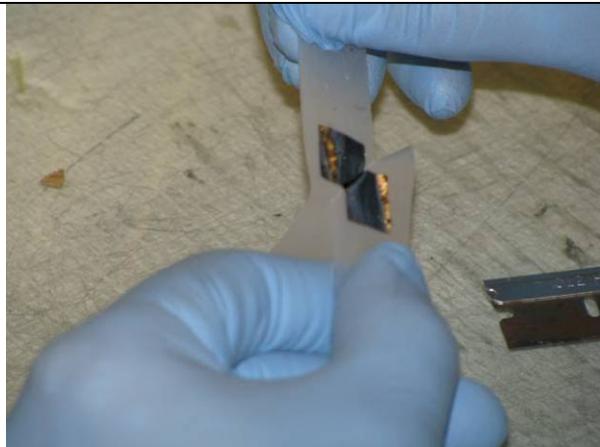


Fig. 5. Researcher slowly pulls the two layers of tape apart, exposing the graphene.



Fig. 6. Gary Casuccio (RJLG) leans in to get a closer look at the work researcher is performing.

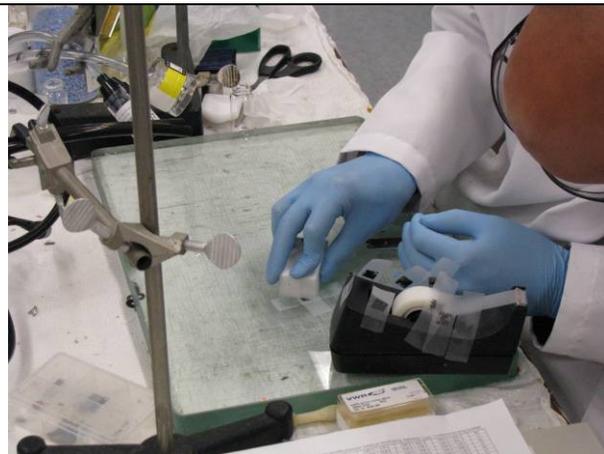


Fig. 7. Researcher repeats the graphene prep multiple times.

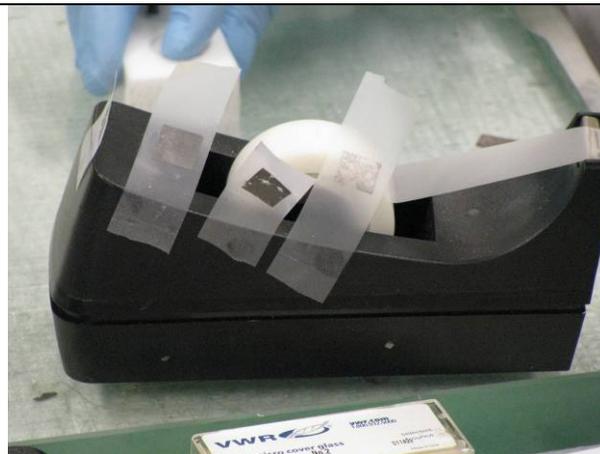


Fig. 8. Various prepped graphene samples were placed temporarily on a tape dispenser after being prepared.

Appendix L

Photos of UNP Research Process: Carbon Black and Fumed Silica in Glovebox, John Kerr's Lab, 62-246 (April 20, 2010)



Fig. 1. John Kerr (LBNL) passes equipment through access panel on the right of the glovebox.



Fig. 2. John Kerr (LBNL) sets up equipment inside glovebox.

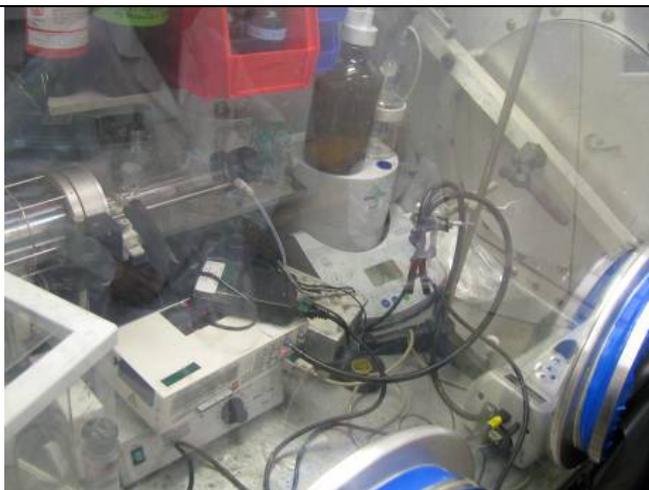


Fig. 3. Placement of samplers in glovebox in relation to work area.



Fig. 4. Mike Wilmoth (RJLG) starts the CPC/OPC with John Kerr observing.

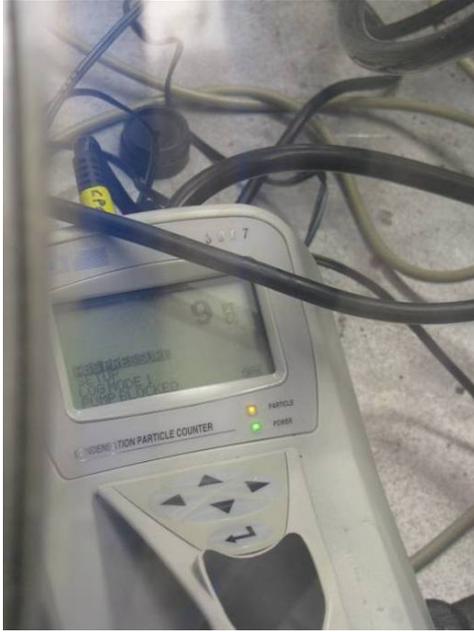


Fig. 5. Close-up of CPC showing 9p/cc in glovebox.



Fig. 6. John Kerr (LBNL) handling weighing pan in the glovebox.

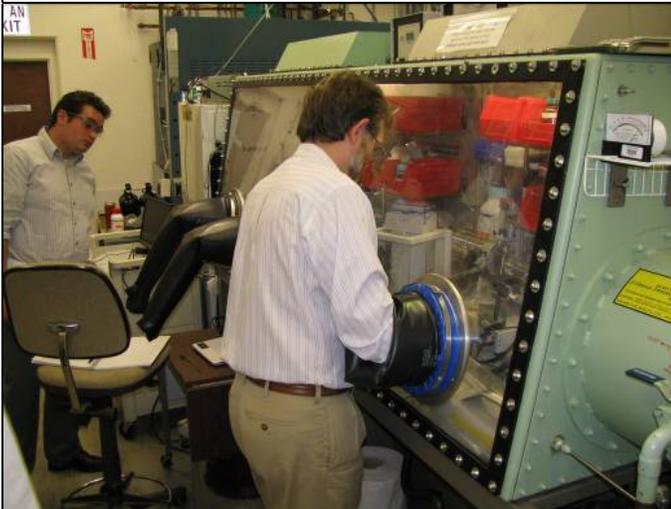


Fig. 7. John Kerr (LBNL) performing process activities in the glovebox while direct-reading data are collected.



Fig. 8. Close-up of samplers and John Kerr's (LBNL) hands in the glovebox.

Appendix M

Photos of UNP Research Process: Carbon Black and Fumed Silica in Glovebox, John Kerr's Lab, 62-246 (April 23, 2010)



Fig. 1. Mike Wilmoth and Gary Casuccio (both RJLG) prepare for the glovebox test.

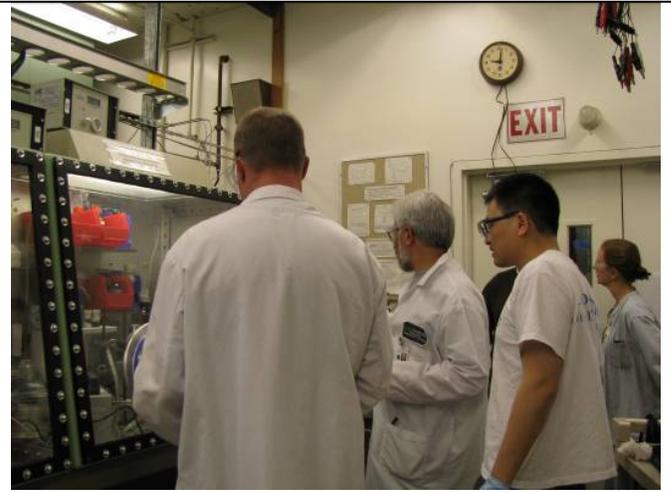


Fig. 2. Gary Casuccio (RJLG) reviews work plan with researcher prior to running test.

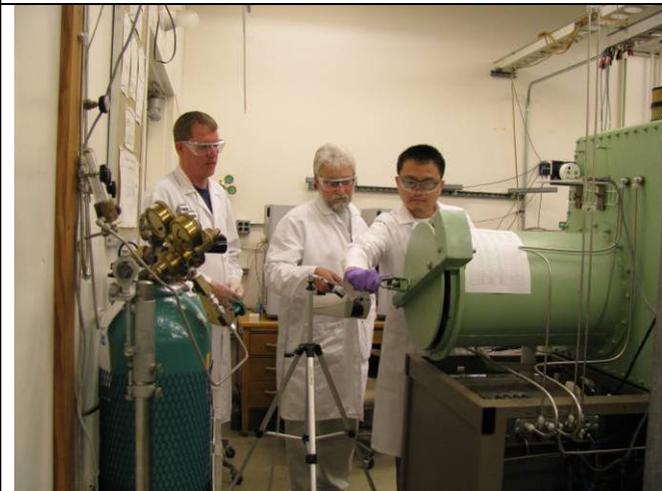


Fig. 3. Researcher opens glovebox access port to put equipment inside.



Fig. 4. Researcher working inside the glovebox during test.



Fig. 5. Close-up of researcher handling weighing pan in glovebox.



Fig. 6. Background samplers outside of glovebox.



Fig. 7. Access port being opened inside the glovebox at the conclusion of process activities.



Fig. 8. Testing concluded and Gary Casuccio (RJLG) reviews notes with researcher.