Environmental Monitoring Plan for Unbound Engineered Nanoparticles

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Acronyms

BEA	Baseline Exposure Assessment
CPC	Condensation Particle Counter
CNT	Carbon Nanotubes
DOE	Department of Energy
EETD	Environmental Energy Technologies Division
EHS	Environment, Health, and Safety
EM	Electron Microscopy
EPA	Environmental Protection Agency
ESG	Environmental Services Group
HEPA	High-Efficiency Particulate Air
ICP	Inductively Coupled Plasma
IHG	Industrial Hygiene Group
ISM	Integrated Safety Management
JHA	Job Hazards Analysis
LBNL	Lawrence Berkeley National Laboratory
NIOSH	National Institute of Occupational Safety and Health
OPC	Optical Particle Counter
UNP	Unbound Engineered Nanoparticles

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1.0 INTRODUCTION

The Department of Energy (DOE), in support of integrated safety management (ISM), has issued the Secretary's Policy DOE P456.1, *Secretarial Policy Statement on Nanoscale Safety* (DOE 2005); DOE Order O456.1, *The Safe Handling of Unbound Engineered Nanoparticles* (approved on May 31, 2011), which replaced the DOE notice of the same title (DOE 2009, DOE 2011); and guidance (*DOE Nanoscale Science Research Centers Approach to Nanomaterial ES&H*, May 2008) on working safely with nanomaterials (DOE 2008). DOE Policy P456.1 specifically states:

> *The Department of Energy (DOE) requires that all work with nanomaterials be conducted in a safe and responsible manner that protects workers, the public, and the environment. Thus, the Department must be prudent and follow a cautious approach in the production, use, and disposition of nanomaterials.*

To satisfy the DOE policy and the order on nanoscale safety and to address the uncertainties inherent in a rapidly developing technological field, a multiphase pilot study has been conducted at the Lawrence Berkeley National Laboratory (LBNL) to evaluate the potential for emissions of unbound engineered nanoparticles (UNP) to the outdoor environment and assess the need for appropriate controls. It is also designed to support the LBNL research organizations by addressing the five ISM core functions and working within existing structures and programs.

The work conducted in Phases I, II and III of the pilot study represents a first effort to evaluate the environmental release of UNP in research environments, with a focus on determining whether emissions from building exhaust are acceptable or compliant.

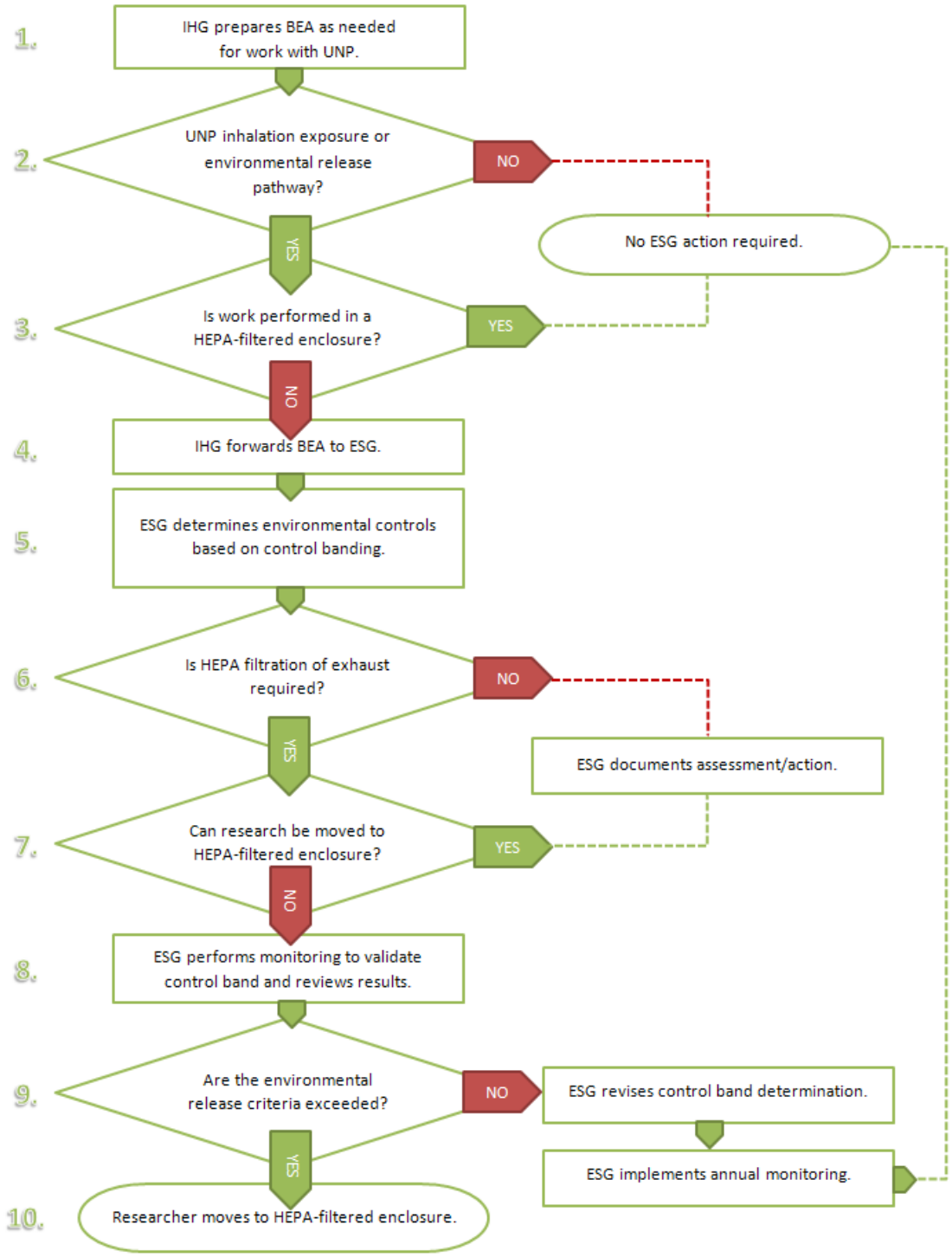
Based on the results obtained in the pilot study, the controls currently used by researchers in the Environmental Energy Technologies Division (EETD) during work with UNP met or exceeded the validated, recommended control level (based on a control band approach). It was also determined that high-efficiency particulate air (HEPA) filtration was not required for the research processes evaluated and that similar control bands can be used for similar processes and controls. A summary of the first three phases and discussion of general observations and lessons learned is provided in Appendix A.

The final phase of the pilot study will provide a plan for implementing an ongoing environmental program for emissions of UNP to the outdoor environment. The plan involves several steps. The first step is for ESG to identify candidate UNP operations by using LBNL's Baseline Exposure Assessment (BEA), an equivalent work planning and control process, or other health and safety information and assessments. The plan includes the use of a control band matrix to identify appropriate control options, discussion of options with researchers and subject matter experts, and any necessary performance of periodic monitoring of long-term research. The plan discusses documentation that will be developed and maintained. The plan also considers potential future changes in the monitoring approach that may be appropriate as the technology for ensuring nanomaterial safety evolves.

2.0 IMPLEMENTATION STEPS

This section provides the steps to implement environmental monitoring for UNP. The methodology was based on evaluation of research processes at LBNL EETD. The flow diagram presented below is appropriate for LBNL research processes involving UNP.

Figure 1. Flow Diagram for UNP Environmental Monitoring



2.1 Identify Applicable Nanoscale Research using the LBNL Baseline Exposure Assessment (BEA)

At LBNL, the BEA is a data collection tool used by the Industrial Hygiene Group (IHG) staff to document and determine the need for worker exposure sampling. The BEA is required when work presents a risk of occupational exposures to hazards. The need for a BEA is identified in the Integrated Safety Management (ISM) process of work planning and review, and is an outcome of the Job Hazards Analysis (JHA) or is requested by a work lead, employee, or industrial hygienist when conditions detailed in PUB3000, Chapter 4.18 are met. A sample BEA is shown in Appendix B.

The completed BEA contains UNP exposure/release data that is important not only in determining risk of occupational exposures, but also in determining the risk of release of UNP to the outdoor environment, especially when there is no filtration of exhausted air. Useful environmental hazard information contained in the BEA includes material name, quantity, frequency, duration, potential exposure route(s), and controls. Ideally additional information such as the relative dustiness of the UNP and a description of the work practices would also be gathered in the BEA. The BEA also contains a section for describing the type of follow up assessment needed. When the BEA is developed for UNP, this section can be used to notify Environmental Services Group (ESG) that additional environmental review is needed. ESG would then use this information to further assess the environmental hazards and to help the researchers enhance controls or determine the need for sampling.

When exposure sampling is performed, the location of air sampling differs between determining occupational exposures (i.e., breathing zone) and the release to the environment (e.g., which is collected at the location of potential release such as within the laboratory hood). Nonetheless, the information gathered during a BEA is useful in determining the potential for the release of UNP to the ventilation system and its availability for release into the ambient environment. The BEA is an excellent way to communicate this information to the ESG staff.

The IHG performs BEAs for operations with higher risks of personal exposure. This is typically UNP work performed outside of ventilated enclosures. For work with UNP performed within ventilated enclosures, the IHG provides ESG with information on work locations, UNP users, and all BEAs and monitoring results (current and past). In the absence of BEA data, ESG will identify and assess other information (as just described) to determine environmental risk.

Following the protocol for evaluation of the environmental release of UNP, when the IHG determines that the work involves UNP, the material presents a possible inhalation exposure or environmental release pathway, and the exhaust air is not HEPA filtered, then the BEA or other information is forwarded to the ESG staff for further review of potential environmental releases.

ESG may also identify applicable UNP research through Berkeley Lab's project planning and review process. This process ensures ESG's early involvement in the planning of new or remodeled facilities.

2.2 Determine Controls Needed to Prevent Environmental Releases

Using information gathered by IHG and documented in a BEA, ESG staff review the research process to determine if there is a reasonable possibility of an environmental release. This review includes applying the following algorithm in support of a control band process:

Figure 2. Risk Algorithm

Environmental Hazard	+	Release Probability	=	Risk (Degree of Hazard) Level

Environmental Hazard categories are based primarily on risk attributes such as dustiness and suspected toxicity of UNP. The following categories are used to classify the environmental hazard.

A. **Low**: No observed or anticipated environmental effects. NOTE: At this time, no UNP are assigned a low ranking.

B. **Medium**: Minor environmental effects due to the presence of the UNP. For instance, the presence of the UNP may be observed as cloudiness in water or dust may be observed in air. If inhaled, the UNP may cause minor irritation, but no systemic reaction is anticipated. NOTE: Naturally occurring nanoparticles such as nanosized amorphous minerals are examples of UNP having only medium environmental effects.

C. **High**: Significant environmental effects where there is evidence of environmental toxicity of the UNP or the parent material. These materials have governmental regulations or have notation of environmental effects in the MSDS. NOTE: The National Institute of Occupational Safety and Health (NIOSH) has a recommended standard for titanium dioxide (TiO_2) and carbon nanotubes (CNT), and thus these materials would be considered as a "high" environmental hazard (NIOSH 2010, NIOSH 2011).

D. **Very high or unknown**: Highly toxic UNP with unknown environmental effects. This risk level includes, for example, UNP from a regulated parent material that is designated as an extremely toxic material such as asbestos, beryllium, cadmium, or radioactive materials.

Release Probability categories are based on the ability of a material to become dispersed. The risk of dispersion into air is based on particle attributes such as dustiness and on the research activities and work practices. The following categories are used to classify the release probability.

1. **Unlikely**: Unlikely to be dispersed into the air (e.g., large, solid or agglomerated particles typically greater than 10 μm and liquids with very low volatility).
2. **Low**: Low likelihood for release (i.e., UNP that are not dusty and tend to agglomerate); however, a small release cannot be ruled out. NOTE: In Phase III, carbon (or acetylene) black, graphene, fumed silica and nanosilicon were manipulated during the research process, but little airborne UNP was detected.

3. **Likely**: UNP that is used in a dusty process (significant manipulation of the UNP for extended periods) or volatile liquid containing UNP with a significant release likely. For example, the UNP is subjected to manipulations that are known to create dust, such as sieving, or hand sanding.
4. **Probable**: Highly volatile liquids containing UNP or use of UNP classified as dusty and consisting of very fine particles (e.g., individual nanoparticles with two dimensions less than 100 nm diameter) and subjected to highly energetic process (e.g., welding or mechanical grinding which can disperse UNP into the air).

The **Risk (Degree of Hazard) Level** rankings range from relatively safe, 1A (from the attributes listed above), to the highest degree of risk, 4D (see Figure 3). The level of control for a process is directly matched to the risk; that is, a low level of control is generally matched to a low level of risk, while higher risk indicates the need for a higher level of control. Controls may exceed the level of risk but should never be less than the level indicated by the risk.

Controls required for each control band category shown in Figure 3, are based on the following:

I. Minimum control; general area ventilation; work on a bench top is acceptable.
II. Work within an approved laboratory ventilation hood required; air cleaning recommended (e.g., HEPA filtration for particles) but not required.
III. Containment, such as a HEPA-filtered hood or glove box, required to prevent release of UNP to the outside ambient environment.
IV. Review by a specialist required (may require full containment of the operation and air-cleaning devices).

The control bands developed for research processes using UNP illustrating the controls needed based on the relationship of the probability of release to the environmental hazard are shown in Figure 3.

Figure 3. Control Band Matrix for UNP Environmental Monitoring

		Release Probability			
		Unlikely (1)	Low (2)	Likely(3)	Probable (4)
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

2.3 Validation of the Preliminary Control Bands

If the research is assigned to a preliminary Control Band III or IV, HEPA filtration of the exhaust air is required. However, the control band approach is conservative and it is possible that sampling of the exhaust air will show that the probability of environmental release is insignificant and HEPA filtration is not necessary. This was demonstrated in Phase III of the pilot study, when validation of the preliminary control band assignments verified that HEPA filters were not necessary.

Until environmental air monitoring/assessments are performed, it is necessary to be conservative in assigning preliminary controls. Air monitoring provides more definitive information for assigning controls, and control bands validated by air monitoring data are normally less conservative than preliminary control band assignments. If a control band has not been assigned and validated, at this point in the process further sampling may be necessary. Validated control bands serve as a basis for assigning the best level of controls for new work. Air monitoring is considered the strongest proof of environmental protection. Validation through air monitoring in the exhaust hood or system and documentation that environmental releases are insignificant and that HEPA filtration is not needed is an alternative to requiring HEPA filtration.

Air monitoring for worker exposures and environmental releases is not a high priority if the attributes of a new research task or project are similar in duration, use similar UNP materials, and involve similar research processes as previously sampled research (such as that performed in Phase III of the pilot study). Phase III sampling of releases into the hoods and modeling of UNP emissions to the outdoor environment indicated that the processes studied resulted in insignificant releases to the outdoor environment; that is, they resulted in release concentrations that were orders of magnitude less than applicable standards or a size-scaled permissible exposure limit. Based on the limited data from Phase III, processes that involve transfer of UNP in milligram or less quantities, processes that are less than 30 minutes in duration, and processes that occur less than a few days a week (from PUB3000, Chapter 4), do not need HEPA filtration.

If sampling is required for a research process involving UNP that is not similar to those evaluated in Phase III, the preliminary control band must be validated in a manner similar to that performed in Phase III. The sampling and analytical methodology developed for use in the pilot study provided the necessary information to make an informed decision on the potential release of UNP to the outside environment. However, it is recommended that it be modified based on lessons learned in previous phases of the study for the following reasons.

Extended sampling durations and increasing sampling flow rates were used in the pilot study in an effort to optimize detection of UNP using filter-based methods. However, even by increasing sampling flow rates and extending research task durations, obtaining sufficiently low detection limits for research tasks was challenging. Generally, only electron microscopy (EM) was able to report values above detection limits. Differentiating between UNP and naturally occurring nanoparticles or those that are produced through incidental processes such as combustion is very important to determine whether controls are needed (e.g., HEPA filtration). The gravimetric and ICP analyses were of limited value from the perspective of environmental release and UNP speciation.

Direct-reading instrumentation provided no information related to specificity of the UNP. This is a significant limitation because the vast majority of the nanoparticles measured by this technology are typically from "background" sources (naturally occurring or incidental nanoparticles such as those produced during combustion). High background particle levels increase the complexity of determining the environmental emissions contributed by research process tasks using direct-reading instruments.

If sampling is required to validate preliminary control bands for research processes involving the use of small amounts of UNP (milligram quantities) for short durations (less that 30 minutes), samples should be collected on track-etched filters and analyzed using EM as described in the Phase III report. Estimates of ambient concentrations should be modeled using the EM data as outlined in the Phase III report. Collection of additional samples for gravimetric and ICP analyses is optional. Measurement of particle concentrations using direct-reading instruments is not required.

2.4 Review Monitoring Results, Determine Potential for Significant Environmental Release, and Revise Control Band as Appropriate

As discussed in Section 2.3, without environmental air sampling data, the initial assignment of control bands is conservative. Control banding is a reiterative process and each time sampling is performed on a control banded process, the sample data should be reviewed to determine if the assignment of controls is optimal.

If sampling data indicate that the probability of a UNP release to the outdoor environment is less than originally predicted, then the process may be assigned to a lower control band and safely performed under less restrictive controls. In many cases, extra precautions, such as using HEPA filtration for exhaust systems, may not be necessary. The requirement for HEPA filtration can be avoided through review of sampling and application or adjustment of the control bands originally assigned to the process.

Two types of air sampling data may be available for review. The BEA may result in development of industrial hygiene sampling and there may be data available from sampling of the process within the laboratory exhaust system/lab hood. Both data sets are of importance in determining the effectiveness of the controls for the research process. If industrial hygiene monitoring indicates controls are inadequate, then research will not be permitted to continue until further research modifications and controls are instituted.

Environmental sampling data for a research process can be compared to existing data (in this case, Phase III data). If the data are of the same order of magnitude as the Phase III data, then compliance is affirmed because sampling data from Phase III indicated that releases from research evaluated in the pilot project were orders of magnitude below potentially applicable regulatory limits.

Since control bands are portable to similar work involving similar materials, when a control band is revised based on a review of sampling results, controls for the similar work may also be revised. Thus, it is possible to use the information from Phase III monitoring to support the

evaluation of research processes as long as research is of a similar duration (e.g., less than 30 minutes), utilizes similar UNP materials in milligram quantities and involves similar work practices.

2.5 Implement Periodic Monitoring for Long-Term Research

When research with UNP is funded for at least one year and planned to be ongoing, then periodic environmental sampling may be required to ensure that UNP emissions to the outdoor environment remain safe and compliant. Periodic monitoring statistically strengthens the results of previous sampling and ensures that any changes to the research do not result in significant differences in emissions. Research involving UNP often requires modification of procedures through trial and error, and staff members performing the research may change frequently. To capture the effect of research changes and to document safety, monitoring of long-term processes is often warranted.

Periodic sampling of long-term processes should be performed using sampling and analysis methodology using EM as described in the Phase III report. Estimates of maximum outdoor concentrations will be modeled using the EM data as outlined in the Phase III report. Collection of samples for gravimetric and ICP analyses, and measurement of particle concentrations using direct-reading instruments is not required for research processes that use small amounts of UNP materials (milligram levels) for short duration (30 minutes or less).

Monitoring of environmental releases is most important where HEPA filtration is not utilized and air monitoring indicates emissions are less than applicable limits or size-scaled permissible exposure limits or where UNP is known to have novel properties (e.g., morphology, toxicology, or dustiness). In these cases, subtle changes in research and personnel could impact emissions of UNP to the outdoor environment.

Periodic monitoring is not a priority if the work has been monitored (and modeled) and found to have emissions that are significantly less than potentially applicable regulatory limits. In addition, monitoring would not be appropriate for short-term projects and tasks, which by their nature end before additional sampling is warranted. A research project would be long-term if the research tasks are sustained for over a year and if there is opportunity for resampling.

3.0 RESEARCH PROCESS REVIEW AND DOCUMENTATION

For research processes involving the use of UNP that were not considered in the pilot study, attention should initially be placed on processes that present a greater potential for release of UNP than those observed in the pilot project. New work with a greater potential for airborne release of UNP than those evaluated in the Phase III would have one or more of the following characteristics (for example):

- processes of longer duration
- processes that occur with a greater frequency
- manipulation of larger quantities of nanomaterials
- more energetic processes
- use of dustier nanomaterials
- nanomaterials of novel morphologies (e.g., CNT)
- nanomaterials with a greater toxicity than the parent material

Since assessments and validation of assessments similar to those performed in the pilot study are resource intensive, prioritization of risk is important. However, in the absence of air monitoring data, it is difficult to prioritize UNP because attributes such as dustiness and toxicity are not yet well defined. Based on the assessments made in the pilot study, LBNL subject matter experts should focus on research activities involving UNP that is of greater potential risk.

The LBNL ESG is tasked with ensuring environmental safety and compliance. To this end, environmental management of the UNP begins with identifying the sources and their significance. The BEA form may provide some information about UNP (see Appendix B), and when the IHG has completed the BEA, more detailed information on occupational exposure becomes available. For work with UNP that does not require a BEA, the IHG provides ESG with information on work locations, UNP users, and all BEAs and monitoring results (current and past).

Berkeley Lab uses a hierarchy for instituting controls and this information is important for the ESG's determination of potential environmental releases. Controls are implemented in accordance with the following hierarchy, when feasible:

- Elimination of a material or process, if it is determined to be unnecessary (this is the preferred method of control)
- Substitution of a less-hazardous method or material
- Engineering controls such as ventilation, containment, or barriers
- Administrative controls such as rotation, job sharing, or training
- Personal protective equipment (PPE) such as clothing, gloves, and respiratory protection

When the researcher is able to effectively control UNP using elimination or substitution, then environmental releases are mitigated, but where engineering, administrative or PPE are the primary controls, release of UNP to the environment should be evaluated

The ESG should track UNP-generating research projects to ensure releases to the outdoor environment have either been monitored or controlled. When monitoring is performed, the data is used to expand the control banding data set and to modify control bands. Determining the UNP projects with the greatest potential for environmental impact requires periodic review of the sources, the controls, and the regulations. Since nanotechnology research is dynamic, a six-month review of data is suggested. The ESG should maintain documentation of the list of projects, their duration, control bands (or equivalent hazard and control information), and environmental assessment results. This information should be communicated to the EHS management. LBNL ESG currently has a format for managing and tracking potential sources of environmental contaminants, such as the LBNL program for managing Diesel Particulate Matter Air Emissions, and a similar format for environmental UNP emissions would ensure that ESG would be prepared for future (potential) reporting requirements.

4.0 IMPROVING THE ENVIRONMENTAL NANOSCALE MONITORING PROCESS

The LBNL UNP pilot study represents a first effort in the evaluation of environmental release of UNP in research environments, with a focus on determining if releases of UNP from building exhaust were acceptable or compliant. The methodology consisted of an understanding of the research process involving UNP, identifying the UNP material(s) used in the process, and monitoring UNP using filter-based sampling and direct-reading technology based on guidance contained in the NSRC Approach document and the Nanoparticle Emission Assessment Technique (NEAT) developed by NIOSH (Methner 2010a; Methner 2010b).

Estimating environmental release of UNP from LBNL research process operations involved monitoring at the point of potential release which was expected to result in the highest concentration of UNP (the worse-case point source location) for the research processes evaluated (e.g., within the fume hood). Monitoring involved the use of direct-reading instruments such as condensation particle counters (CPCs) and optical particle counters (OPCs), and time-integrated filter samplers at the release location and at a background location. Analysis of the filters was performed using gravimetry, ICP and EM. However, because small amounts of UNP were used over short periods of time, only EM was able to report values above detection limits. The EM results were modeled to estimate UNP concentrations on the ambient environment.

Although modeling (rather that ambient monitoring) was used to determine impact of UNP from LBNL research processes, it represents the state of the science at this time. Establishment of an UNP ambient sampling network was considered as an alternate approach to electron microscopy/modeling but deemed to be not feasible due to complexities with background nanoparticles and costs related to development of ambient sampling technology appropriate for UNP. Simply put, based on data obtained in Phase III, the ambient concentrations of UNP generated from research processes at LBNL will be below the sensitivity of the technology used to analyze the samples (including EM). It will be virtually impossible to obtain any data on the impact of UNP release to the ambient environment from research processes of short duration with a high degree of confidence based on ambient sampling at outdoor locations. Thus, the methodology developed and lessons learned in Phase III related to monitoring UNP provides the foundation to improve the process of estimating the environmental impact of UNP in future studies.

With respect to improving the environmental nanoscale monitoring process, it is important to note that nanotechnology and potential issues related to EHS of UNP are evolving at a rapid pace. As such, the methodology used to sample and analyze UNP needs to be flexible so that the methods can be adjusted and modified as technology and knowledge related to the environmental aspects of nanoscale materials evolves. Although the roadmap for monitoring UNP that has consensus of the scientific community has yet to be established, interim guidelines from the U.S. Environmental Protection Agency (EPA) and NIOSH advise the use of both direct-reading instruments and electron microscopy to assess the presence of airborne nanomaterials in workplaces. Direct-reading monitors such as CPCs and OPCs, however, cannot speciate

particles and are limited in their ability to detect the presence of aerosols that are composed of airborne nanomaterials alone or as a mixture within a complex atmospheric aerosol. Thus, it appears that filter-based sampling will play a dominant role in monitoring for UNP in the U.S. For example, NIOSH has issued bulletins with recommended occupational exposure limits for fine and ultrafine (including engineered nanoscale) TiO_2 (NIOSH 2011) and CNT (NIOSH 2010). Recommended monitoring for TiO_2 and CNT in occupational environments includes sampling using filter-based methods with confirmation using EM.

The methodology used in the pilot study to monitor environmental release, validate the preliminary control bands, and establish a periodic monitoring program was developed with a focus on the ongoing activities involving EHS of nanoscale materials. As noted, methodologies for monitoring UNP are evolving and as such the improvements in environmental and occupational monitoring will evolve as monitoring technology advances and sampling and analytical methodologies become more established. In the meantime, it has been proposed by Hoover that monitoring be subdivided into three primary categories by intent: screening, extensive characterization, and periodic sampling (Hoover and Maiello 2010, Kulinkowski and Lippy 2011.

Screening involves the initial assessment to determine whether the UNP disperses into the workplace or has the potential for release to the outside environment. For this purpose, direct-reading instruments such as CPCs can be used as a relatively cost-effective means to screen a workplace for particle concentrations and to identify areas with elevated particle concentrations. While direct-reading instrumentation can provide useful information on potential particle release in real time, these instruments are not specific for UNP.

Once areas of interest have been identified, extensive characterization using filter-based sampling is needed so that UNP can be analyzed chemically and speciated. Extensive characterization involves the detailed measurement of airborne particle concentration by size, shape, and composition for the purpose of documenting morphological and chemical characteristics which can be used to speciate UNP on filter samples.

Periodic sampling is performed to ensure that airborne concentrations of UNP stay below acceptable levels established by government agencies or the facility if no guidance is provided by the government. Depending on the application, periodic sampling can involve collection of data from direct-reading monitors and/or time-integrated filter samplers, which allows the workplace concentration of UNP to be established. Both screening and extensive sampling of selected EETD research processes were performed in the pilot study. For future periodic environmental sampling of research processes involving UNP, the methodology should be modified based on lessons learned in Phase III. Specifically, the monitoring should be performed using filter-based sampling at the process source locations, and the samples should be analyzed and speciated for UNP using EM techniques. Estimates of maximum UNP concentration to the outdoor environment can be made through modeling of the EM results following the approach outlined in the Phase III report.

While this approach will provide the needed information related to environmental release of UNP from research processes, new and more efficient approaches and tools are needed for evaluating the safety of nanomaterials. In particular, a standardized, screening-level tool is needed for assessing the potential for airborne exposure to any UNP of interest.

In the pilot study, the potential for release was based on a dustiness value which was used as a subjective description of the likelihood that a solid particulate material may become airborne when disturbed. Systematic assessments, such as control banding, require assignment of toxicity and a value for dustiness for solid particulate materials and volatility for liquid materials. The control bands developed for LBNL EETD research processes in the pilot study were based on an estimated toxicity of the UNP and the potential for exposure/release. Since the toxicity associated with UNP is not currently known, it was assumed to be "high" or "very high." For dry UNP powders evaluated in the pilot study, the UNP was assumed to be "dusty." Thus, qualitative worst-case estimates were used in the development of the control bands in this pilot project, which resulted in control band levels that are more stringent than what may be actually needed for LBNL research processes involving UNP.

The control band process can be improved through incorporation of quantitative values of toxicity and dustiness. While it may be many more years for essential toxicological information and environmental and occupational exposure limits to become available, the measurement of dustiness for UNP could be developed at this time. With a more accurate rating of dustiness, there would be a more accurate assignment of risk levels and subsequently environmental controls would not be overly conservative.

Further, incorporating a quantitative dustiness value with data obtained from point source sampling of research processes evaluated in the pilot study will enable predictions to be made as to potential for environmental release from other UNP research processes that are similar to those evaluated in the pilot study. For example, for the UNP types that were evaluated in the pilot study there is minimal potential for environmental release and thus HEPA filtration is not needed. If a quantitative measure of dustiness is obtained for the UNP materials evaluated in the pilot study, then that dustiness value can be compared to the dustiness value of a UNP material used in a similar research process to predict potential for environmental release. That is, UNP that has a dustiness value equal to or less than the dustiness of one of the UNP types evaluated in the pilot study (e.g., fumed silica) should result in an environmental release similar to that obtained for UNP material evaluated in the Phase III study (assuming the processes are similar). The working hypothesis is that UNP possessing similar dustiness values will exhibit similar airborne concentrations, just as solvents with similar vapor pressures would have the same volatility. The dustiness can then be used initially as a screening tool to predict potential exposure to UNP and inform management decisions. For control banding, it would then be possible to immediately assign risks and controls for similar materials without extra validation and without being overly conservative.

A metric based on a quantitative measure of dustiness could be used to estimate the potential for exposure to airborne concentrations of UNP. This metric would be a tool for both researchers and ESH subject matter experts. By understanding which materials present the greatest

likelihood of release, the safest materials can be selected for work and dustier materials can be the focus of the higher degree of control (this concept is currently applied to chemical solvents, where vapor pressure gives an indication as to how likely a solvent would be to vaporize and be present in air). Over time, a database could be developed of UNP and their specific dustiness indices. The extrapolation from dustiness to potential airborne concentrations could be achieved by quantifying, under real-world conditions, the airborne concentrations of a selected UNP with known dustiness indices. Ultimately, dustiness may evolve as a component of the material safety data sheet (MSDS).

Finally, since nanotechnology is a new and dynamically evolving field review of toxicity and governmental standards/recommendations related to UNP should be conducted on a periodic basis. This activity is an important component of the DOE policy on nanoscale safety (DOE P456.1).

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APPENDIX A

Worker and Environmental Assessment of Potential Unbound Engineered Nanoparticle Releases: Lessons Learned in Phases I, II and III

RJ LEE GROUP
DELIVERING SCIENTIFIC RESOLUTION

August 10, 2011

Ms. Linnea Wahl
Pilot Study Project Manager
Ernest Orlando Lawrence Berkeley National Laboratory
One Cyclotron Road
Berkeley, California 94720

Re: Worker and Environmental Assessment of Potential Unbound Engineered Nanoparticle Releases: Lessons Learned in Phases I, II and III

Dear Linnea:

A multiphase pilot study is being conducted at the Lawrence Berkeley National Laboratory (LBNL) Environmental Energy Technologies Division (EETD) to evaluate the potential for worker exposure and emissions to the outdoor environment of unbound engineered nanoparticles (UNP). LBNL management stipulated that the pilot study comply with Department of Energy (DOE) Notice N456.1, *The Safe Handling of Unbound Engineered Nanoparticles* (the DOE Notice N456.1 is being replaced with DOE Order 456.1, *The Safe Handling of Unbound Engineered Nanoparticles*, released on 5-31-2011) as follows:

- Conduct a worker safety and environmental exposure assessment for the potential release of UNP.
- Assess the need for appropriate controls for worker safety and environmental protection (including the use of high-efficiency particulate air [HEPA] exhaust filtration to protect the environment).
- Establish an environmental monitoring program for UNP based on preliminary exposure assessment and guidance provided in the DOE Nanoscale Science Research Centers (NSRC) Approach document[1].

To address these requirements, RJ Lee Group (RJLG) developed a multiphase pilot study. In Phase I, activities involved the collection of information that was used to develop the preliminary Control Bands. Work in Phase I involved discussions with researchers and observation of processes involving fume hoods, glove boxes, counter tops, and ablation systems, and the collection and characterization of UNP starting materials. Phase II 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 in all cases, the actual controls used by researchers, during work with UNP, met or exceeded the validated control bands, none of the researchers were exposed to significant

[1] Department of Energy, *Nanoscale Science Research Centers: Approach to Nanomaterial ES&H*, Revision 3a, DOE Office of Science, 12 May 2008.

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levels of airborne UNP during the evaluation, and none of the processes evaluated resulted in significant emissions to the outdoor environment (see the Phase III report at http://www.lbl.gov/ehs/esg/).

The next phase of this pilot study (Phase IV) will recommend a program to monitor and assess emissions of UNP to the outdoor environment on a periodic basis. One focus of this program will be to determine if HEPA filtration is required to control airborne releases to the environment. As a first step in this process, this letter report addresses "lessons learned" in the Phase I, II and III efforts and focuses on aspects related to environmental release and control of UNP . At LBNL, both environmental safety and occupational safety aspects are controlled through the LBNL Integrated Safety Management (ISM) program processes. Note that this report does not specifically discuss the compliance status of the LBNL occupational health, medical, training, or industrial hygiene programs with respect to DOE Notice 456.1 or DOE Order 456.1.

Listed below is a summary of general observations and lessons-learned during the course of the Phase I, II and III studies.

General Observations

Throughout the project, RJLG staff had access to LBNL research and support staff, and to the laboratories where the research was conducted. Below is a list of general observations that were compiled during the study.

- LBNL EETD researchers involved in this study were forthcoming and demonstrated a working understanding of the ISM processes as related to their research.
- Researchers wore lab coats, safety glasses, and polymer gloves when working with potential UNP materials.
- EETD staff were aware that UNP waste must be in compliance with LBNL's system for managing and disposing of these materials as hazardous waste. Liquids that may contain UNP are bottled, contained, and labeled as required by LBNL rules.
- LBNL staff were aware that sinks and drains must not be used to dispose of liquids that could contain UNP.
- Solid waste with potential UNP are managed through the LBNL-wide hazardous waste system.
- Laboratory interviews with researchers and observations of process activities indicated LBNL (nanoscale research related) rules are being followed.
- It was apparent that researchers had worked with their LBNL safety support and subject matter experts in planning, hazard identification, workplace monitoring, and performance of work, and there was an excellent line of communication established between researchers and ESH personnel.

- The LBNL ESH personnel involved in this project were well versed on the nature of hazards associated with nanotechnology research.

- LBNL EETD laboratory exhaust systems that were evaluated in the pilot study do not incorporate HEPA filtration. In general, this is typical of governmental and academic laboratories.

- Based on the observations of research processes in Phase I and sampling and analysis conducted in Phase III, research process activities with UNP at LBNL EETD appear to be well planned, reviewed, and controlled.

- LBNL research staff raised questions as whether some materials meet the definition of UNP. The LBNL subject matter experts and the support staff were well versed on these issues.

Lessons-Learned

The work conducted in Phase I, II and III of the pilot study represents a first effort in evaluation of environmental release of UNP in research environments. The primary focus of the pilot project was to determine if environmental releases of UNP from building exhaust was acceptable/compliant. The methodology used in the evaluation of UNP environmental release consisted of an understanding of the research process; the UNP material(s) used in the process; use of control bands based on potential for release/exposure to the UNP and hazard associated with the UNP; and monitoring of UNP using filter-based sampling and direct reading technology based on guidance to NSRC Approach document.

It was recognized that the highest concentration of UNP (that is the worse-case point source) for the research processes evaluated was inside laboratory fume hoods. Since there was no active filtration for the exhaust system, monitoring in the hoods provided information on potential worse-case environmental concentrations.

Since this was a pioneering effort, much was learned during the course of the study. Lessons learned in this pilot study which can be used to guide future studies of this nature include:

- Control Banding was used to evaluate or rank the risk and assign controls for the use of UNP in research activities evaluated in this pilot study. Control Banding provides a uniform approach to determining risk attributes and identifies a commensurate level of control. Attributes such as dustiness and toxicity are critical factors to consider in the Control Banding approach. There is little toxicological information for specific UNP and until more toxicological testing of nanomaterials is completed it will be necessary to consider untested materials as being of unknown toxicity and assume that UNP are of a high-level of toxicity. Although there is not a standard method for quantifying the dustiness of UNP, methods to measure dustiness have been developed which make it feasible to quantify or rank dustiness and thus improve the Control Banding approach for UNP.

- To validate the adequacy of the Control Banding approach used in the pilot study, the sampling and analysis methods presented in the NSRC Approach document were used. Where standard methods (such as NIOSH and OSHA methods) were available, they were followed to ensure data met monitoring requirements. Extended work and sampling durations and increased sampling

flow rates were used to optimize detection of UNP using filter-based methods. In addition, researchers replicated the tasks and processes that are most likely to generate emissions of UNP (for example, cleaning up a simulated spill inside a glove box) to further optimize detection. However, even under these extraordinary conditions, obtaining sufficiently low detection limits for research tasks was challenging. Generally, only electron microscopy was able to report values above detection limits. This demonstrates that since worker exposures were insignificant under worst-case work conditions, exposures under normal operating conditions would also be negligible.

- Air monitoring of employees indicated there were no significant exposures (analytical results obtained in Phase III indicate low or unmeasurable levels of worker exposure). Based on this data, the observed work practices and associated controls are deemed effective.

- For the nanoscale research tasks evaluated in this study, air sampling indicated negligible emissions of UNP to the outdoor environment.

- The controls used by researchers, during work with UNP, met or exceeded the validated, recommended control level based on a control band approach.

- Direct reading instrumentation can be used to provide insight on UNP release by comparing data obtained during the process to background. However, direct reading instrumentation provides no information related to speciation of UNP. This is a significant limitation of this instrumentation as the vast majority of the nanoparticles counted at Buildings 62 and 70 are introduced into laboratories from the building air supply (outside environment). Note: Natural or background UNP is currently not the subject of standards and regulations, but high background particulate levels increase the complexity of determining the emissions arising from (contributed by) research tasks. The low background enclosure developed at LBNL has proven to be effective in minimizing or eliminating interfering background particles.

- There is no regulatory requirement for HEPA filtration for research laboratories. (While DOE Notice 456.1 did require an assessment of the need for HEPA controls, this is currently not required by DOE Order 456.1.) None of the research activities evaluated in this study were sources of significant environmental releases of UNP. As such, HEPA was not recommended for any of the research processes that were evaluated in this pilot study.

- 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 result in similar exposure results.

- It is critical in studies of this nature to have a good understanding of the morphological and chemical characteristics associated with the UNP. This information is used to define a signature of the UNP material which can then be used to identify UNP on environmental samples. This approach worked well in this study and should be followed in future studies of this nature.

- The HEPA-filtered enclosure system developed by LBNL staff to reduce interfering background airborne particulate was employed on two research processes during Phase III sampling. Although the enclosure reduced background significantly, the system was not essential to

resolving particle presence and identity of UNP when using the sampling and analytical methods used in the Phase III study.

- Since LBNL conducts nanoscale research using unfiltered exhaust systems, the research review process must consider the toxicity of the materials and the potential for release. Activities that the environmental monitoring program identifies as emitting unacceptable quantities of UNP should be controlled (for example, by performing the work using HEPA filtered exhausts; reducing the quantity of the materials; or using other methods of controlling emissions). The environmental monitoring program that RJLG develops for LBNL will consider these and other possible controls. The LBNL ISM system for review of research was observed to work well at LBNL and appears to provide a good level of administrative control and is suitable for ensuring control of emissions.

In summary, LBNL management recognizes the need to assess Environmental, Safety, and Health aspects of nanoscale research projects as required by DOE Policy, Notice and Orders and addressed this requirement through the conduct of this pilot project. Since LBNL has an effective Integrated Safety Management System for review of research, it is recommended that this program serve as the basis for compliance with the environmental aspects of DOE Order 456.1, *The Safe Handling of Unbound Engineered Nanoparticles* (approved: 5-31-2011). The earlier phases of this project employed the use of common occupational health/industrial hygiene evaluation techniques in a Control Banding approach to rank the risk of environmental release of UNP and to suggest the appropriate level of control. Occupational exposures and environmental air emissions share risk attributes. For example, as utilized in the earlier phases of this project, industrial hygiene assessments using material characteristics/attributes such as degree of dustiness to rank the risk of airborne releases can be modified to determine the potential for both occupational and environmental UNP releases. In essence, the dustier the process the greater the risk of airborne exposures to workers and the greater the risk of release to the environment, where ventilation systems are not filtered. Similarly, the greater the toxicity of a material, the greater potential risk to both workers and the environment. The environmental monitoring program that RJLG develops for LBNL will take these and other risk attributes into consideration.

The implementation plan presented in Phase IV will suggest expanding the exposure assessment approach, to not only ensure occupational safety, but also to capture basic environmental risk attributes. Where environmental release of UNP is deemed likely, air monitoring or increased controls (such as HEPA filtration) would be utilized to ensure compliance and risk mitigation.

Should you have any questions related to this report, please do not hesitate to contact me.

Sincerely,

Gary S. Casuccio Randall Ogle

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Appendix B

Sample Baseline Exposure Assessment Form

SAMPLE *LBNL Baseline Exposure Assessment Form*

Division: XYZ
Location(s): B1000, R1000
SEG:

Primary Hazard Categories: Engineered nanomaterial
Work Authorization Documents: N/A
Medical Surveillance Group (if any):

Activity : Weighting of multi-walled carbon nanotubes (CNTs) on a precision scale located on a lab bench top followed by manipulation of CNTs in a fume hood

☐ Observed ☒ Discussed ☐ Simulated

Person(s) interviewed: JD PI

Work Supervisor(s): JD Supervisor

Hazard Information

Material/Agent	Quantity or other Information	Frequency (Days/Year)	Duration (Hours/Day)	Potential Exposure Route(s)	Current Controls	Is Activity considered "Low Risk" (as defined in the instructions, < 80 dBA or other)
1. Multi-walled CNTs	5 mg	100	0.01	☒ Inhalation ☐ Injection ☐ Splash ☐ Noise ☐ Dermal Absorption ☐ Other:	☒ Engineering. Fume hood ☐ Admin. ____ ☒ PPE Safety Glasses, lab coat, nitrile gloves ☐ None	☐ No ☒ Yes (enter criteria): 2 ☐ Data was used-enter specific information in the comments section.
2.				☐ Inhalation ☐ Injection ☐ Splash ☐ Noise ☐ Dermal Absorption ☐ Other:	☐ Engineering. ____ ☐ Admin. ____ ☐ PPE ____ ☐ None	☐ No ☐ Yes (enter criteria): ☐ Data was used-enter specific information in the comments section.
3.				☐ Inhalation ☐ Injection ☐ Splash ☐ Noise ☐ Dermal Absorption ☐ Other:	☐ Engineering. ____ ☐ Admin. ____ ☐ PPE ____ ☐ None	☐ No ☐ Yes (enter criteria): ☐ Data was used-enter specific information in the comments section.
4.				☐ Inhalation ☐ Injection ☐ Splash ☐ Noise ☐ Dermal Absorption ☐ Other:	☐ Engineering. ____ ☐ Admin. ____ ☐ PPE ____ ☐ None	☐ No ☐ Yes (enter criteria): ☐ Data was used-enter specific information in the comments section.

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SAMPLE *LBNL Baseline Exposure Assessment Form*

Use Additional Sheet for Additional Materials or Agents

Follow Up Assessment Needs	
Type of Assessment Needed	Priority 1 – 5 (1 is lowest...)
Evaluate airborne levels of particles released during weighing using air sampling equipment	2
Unbound engineered nanoparticles (UNP) are being handled in a fashion that needs additional review by the Environmental Services Group	

Other Comments, Observations, or Recommendations
Weighing is performed on a lab bench top outside of a fume hood or glove box. Other activities involving manipulation of the CNTs are performed in a fume hood with no HEPA filtration.

Evaluated by: IH 1 Date: 8/23/11

Reviewed and approved by: _____ Date: _____

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