THESIS

CHARACTERIZATION OF NANOPARTICLES GENERATED FROM DRILLING ACTIVITIES WITHIN A SUB-SURFACE MINE USING A NOVEL SAMPLER

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ABSTRACT

CHARACTERIZATION OF NANOPARTICLES GENERATED FROM DRILLING ACTIVITIES WITHIN A SUB-SURFACE MINE USING A NOVEL SAMPLER

This study employed nanoparticle sampling techniques to characterize the aerosol generated from a routine mining activity. A preliminary survey of the particle emission from the feed-leg drilling activity was conducted in the excavations of an experimental mine. The level of particulate exposure was sampled using a novel sampler for respirable and nanometer sized particles; and monitored by direct reading real time instruments. A NanoScan scanning mobility particle sizer (measurement range 10-420 nm) and an optical particle sizer (measurement range 0.3-10 µm) were used. Particulate morphological and structural examination of samples collected with the novel nanoparticle sampler and a thermophoretic sampler was conducted through transmission and scanning electron microscopy and x-ray dispersive analysis. Based on the real-time instrument data, the researchers found high concentrations (> 3.5 x 106 particles/cm^3) of ultrafine/nanoparticles generated from the drilling activity. A large amount of submicron silica, spherical primary and agglomerated particles rich in carbon were discovered via analysis of particle sampler specimens with energy-dispersive x-ray spectroscopy. Many particle agglomerates contained primary particles less than 100 nm. Exposure to particles in the nanometer size from various sources within the mining environment has not been well characterized and may be associated with respiratory and systemic disease among miners.

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INTRODUCTION

Exposures to mine dust have been measured and evaluated for decades using gravimetric measurements, and it was found that exposures to aerosolized dust particles such as coal or silica can cause diseases in the lung and other organs[1-7]. One method that the Mine Safety and Health Administration (MSHA) uses to characterize inhalation exposures within the mining environment is the measurement of the respirable dust mass concentration within the breathing zones of workers[8]. Respirable particulate matter (RPM) is of great concern due to its ability to deposit in the alveolar region of the lungs[9, 10] where it can affect respiratory function. Interventions championed by MSHA in the past few decades have greatly reduced the prevalence of coal workers pneumoconiosis (CWP) and progressive massive fibrosis (PMF). Although great progress has been made, the prevalence of CWP and PMF appears to be trending upwards since the mid-1990s and the measured increase in prevalence is not elucidated in RPM measurements[11, 12]. The presence and risk associated with ultrafine particles such as emission from diesel engine within the mining environment has been previously established[13, 14].

Nanometer sized particles, in the range of ultrafine particles (<1 µm), fall within the RPM size range and have been found to deposit in all regions of the respiratory tract[15, 16]. Nanoparticles are commonly accepted as particles that are greater than 1 nm in two or three dimensions but smaller than 100 nm[17]. Once in the lungs, nanoparticles can enter the blood stream[18] and selectively affect organ systems such as the respiratory and cardiovascular system along with other target organs including the liver, bone marrow, lymph nodes, spleen, and brain[15, 16, 19]. The size of nanoparticles has been shown to correlate with their translocation behavior on secondary target organs[20, 21]. There is strong evidence that the clearance mechanisms used to rid the lungs of particulate matter are not as effective on nanometer sized particles, leading to a greater fraction of never-cleared particles which may enhance disease development[20]. Researchers have demonstrated that nanometer sized particles have unique properties [22-24] whose adverse health impact is greater than what has been found with micrometer sized particles of the same type[25-28]. The large ratio of surface area to mass compared to larger particles is believed to make nanoparticles a greater hazard. Using mass to measure these types of exposure would be very difficult to accurately characterize the quantity of such small particles present within the air and may overlook the health impact posed by very fine particles. Due to the relationship between mass and volume of aerosol particles, a particle that is one tenth in size of another particle will have one-millionth the mass of the larger particle. This quantity of nanometer sized particles makes characterization via measuring the mass of RPM inappropriate.

Effective characterization of nanoparticle exposures requires the use of size selective sampling techniques. Traditionally a respirable mass exposure is determined by impacting respirable sized particles onto a filter sample using a nylon cyclone to exclude the collection of particles that are larger than the respirable size range. As previously stated, there are many issues with this mass-based approach. In response to this challenge, several samplers have been developed that are designed to directly collect nanoparticles on substrates including a mesh screen, filter, or transmission electron microscope grid (TEM) to characterize nanoparticles by number count. These samplers employ a variety of particle collection mechanisms including impaction, electrostatic precipitation, sieving, diffusion, and thermophoretic precipitation [29-33] to achieve size-selective nanoparticle collection.

This researchers of this pilot investigation seek to examine the hypothesis that drilling within a mine produces a high number of nanometer-sized particles that are not well characterized by traditional gravimetric methods of measuring RPM.

METHODS

Sampling Site and Study Design

This preliminary investigation was conducted at Edgar Mine operated by Colorado School of Mines. The drilling activity was performed using a pneumatic feed, leg jack drill and was evaluated for aerosol generation and exposure simulation in the drilling area. The drilling site was a dead-end excavation, approximately 9 m x 5 m x 5 m (30 ft x 16 ft x 16 ft), located roughly 250 m (820 ft)down the main portal into the underground mine. The drilling air samples were collected 2 m (7 ft) from the site of drilling action and 1.5 m (5 ft) above the ground to simulate the breathing zone location of a worker near the activity, as illustrated in Figure1. A control sample was collected approximately 15 m (50 ft) upwind from the drilling site in the main shaft with an area of 1.5 m x 1.5 m (5 ft x 5 ft). The air velocity through the main shaft was approximately 1 m/s (215 ft/min). Once drilling began, four consecutive holes were drilled in the excavation wall 10 minutes apart. Each hole represented approximately one to three minutes of drilling.

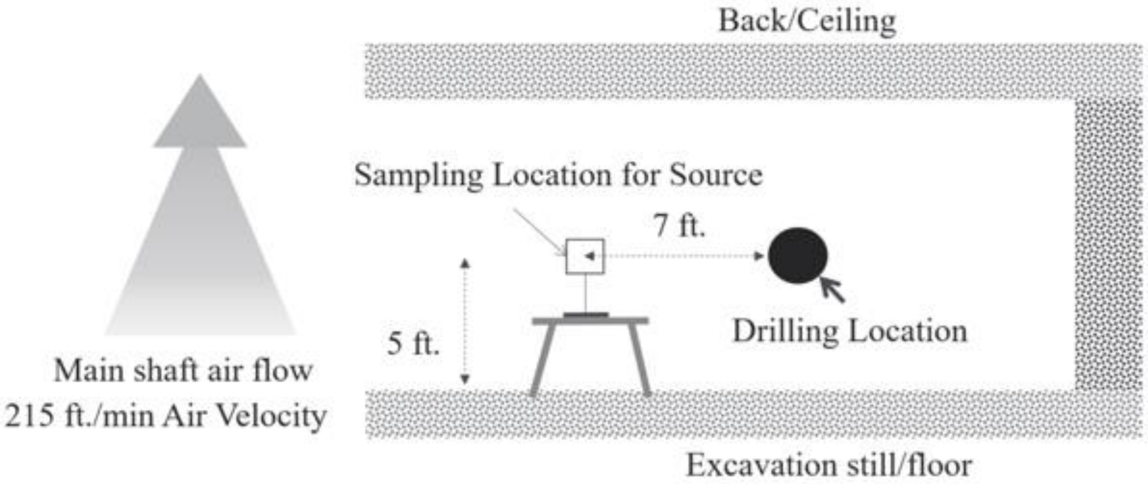


Figure 1. Side view of excavation and drilling location

Exposure Evaluation

Particle size distribution and concentrations were monitored using direct-reading real-time instruments (RTIs) including a NanoScan scanning mobility particle spectrometer (SMPS) (model 3910, TSI Incorporated, Shoreview, Minnesota, USA) and an optical particle sizer (OPS) (model 3330, TSI Incorporated, Shoreview, Minnesota, USA). The NanoScan SMPS has a measurement range of 10-300 nm with a recommended maximum concentration measurement of 1×10^6 particles/cm^3. The OPS has a measurement range of 0.3-10 µm with a recommended maximum concentration measurement of 3,000 particles/cm^3. The normalized concentration of each particle size bin and total particle number concentrations were exported to Excel (Microsoft, Redmond, Washington, USA) to examine the size distribution curves. The normalized number concentration is the measured number of particles for each size channel, divided by the log (base 10) of the size channel width times the midpoint particle diameter for that channel. By utilizing both the NanoScan SMPS and the OPS, the researchers were able to measure particle concentrations and size distributions for three orders of size magnitude from 10 nm to 10 µm. The RTIs began sampling 35 minutes prior to the drilling activity to establish the baseline total particle concentration and particle-size distributions that were present in the background conditions of the mine. Following the establishment of the mine ambient atmospheric aerosol concentration baseline, the drilling activity began for which the RTIs scans were conducted. The RTIs sampled for a total of 84 minutes which included 35 minutes of pre-drilling background, 40 minutes of drilling and 10 minutes of post drilling background. Environmental conditions were monitored with a Velocicalc air velocity meter (Model 9545, TSI Incorporated, Shoreview, Minnesota, USA).

A nanoparticle sampler named the Tsai Diffusion Sampler (TDS) was used for collecting particles in the nanometer and respirable size scale[33]. The TDS was designed to directly collect particles on a polycarbonate membrane filter (25 mm D, 0.22 µm pore) for respirable sizes and a TEM grid for nanoparticles through sieving and Brownian motion/diffusion. A combination of the inlet diameter, geometry of the sampler, and operating flow rate results in the collection of a size-selective sample[33]. The TDS collection efficiency was established experimentally and followed a sigmoidal curve with a cut-point diameter (d_{50}) of 3.8 µm, expressed as a mass median aerodynamic diameter (MMAD)[33]. The TDS cut point diameter closely mirrors the respirable fraction cut point diameter (d_{50} = 4 µm) of the American Conference of Governmental Industrial Hygienists (ACGIH) particle size-selective sampling criteria for airborne particulate matter[34]. Use of the TDS allowed for respirable particle sampling while retaining the ability to characterize collected nanoparticles.

Two additional samplers were used to provide additional aerosol characterization. A thermophoretic sampler (TPS) (RJ Lee, Monroeville, Pennsylvania) was used to collect nanoparticles, along with a respirable cyclone sampler, which was operated in accordance with the NIOSH Manual of Analytical Methods (NMAM) sampling method 7500 for measuring respirable particles in mass. The TPS collects particles on a carbon-coated nickel TEM grid. The grid samples from the TDS and TPS were analyzed using a transmission electron microscope (JOEL JEM-2100F, JOEL Peabody, Massachusetts, USA,). Additionally, the TEM grid samples were analyzed for chemical composition through energy dispersive spectroscopy (EDS) on the TEM. Particles on the filter samples collected by the TDS were examined using scanning electron microscopy (SEM) (JOEL JSL-6500F, JOEL, Peabody, Massachusetts, USA). The filter samples from the respirable cyclone were analyzed via gravimetric weighing using a microbalance (Mettler-Toledo MX5, Columbus, Ohio, USA) to determine the mass collected and to estimate the mass concentration.

The researchers collected samples at several intervals throughout the drilling activity as listed in Table 1. Four TDS samples were collected : Sample 1 collected aerosols for the first 10 minutes of drilling; Sample 3 collected aerosols for the last 10 minutes of drilling; Sample 4 collected aerosols for the entire 40-minute drilling process; and Sample 2 collected aerosols for 18 minutes during the second and third drilling sessions. Additionally, the researchers collected three TPS samples: Sample 1 collected aerosols for the first 10 minutes of drilling; Sample 2 collected aerosols for the next 20 minutes of drilling; and Sample 3 collected aerosols for the final 10 minutes of drilling. One respirable cyclone sample was taken for the complete 40-minute drilling activity.

An environmental aerosol sampling station used for control samples was set up approximately 15 m (~50 ft) upwind from the drilling location. At the control sampling location, the researchers collected a TDS and a respirable cyclone sample to establish the background level of ambient aerosols maintained by the general exhaust ventilation (GEV) system in the mine. Additionally, the researchers collected a background sample by disturbing the settled dust within the mine by driving a golf cart through the mine excavation which is routinely done within the mine. The disturbed dust was examined with a TDS, TPS, and respirable cyclone.

Table 1. Timeline and sample summary of drilling activity

Processes	TDS		TPS	Rep. Cyclone	RTIs
Background 9:35-10:09					Monitoring 9:35 - 10:59 (84 min)
Drilling 1 10:10-10:13	Sample 1 10:10 - 10:20 (10 min)	Sample 4 10:10 – 10:50 (40 min)	Sample 1 10:10 - 10:20 (10 min)	Sample 1 10:10 – 10:50 (40 min)	
Drilling 2 10:21-10:22	Sample 2 10:21 - 10:39 (18 min)		Sample 2 10:21 - 10:39 (18 min)		
Drilling 3 10:30-10:31					

Drilling 4 10:40-10:44	Sample 3 10:40 - 10:50 (10 min)		Sample 3 10:40 - 10:50 (10 min)		
Post drilling 10:50-10:59					

RESULTS

Particle Concentration and Size Distribution

The background aerosol concentrations measured by Nanoscan SMPS and OPS before drilling were found to be relatively low and stable prior to drilling as seen in Figure 2a. The average background particle concentration measured by the OPS for this period was approximately 30 particles/cm^3, and the concentration measured by the NanoScan SMPS was 6000 particles/cm^3 as seen in Figure 2a. Once drilling commenced, there was a clear increase in atmospheric aerosol concentration. The aerosol concentrations quickly exceeded the recommended operating range prescribed by the RTIs manufacturers. The aerosols generated in the 0.3-10 µm range (OPS) remained consistent from the first-hole drilling until the third-hole drilling at which point the oil for the drill bit began to burn as evidenced by a cloud of smoke. The burning oil created greater particle concentrations in the 0.3-10 µm range and it took longer for the GEV system to return the atmospheric aerosol conditions to near background levels. A relative humidity of 33-38% and a temperature of 8.9 °C was measured in the mine.

By evaluating the particle size distribution measured in the aerosol size range below 420 nm by the NanoScan SMPS, the researchers determined the aerosol generation to be unimodal, predominantly in the sub 100 nm range with the peak concentration near 30 nm diameter particles. As the drilling session progressed, the width of the size distribution curves widened within the 10-420 nm range as evidenced by the NanoScan SMPS. For the fourth hole, a high concentration of particles below the100 nm diameter range can be seen, however additional modes developed with the maximum concentration near 50 nm and 100 nm (Figure 2b). The particles measured in the sub-micron range peaked at 3.5 million particles/cm^3 for the first hole drilled. This concentration is three times the recommended operating limit for the NanoScan SMPS. The OPS particle size distribution data showed that most particles sampled by the OPS were less than 500 nm in size (Figure 2c). Throughout the drilling session, the OPS particle concentrations appeared to increase, however the size distributions were consistent throughout sampling time.

Particle Structure and Morphology

The researchers observed high particle deposition on the TDS TEM grid sample for the first 10 minutes of the drilling activity as seen in Figure 3a. The collected particles appeared to have a bimodal distribution with many particles in the micrometer range and many others in the nanometer range (Figure 3b). The researchers identified many silica-rich particles through EDS analysis (Figure 4b). Several particles examined through EDS displayed a significant carbon signal along with the silica rich stone particle signal observed. These particles were also rich in sulfur and iron (Figure 4a). The researchers observed a wide variety of particles through SEM imaging of the TDS filter samples as shown in Figure 3e. Many large agglomerates were observed on filter images, which were comprised of very fine particles with a primary size smaller than 20 nm as seen in Figures 3g and 3h. The grid samples collected by TPS for this period also showed many carbon-rich particles in the 100 nm or smaller size range (Figure 6).

The 20-minute TDS sample included the drilling of two consecutive holes approximately 10 minutes apart. During the second hole for this sampling session, the researchers observed that the oil lubricating the drill began to burn, creating a significant cloud of smoke. The TEM grid sample had an extremely high number of particle deposition with much of the grid overloaded. Three distinct groups of particle types were observed with TEM/EDS analysis; silica-rich stone particles, spherical primary particles and agglomerated carbon-rich particles (Figure 5).

The grid sample collected by the TPS during 20 minutes of the drilling activity (holes two and three) showed a uniform distribution of one particle type consistent with the particles collected in the first 10 minutes of drilling (Figure S3). These particles were within 100 nm in size and EDS analysis identified them to be rich in carbon. The TDS sample for the control station collected very few particles. Most of the TEM grid space had no particle deposition whatsoever that indicated clean, fresh air at the control sample location. The particles collected through disturbing the settled dust within the mine excavations were found to be exclusively silica-rich stone particles with trace minerals consistent with rock dust. The gravimetric samples collected with the respirable cyclone to characterize RPM were below the limit of detection.

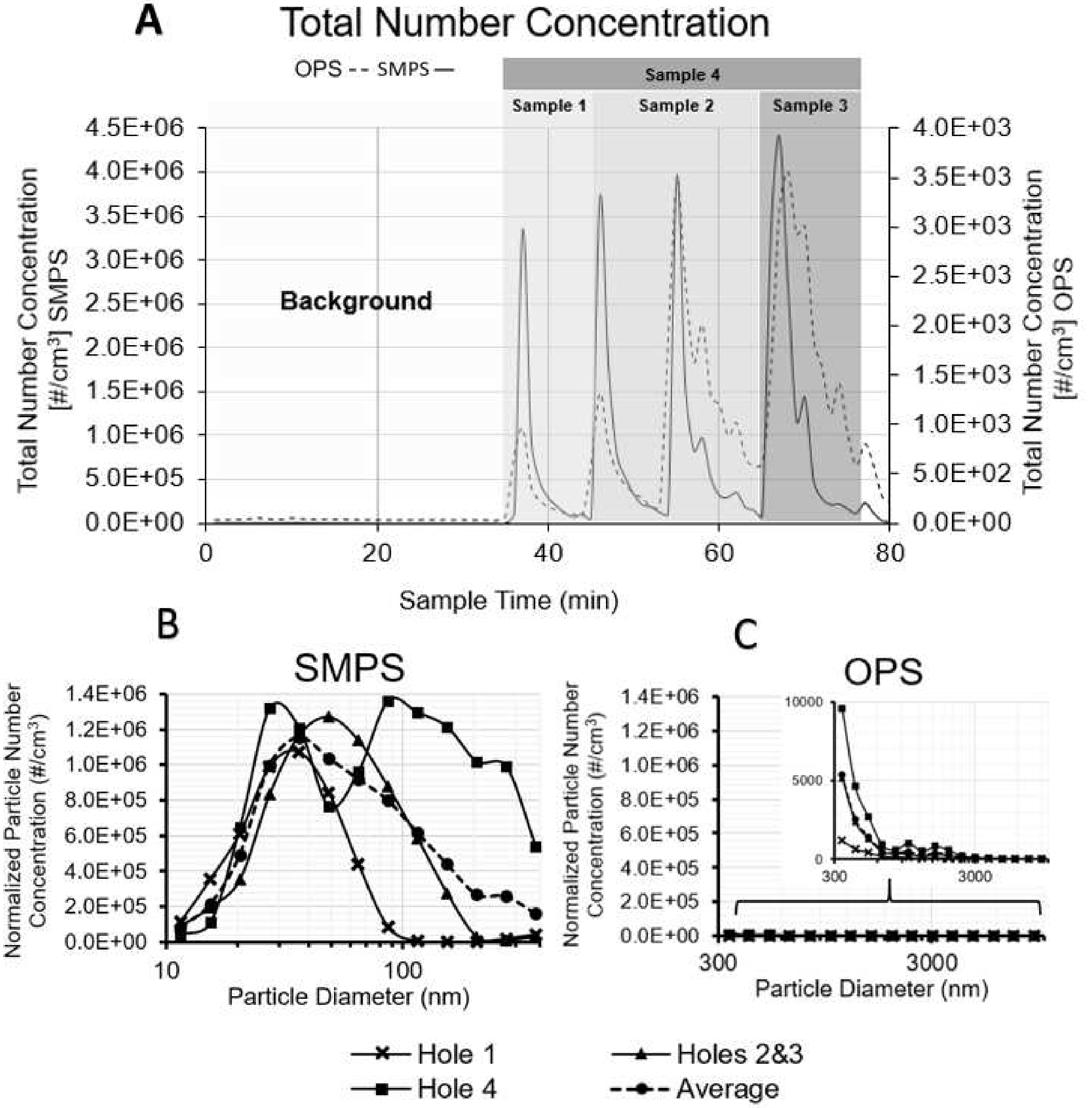


Figure 2. NanoScan SMPS and OPS data for drilling activity. A) Total particle concentrations during sampling periods, B) Particle concentration and size distribution of NanoScan SMPS, C) Particle concentration and size distribution of OPS

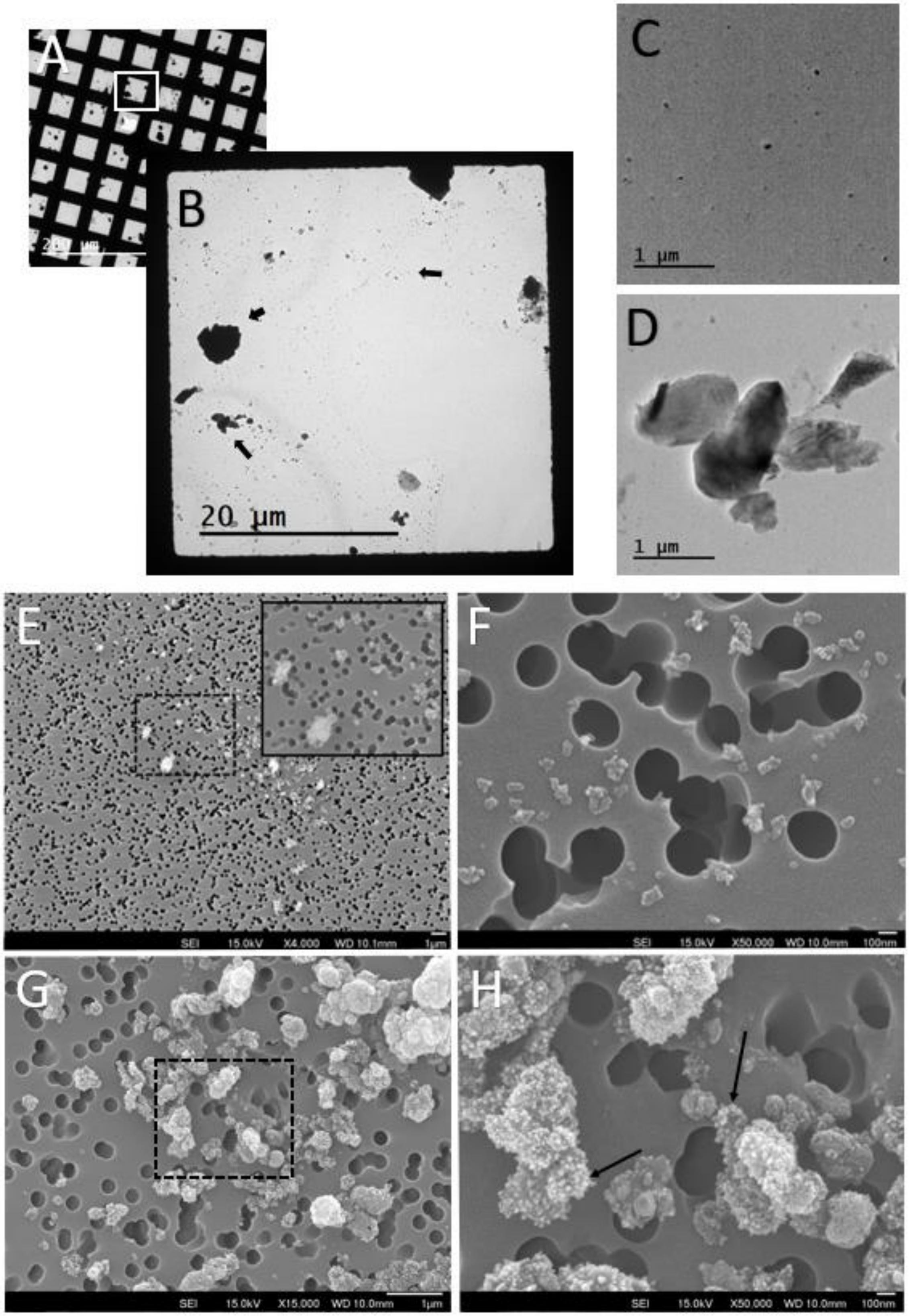
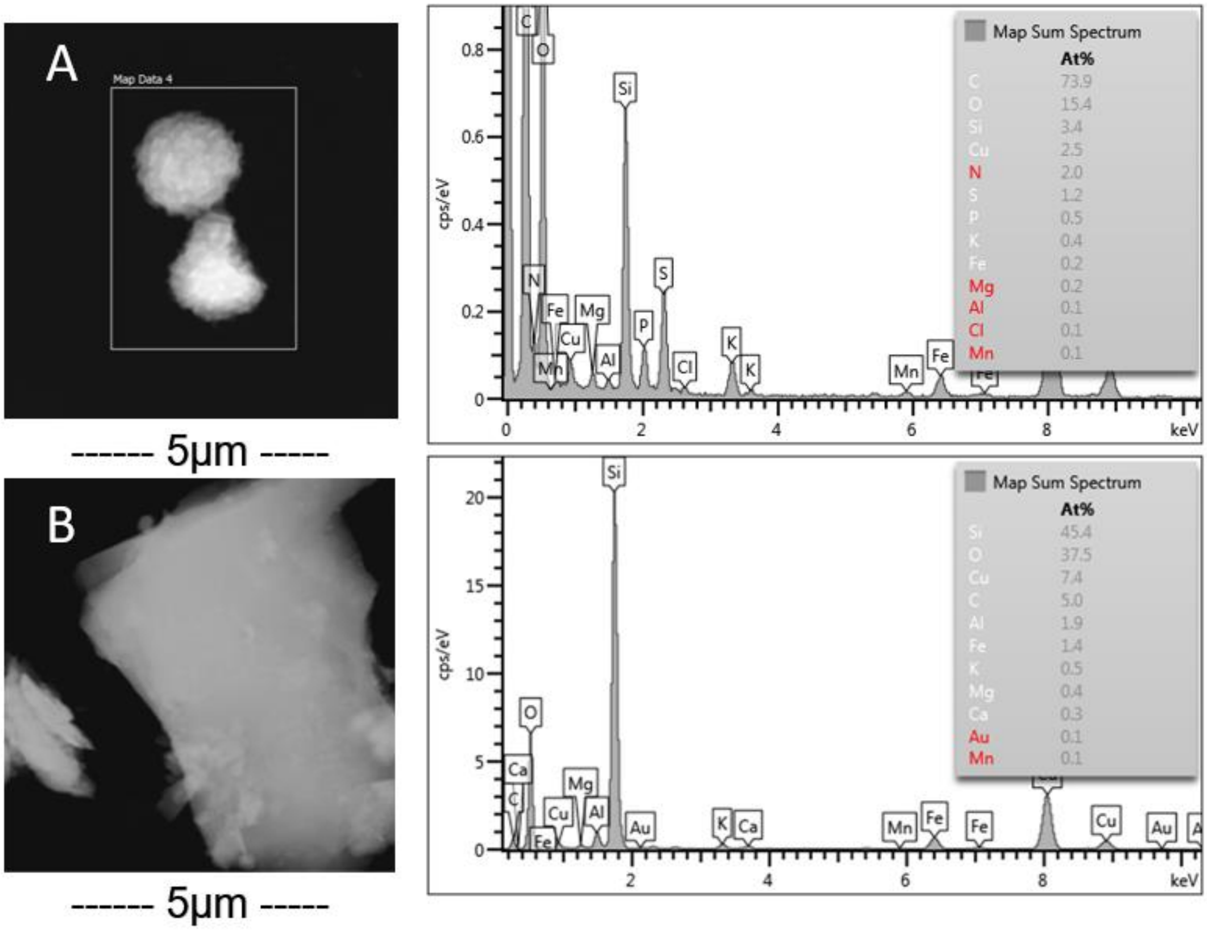

A
200 µm
B
20 µm
C
1 µm
D
1 µm
E
SEI 15.0kV X4,000 WD 10.1mm 1µm
F
SEI 15.0kV X50,000 WD 10.0mm 100nm
G
SEI 15.0kV X15,000 WD 10.0mm 1µm
H
SEI 15.0kV X50,000 WD 10.0mm 100nm

Figure 3. Image analysis of the TDS sample of the first ten minutes of drilling. A) Overview image at 50x of the center of a TEM grid showing heavy particle deposition. B) Image of one grid space viewed at 400x where a bimodal particle distribution can be seen. C) TEM image take at 6000x showing very fine particulate less than 100 nm in diameter. D) TEM image taken at 6000x of agglomerate. E) SEM imaging of TDS filter showing the collection of very fine particulate, with a scale bar of 1 um. F) SEM image showing very fine particles with a scale bar of 100 nm. G) SEM Imaging of TDS filter showing large agglomerates with a scale bar of 1 µm. H) Close up image of agglomerate microstructures with a scale bar of 100 nm



Map Sum Spectrum

	At%
C	73.9
O	15.4
Si	3.4
Cu	2.5
N	2.0
S	1.2
P	0.5
K	0.4
Fe	0.2
Mg	0.2
Al	0.1
Cl	0.1
Mn	0.1

Map Sum Spectrum

	At%
Si	45.4
O	37.5
Cu	7.4
C	5.0
Al	1.9
Fe	1.4
K	0.5
Mg	0.4
Ca	0.3
Au	0.1
Mn	0.1

Figure 4. EDS analysis of the TEM grid from the first 10 minutes. of drilling sampled by the TDS showing A) spherical primary particle rich in carbon and sulfur and B) silicon-rich stone dust

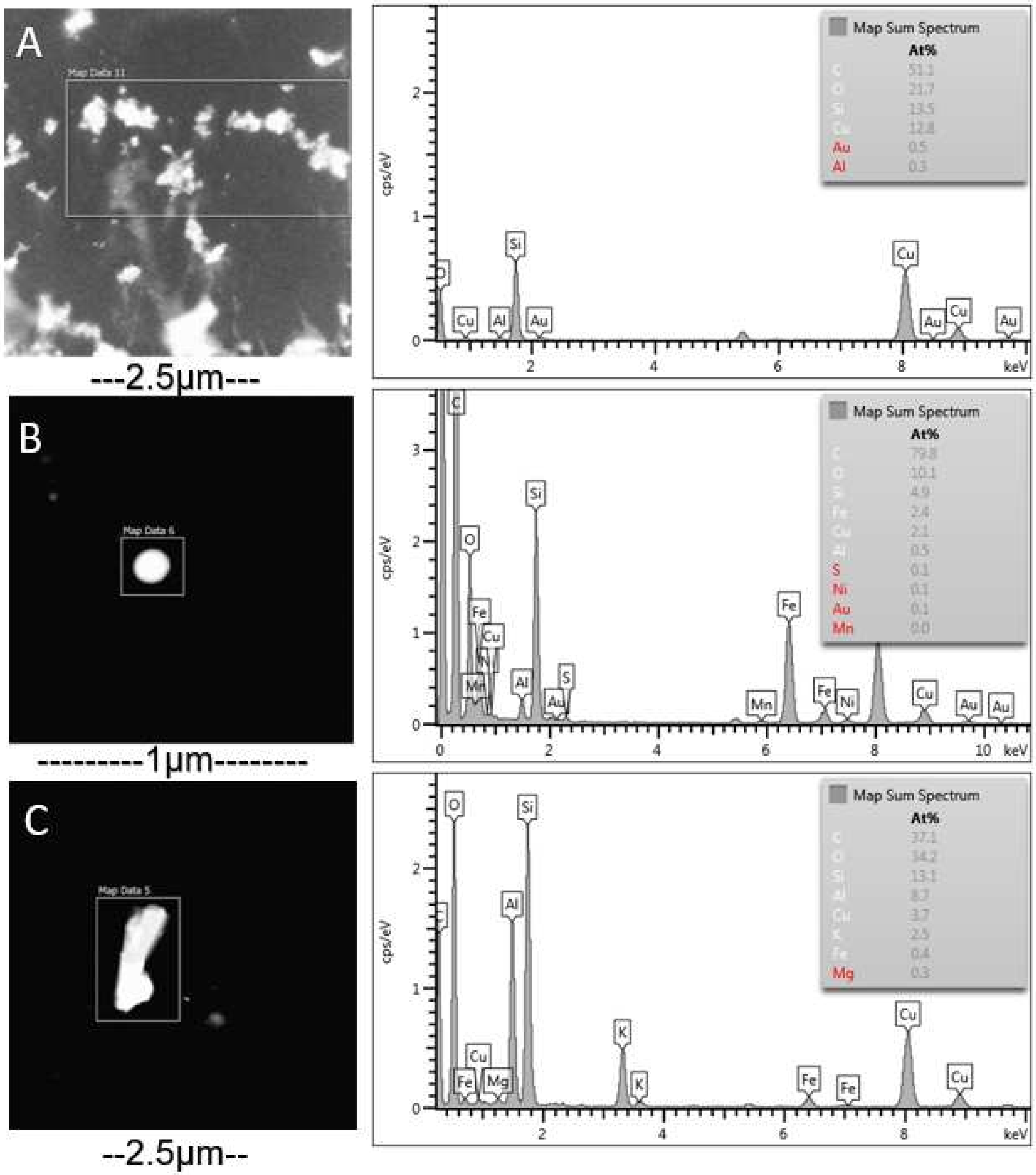


Figure 5. EDS analysis of TEM grid from 20 minutes. of drilling sampled by the TDS. A) Fine particulate matter rich in carbon. B) Very fine spherical particle rich in carbon and iron. C) Silicon-rich stone dust particle

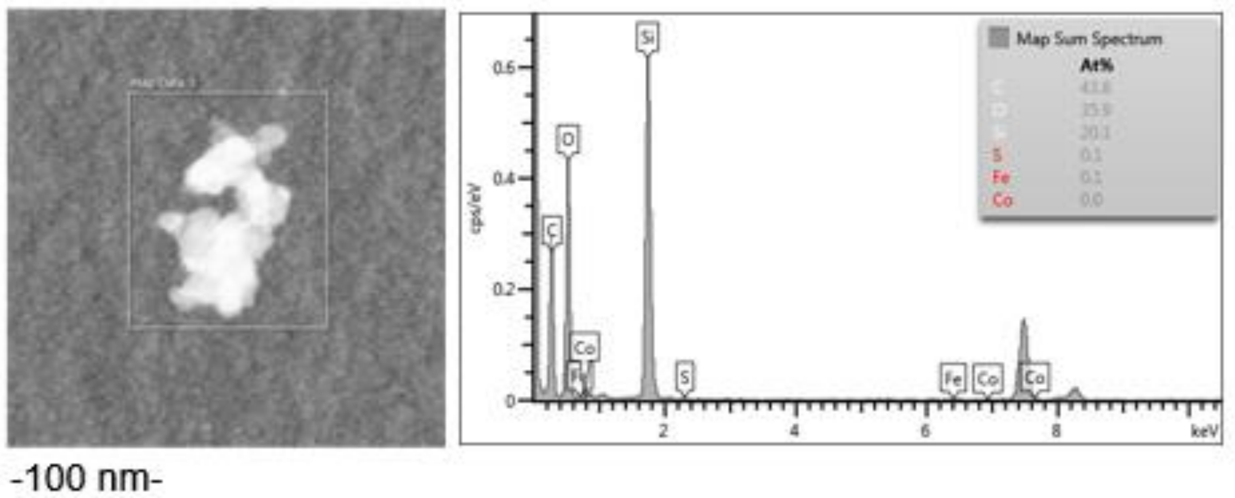


Figure 6. TEM image and EDS analysis of a typical particle collected by the TPS during the drilling activity

DISCUSSION

Based on the aerosol data, the researchers showed that there was a significant release of nanoparticles during the drilling activity. The aerosol concentrations remained relatively high throughout the drilling activities and subsequently decreased following the cessation of drilling. The majority of the particles measured in this study were below 100 nm in size and would therefore be able to deposit in all regions of the respiratory tract. The existence of these particles raises concern for respiratory and systemic impacts that this exposure can cause. The health effects of silica[35-38]**,** and carbon-rich soot[39, 40] have been established for some time. The presence of high concentrations of these particles indicate the existence of a potential hazard that could result in respiratory and systemic health effects to miners.

The four holes drilled represent a relatively small amount of drilling compared to the work done by miners during a full work shift. Given the limitations of this study, the authors could not determine the time weighted average (TWA) exposure during a full shift of drilling. Further investigation should be made into the carbon-rich particles observed during drilling in this study to clearly identify their representation in the particle sized distributions observed. Since it was difficult to quantitatively describe the rate and frequency at which the lubrication oil would burn for any given drilling session, the analyses resulting from this study were further complicated by the oil mist generated during the drilling process. The oil effectively covered the entire sample resulting in a high carbon signal in the EDS analysis.

The researchers consistently identified, through EDS analyses, a variety of particle types present within the mine atmosphere during the drilling session. These particle types included silicon-rich stone, spherical primary and agglomerated carbon particles. The silicon observed through EDS analysis is present in abundance in the Earth's crust[41], however, the spherical soot-like carbon particles and fractal agglomerates of these particles appear to have been created during the drilling process, not simply liberated from the mine substrate.

The investigators of this study have demonstrated the value in examining potential nanoparticle generation in areas where occupational exposures are difficult to elucidate. However, several limitations must be acknowledged when considering these findings. This study was conducted in a metal mine examining the controlled activity of a pneumatic feed leg drill. Varying the type of mine or activity may result in different findings. No duplicate samples were collected; therefore, these results may not fully represent the conditions within the mine. The sample volumes collected for the respirable cyclone were far below the minimum sample volumes required for the analytical method. The researchers should have predicted that these samples would be below the limit of detection and adjusted the sampling method accordingly to collect an acceptable sample volume. Furthermore, the sampling methods used in this study were not exhaustive. Additional methods and equipment could have been used to characterize the aerosol generated within the mine. The real time instruments measured the aerosol to be significantly higher than the recommended measurement limits. These data only represent an indication of what the actual particle counts and particle size distributions may be and must be considered with caution

Based on the results of this study, the authors demonstrated that new nanoparticle sampling techniques, such as the TDS methodology, successfully collected various particles in very fine sizes and can be used to characterize the morphology and composition of aerosolized nanoparticles associated with mining activities. When evaluating aerosol exposures within workplaces, nanoparticle sampling techniques should be employed alongside traditional characterization methods in order to accomplish a comprehensive exposure assessment.

CONCLUSIONS

The hazards associated with mining have been acknowledged for centuries. Although in modern times great efforts have been taken to protect the health of miners, occupational illness associated with the profession is still a great challenge. Despite rigorous sampling and protection methods employed by the MSHA, miners are still suffering from respiratory diseases. The authors conclude that there is a significant nanoparticle inhalation risk in the mining environment that is not well characterized by the current employed methods of investigation, such as gravimetric analysis. The highest concentration measured for the drilling activity in the 10-420 nm range was 4.4×10^6 particles/cm^3 and 3.5×10^3 particles/cm^3 in the 0.3-10 μm range. These particles were identified to be composed of silicon, carbon, and trace minerals. Nanoparticles found from drilling were not present in the background concentrations within the mine. Regardless of the relatively high concentrations, these fine particles are effectively massless when examined by gravimetric methods for evaluation levels of RPM. The effects of exposure to a nanoparticle-rich atmosphere, as identified in this study, need to be further understood. Methods for examining these particles should be considered when conducting exposure assessments within mining environments. The association between the exposure to a relatively high concentration of nanometer-sized particles and respiratory and cardiovascular system health effects to miners needs to be further investigated.

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