

PROJECT FINAL REPORT

Project Title: Quantification of road dust and its effect on soil

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1) Project Summary:

Western North Dakota, USA is experiencing economic growth due to the rapid oil development. The increased oil activities are also causing heavy vehicle traffic on the unpaved roads. Unpaved road traffic may create coarse particulate matter (PM₁₀) and fine particulate matter (PM_{2.5}), and Total Suspended Particles (TSP) emissions, and deposit them in adjacent areas. These PMs may affect human and animal health, and soil quality. To address this issue, a study was conducted to characterize and quantify PM₁₀, PM_{2.5}, and TSP generated from unpaved roads surrounding oil development areas. Particulate matter concentrations were measured from two different sites using the miniVOL™ portable air samplers (Air Metrics, Springfield, OR, USA) at three pre-selected distances from the road using the Federal Equivalent Method. Additionally, composite soil samples were collected at the same location of PM sampling location in one site (site 2) only. Scanning Electron Microscopy (SEM) was done on dust samples to determine particle elemental compositions and X-Ray Diffraction (XRD) to identify minerals present. Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) was performed on soil samples taken from the same location as dust samples to determine the elemental composition. The pooled average PM₁₀ and PM_{2.5} concentrations were $30.84 \pm 14.19 \mu\text{g}/\text{m}^3$ and $14.08 \pm 6.56 \mu\text{g}/\text{m}^3$ from a periodically treated road (Site 1), respectively; the pooled average PM₁₀ and PM_{2.5} concentrations were $70.42 \pm 38.37 \mu\text{g}/\text{m}^3$ and $19.60 \pm 7.51 \mu\text{g}/\text{m}^3$ from an untreated loose gravel road (Site 2), respectively over a two-year sampling period. Magnesium chloride was found to be the most effective treatment in reducing PM. Scanning Electron Microscopy (SEM)/ Energy Dispersive Spectroscopy (EDS) analyses revealed that most of the particulates were quartz (46%) or silicates (36%) minerals or biogenic particles (9%). Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) analyses on soil samples revealed that concentrations of most elements were below the reference level measured by United States Geological Survey National Geochemical Survey (USGS – NGS). This study improves our understanding of PMs in Western North Dakota, USA and suggests avenues for future research to be taken for more in-depth study.

Overall goals and objectives

The overall goal of this project is to quantify road dust emission, especially PM_{2.5} and PM₁₀ concentration, in western North Dakota due to road traffic in the oil development area. Specific objectives are:

- i) Quantification of PM_{2.5} and PM₁₀ concentration,
- ii) Quantify elemental composition of dust, and
- iii) Quantify dust impacts on roadside soil quality and elemental composition of soil

2) Introduction and Rationale

Unpaved road traffic is a major source of dust nuisance and road traffic may emit considerable amounts of coarse particulate matter (PM₁₀) and fine particulate matter (PM_{2.5}) emissions. Particulate matter has been recognized as an air pollutant due to nuisance and its adverse impact on the environment, and can be a pulmonary health risk (Mao et al., 2013; Pattey and Qiu, 2012). Fine particles (PM_{2.5}) result from fuel combustion from motor vehicles and power generation, while coarse particles (PM₁₀) are generally emitted due to vehicles traffic on unpaved roads, and materials handling, and as well as windblown dust. Inhalable PM includes both fine and coarse particles. Small particulates (PM_{2.5}) can be inhaled, resulting in respiratory diseases and premature death (Gonzales et al., 2011; Pattey and Qiu, 2012; Samet and Krewski, 2007; Saxton et al., 1999; Donham and Thelin, 2006). Fine particulate matter on the road surface is also a significant source of air pollution (Gunawardana et al., 2012). These particles can deposit in the respiratory system and are associated with numerous health effects. Exposure to coarse particles is primarily associated with the aggravation of respiratory conditions, such as asthma. In addition to health problems, PM is the major cause of reduced visibility (USEPA, 2016). Increased dust in Western North Dakota, USA, from unpaved road traffic is an inevitable consequence of increasing traffic from oil activities. The rapid growth

of transportation activities is causing and releasing numerous pollutants to the environment and depositing on the nearby road or crop land. Dust may contain heavy metals that may be toxic when their concentrations exceeded certain thresholds (Guney et al., 2010). The amount of dust emissions from the unpaved road is dependent on vehicle type, weight and speed of vehicle, wind speed and condition of the road (Mao et al., 2013).

Road dust may affect plants, animals and humans that are exposed to it. Road dust is believed to affect both the yield and/or marketability of crops grown alongside unpaved roads due to both physical and chemical impacts. Dust can physically block stomata of plants and chemical characteristics of dust may affect either soil or plants (Farmer, 1993). Dust cover on leaf surfaces may affect yield in a variety of ways, with the yield reduction depending upon the thickness of cover and to an extent, the type of plant (McCrea, 1984). The effect is likely to be greater on plants with young leaves as these retain a greater amount of dust, even after a moderate rainfall. Similarly, dust may carry and cause plant disease and increased pest infestation. Additionally, dust may also cause depressed appetite in livestock, which may result in a retarded growth rate of around 20% for each day the animal is kept on the contaminated pasture (McCrea, 1984). Agricultural worker exposure to dust or particulate matter is likely to result in mild to chronic respiratory illness (Canadian Center for Occupational Health and Safety, 1999; Pattey and Qiu, 2012). It is reasonable to postulate that oil field workers, truck drivers, and local residents similarly exposed would exhibit these symptoms. Therefore, it is important to carefully quantify dust emission rates to assist in the development of techniques or technologies to control dust from the source.

According to the US Energy Information Administration (USEIA, 2014), North Dakota's oil production topped 1 million barrels per day in June, 2014, compared to 315,000 barrels per day only four years previously in June, 2010. This significant increase in oil production has concomitantly increased oil rig activities and traffic volumes in western North Dakota which is also causing noticeably increased dust emission.

The chemistry of dust is important since it may contain a number of metals and elements which may be concentrated in the smaller particles and they may travel further (Farmer, 1993). Studies suggest that heavy metals may be concentrated within the first few meters of the roadside and their concentration may decrease with distance from the road (Guney et al., 2010). However, their concentration in soil may increase over time. Impacts of road dust due to oil exploration and production activities on surrounding landscapes and vegetation are not well understood.

There is one recent study on dust control technology in North Dakota (Schwindt, 2013). However, that study neither quantified the dust emissions nor measure the impact of dust on crop, soil, animal, and human health. Prior to this study, no scientific data were available in western North Dakota on dust emissions and their impact on soil health.

Therefore, there is an urgent need to quantify the dust emissions and adapt appropriate technology to mitigate environmental impact. In this study diurnal dust deposition in a nearby livestock grazing area due to traffic on an unpaved road was quantified and its impact on soil quality was monitored. This work evaluated impacts of dust on landscapes surrounding oil field roads and/or drilling sites particularly with regard to the distribution of potential elemental contaminants in dust distributed with distance across the adjacent landscapes. The work evaluated any changes in the elemental composition of soil from the beginning of the construction of the road out to areas up to 200 m from the road. In addition, changes in soil organic matter, salinity and sodicity were evaluated.

Therefore, the objectives of this study were to i) quantify $PM_{2.5}$ and PM_{10} concentration, ii) quantify elemental composition of $PM_{2.5}$ and PM_{10} , and iii) quantify dust impacts on roadside soil quality and elemental composition of soil.

3) Method

Dust sampling

This study was conducted near the North Dakota State University Dickinson Research Extension Center Manning Ranch Headquarters (Latitude: 47°12' N, Longitude: 102° 50' W), located in Dunn County about 35 kilometers north of Dickinson and 5 kilometers west of Manning, North Dakota, USA (Figure 1) (Site 1 and 2). Site 1, at the first location, was approximately 7 kilometers away from site 2. Monitoring sites were established at DREC Manning Ranch, where one site is next to cropping trials and the another site is on forage land. In both locations four EPA approved MiniVol portable air samplers (Airmetrics, Springfield, OR, USA) were deployed. Samplers were swapped between sites. Initial sampling began with Total Suspended Particles (TSP) to measure total dust accumulated on the filter in 24 hours. TSP contains particulate matter up to a size of 45 micrometers (μm) in diameter. As the project moved forward, the TSP sampling head was replaced with $\text{PM}_{2.5}$ and PM_{10} sampling heads.

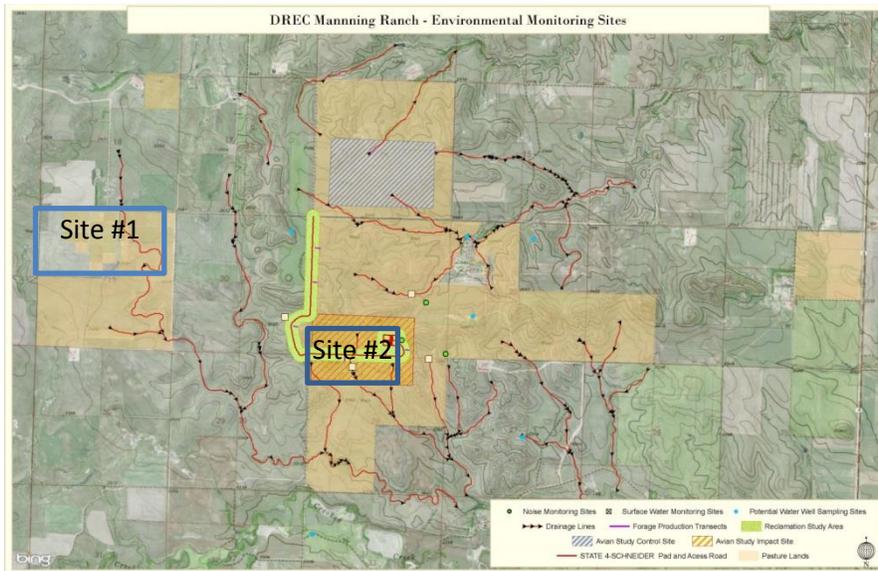


Fig. 1. Sampling locations at Manning ranch are shown with blue rectangular boxes. Site#1 has significant well development; and Site#2, no well development yet

Sampling was carried out on the following dates (a table, or is this something for an appendix?)

Out of four MiniVol samplers, one sampler was installed upwind and three others were installed downwind of the road sites depending on the prevailing wind directions at the monitoring sites to collect PM_{10} and $\text{PM}_{2.5}$ samples over 20 hour periods (Figure 2). Downwind samplers were installed at different distances from the unpaved traffic to measure PM_{10} and $\text{PM}_{2.5}$ deposition. The sampler was mounted to a pole vertically as shown in Figure 3. After several samplings, the impactor was cleaned and greased for the next sampling.

Before installing samplers in the field, 47 mm glass fiber filters or quartz filters were labeled with ultra-fine Sharpie® pen while wearing latex gloves, stored in petri-dishes (48 mm in diameter), and conditioned in an environmentally controlled room (relative humidity = $50.5 \pm 0.2\%$, temperature = 22.6 ± 1.4 °C) at the Nanoscale Science and Engineering (CNSE) Research lab at NDSU. Pre- and post-sampling weight of

filters were taken by a microbalance (Sartorius CP2P) in an environmentally controlled room to determine particulate matter mass with a resolution of $1 \mu\text{g}$ (0.001 mg).

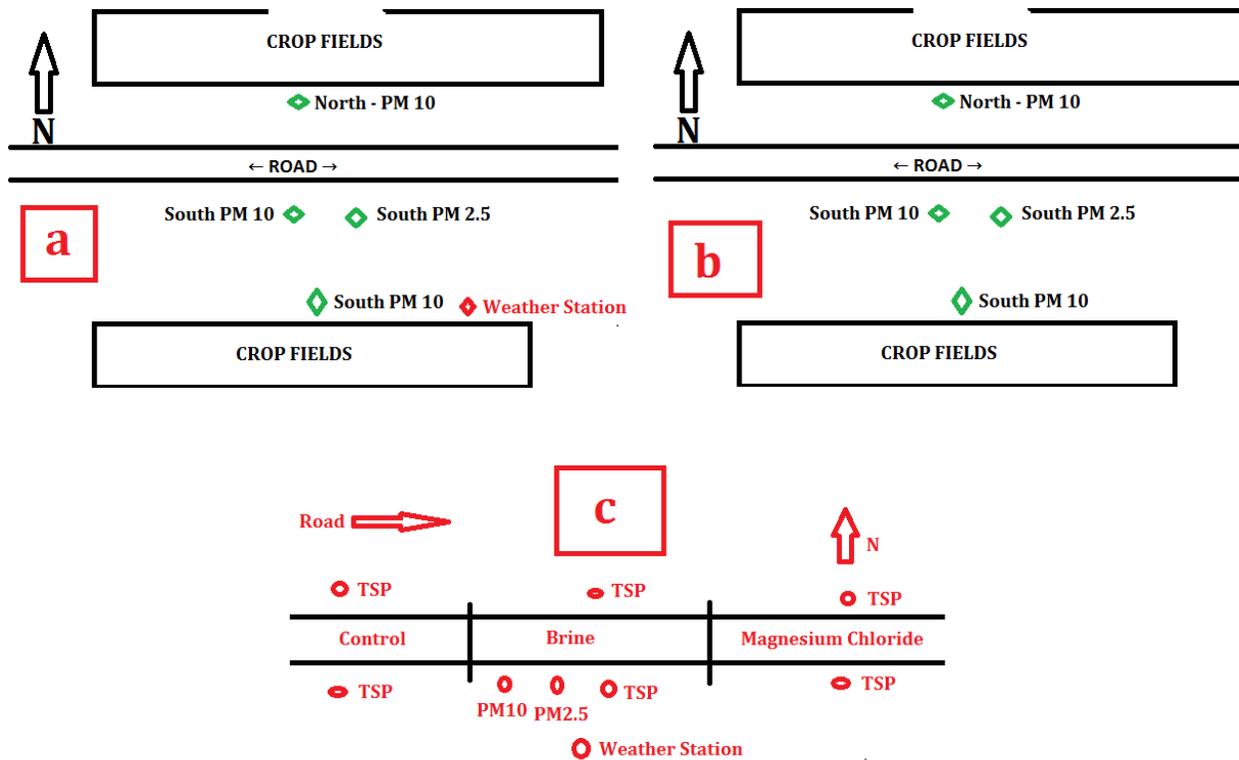


Figure 2. Experimental setup of different locations: a. site #1; b. site #2; c. site #3



Figure 3. MiniVol™ Portable Air Sampler in operation at site #1 (vertically mounted)

To avoid static, a polonium bar at the back of the microbalance was used. During conditioning, filters were reweighed 2-3 times for consistent weight. The differences in weight after each measurement should not exceed 0.5% of the previous weight. After conditioning, filters were used within 7 days and protective

holders were used during transportation. In the field, a cassette separator was used for insertion and removal of these filters to and from the cassette. After inserting the filter, a pre-calculated actual air flow rate was adjusted for the sampler and sampling was started.

During sampling, an air sample was drawn at 5 L/min, which is the recommended flow rate for PM_{2.5} and PM₁₀ using the MiniVol air sampler. A flow rate check was performed before and after each deployment of samplers. All samples were protected in petrislides filter holders before and after sampling and weighed twice in a 24-h period in order to obtain more accurate results.

Soil Sampling

Besides the dust sample, composite soil samples (a mixture of three samples) were collected at site 2 at different distances (12 m, 30 m, 60 m, 90 m from the center of the road on both south and north side) using a 25.4 mm soil core sampler (inside the cutting tip, diameter = 19 mm). Each soil core was taken at a 150 mm depth. Before collecting the soil sample in sampler bags, vegetation and ground litter were removed to avoid contamination by plant materials. Then, the cores were stored in ziploc bags and labelled with a unique ID. The sampling was done on a monthly basis to see the impact of dust on soil quality. These soil samples were analyzed for potential changes in soil elemental composition over time as well as for potential chemical changes that could be used as “fingerprints” for evaluating dust issues in future studies.

Traffic Monitoring

Two battery-operated Simmons Whitetail Cameras (119234C) (Simmons Outdoor Products, Overland Park, KS, USA) were used for tracking the number of vehicles passing through the study site (Figure 4). Cameras were equipped with motion sensor and night vision (Infra-red) capabilities for capturing photos of a passing vehicle even during night time. These cameras were set up on the same pole as the air sampler in such a way that they would pick up both fast and slow moving objects. After each sampling, the number of vehicles passed during the sampling period was counted and correlated with total dust emission during the sampling.



Figure 4. Simmons Camera (deployed on site #2)

Meteorological Data

In-situ meteorological data (e.g., temperature, relative humidity, pressure, wind speed, gust speed, and wind direction) were collected on site 1 using Hobo micro weather station data logger (H21-002) (Onset, Bourne, MA, USA) (Figure 5). Additionally, weather data were also downloaded from North Dakota Agricultural

Weather Network (NDAWN) and National Weather Service (NWS) to correlate important factors with the dust emissions.



Figure 5. Onset Hobo Data Logger (H21-002) (Image partially from Onset Website – www.onsetcomp.com)

Sample analysis

After sample collection, filters were transported back to NDSU and conditioned in the same pre-sampling environment. During weighing and handling of filters, identical pre-sampling room conditions were maintained and polonium sources were used to avoid any static during weighing of samples. To calculate PM concentration for a sample taken with the MiniVol sampler, the volume of air that passed through the filter at standard conditions, V_{std} , or at ambient conditions, V_{amb} , was calculated as follows:

$$PM_{act} = \frac{M_{PM}}{V_{act}}$$

Where: PM_{act} = actual PM concentration, $\mu\text{g}/\text{m}^3$ (actual condition); M_{PM} = PM concentration, $\mu\text{g}/\text{m}^3$ (Standard condition); V_{act} = Volume of air, m^3 (actual condition)

The volume of actual air passed through the filter during sampling period at actual ambient condition would be calculated as:

$$V_{act} = \frac{60 \text{ min/hr} \times Q_{act} \times t_{hr}}{1000 \text{ l/m}^3}$$

Where: Q_{act} = Flow rate of the sampler, liters/min; t_{hr} = Sampling period, hr

After weighing, particles from selected dust filters were analyzed for their physical and chemical characteristics using Scanning Electron Microscopy (SEM), and Electron Dispersive Spectrometry (EDS) (Pachauri et al., 2013; Tasic et al., 2006). Use of these complimentary methods was done to identify particles (biogenic, geogenic, or anthropogenic), their grain sizes and size distribution, and their chemical composition. SEM-EDS analysis was carried out for phase identification and semiquantitative chemical characterization using a JEOL JSM-6490LV SEM at NDSU's Electron Microscopy Center. Energy-dispersive X-ray information was collected using a Nanotrace EDS detector with a NORVAR light-element

window and Noran System Six imaging system (ThermoFisher Scientific, Madison WI, USA) at an accelerating voltage of 15keV for the JSM-6490LV. In this analysis, samples were not coated with carbon or gold because of the possibility of having biogenic organisms in the filters, because biogenic organisms are basically made of carbon and oxygen ($C + O > 75\%$ of the total molecular weight), which may bias the quantification (Figure 6). During EDS analysis, when the carbon was $<10\%$, the carbon was excluded from 'quant spectrum' option. About 10-20 images were taken per sub-sample and when necessary, EDS was done on the image by picking up several points. The magnification level used for taking the images was $\times 1500$. The magnification level and spot size was fixed according to particles countered in the filters.

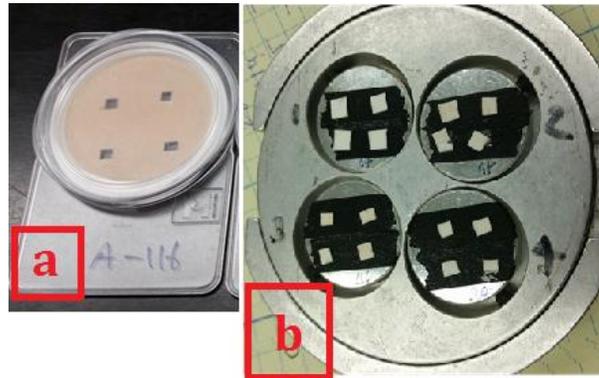
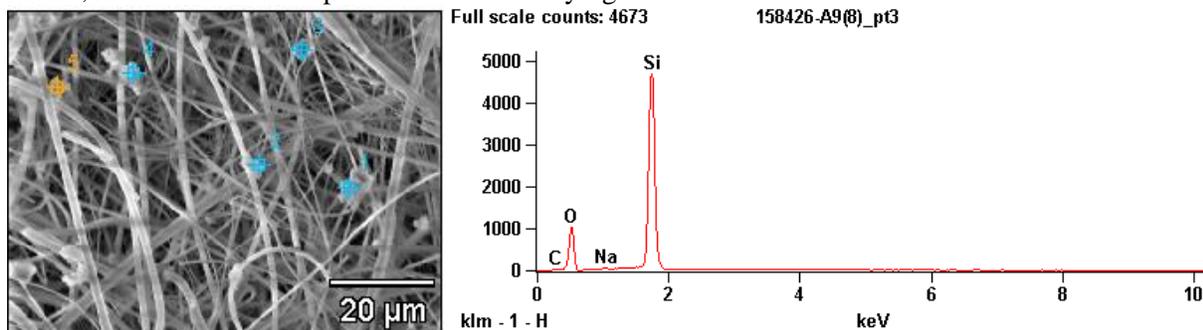


Figure 6. Sample preparation for SEM analysis: a. small sections cut from filter; b. sections placed on carbon tape on cylindrical mounts

After collecting the soil cores from site 2, soil samples were air dried for at least 72 hours before processing. The soil was hand crushed to pass through a 2 mm sieve and plant residues and rock fragments were removed. A 10 g subsample of soil was taken from the bulk samples for ball-milling. The soil subsamples were milled to pass through a No. 80 (80-mesh opening = $180\ \mu\text{m}$). Then, the prepared samples were analyzed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) at Activation Laboratories Ltd (Ancaster, ON, Canada) using the Ultratrace 2 method (aqua regia digest).

Identification of mineral phase from SEM results

Relative atomic weight percentages were taken from SEM results to calculate approximate empirical formulas. In the ideal case, each coefficient for a crystallographic site will be a whole number, and will give the accurate mineral formula. SEM/EDS outputs data as percentage weight of atoms or oxides present in the sample. These data together with the atomic mass of corresponding elements are used to calculate the empirical formula of the mineral. The procedure is simple for pure phases and complex with phases with impurities and trace elements. Figure 7 shows a sample SEM image and the EDS spectrum of quartz mineral, and the calculation procedure for identifying the mineral.



Elements	O	Si	Na	Notes
wt. %	53.06	46.40	0.54	Mineral: Quartz (SiO_2); Major elements: O, Si; Trace elements: Na;
grams/mol	16.0	28.09	22.98	
mols	3.32	1.65	0.02	
Normalized mols	2	1	Negligible	Nearly Spherical particles; Formula: 2 O, 1 Si

Figure 7. Top: SEM image of filter showing particles, along with an EDS spectrum of a particle. Bottom: Example calculation of possible mineral/phase group from SEM data (Quartz)

Reported weight percentages were divided by atomic mass to obtain the number of moles normalized. This particular sample had the ratio of 1 mol Si and 2 mol O (and a trace amount of Na). So, it was determined to be quartz. The procedure is similar for a complex mineral oxide weight as shown in Figure 8. In this case, molar mass of oxide is used instead of the atomic mass. If the number of moles could not be brought to a whole number, an approximate empirical formula is calculated. Morphology and knowledge in mineralogy and crystallography can be beneficial in this case for identification. Figure 8 shows the calculation for an aluminosilicate mineral phase. The mole numbers may not be brought to whole numbers which could be due to the electron beam accuracy of the EDS method on small particles, and fluorescence from silica filters.

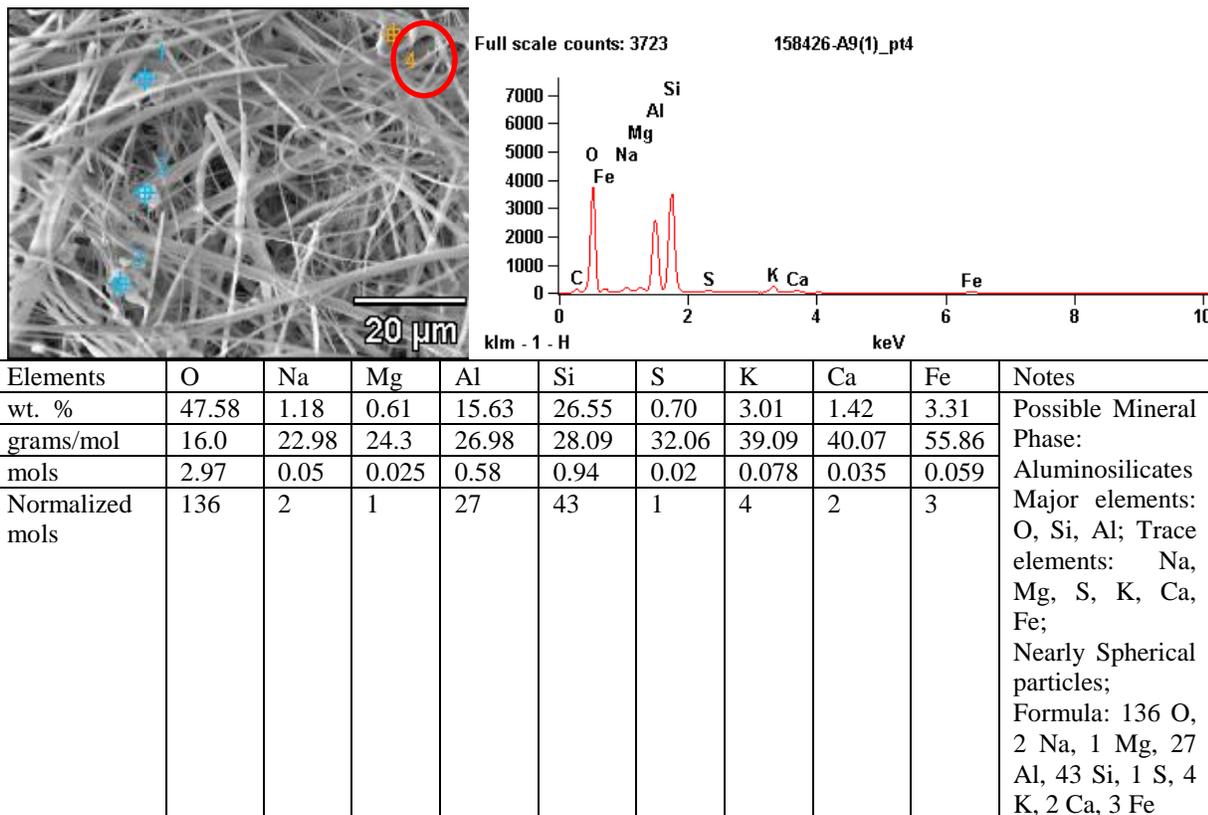


Figure 8. Calculating possible complex mineral formulas from SEM data (Aluminosilicates)

RESULTS AND DISCUSSION

Particulate matter concentrations

Particulate matter (PM) is one of the Ambient Air Quality Standards (AAQSs) pollutants and constitute a major class of air pollution (Cooper & Alley, 2002). Figure 9 shows the average PM concentrations (PM_{10} and $PM_{2.5}$) measured at site 1 over two years with respect to the number of vehicles and the amount of rainfall during the corresponding sampling dates, while, Figure 10 shows the yearly average PM concentrations (PM_{10} and $PM_{2.5}$). Table 1 shows the stepwise regression analysis of PM at site 1.

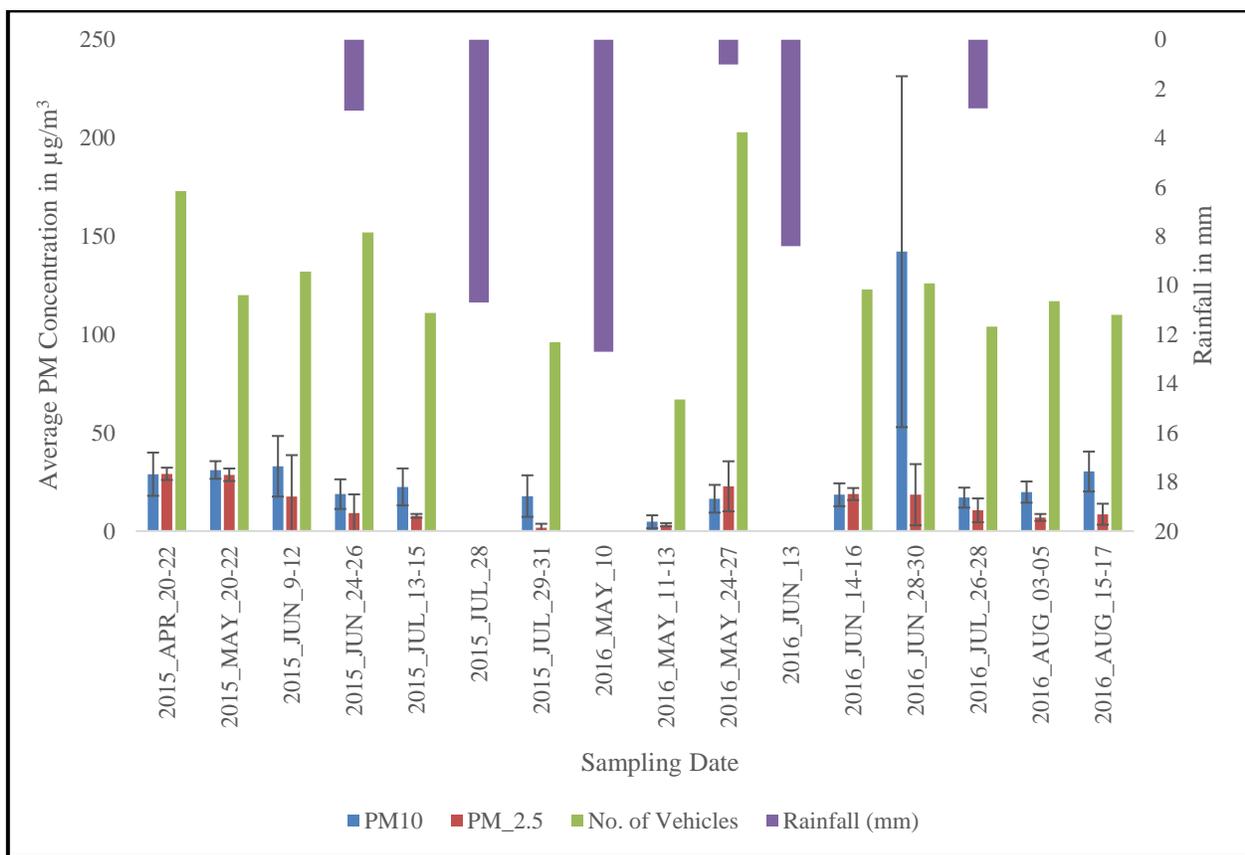


Figure 9. Average PM concentrations with respect to traffic and rainfall at site 1.

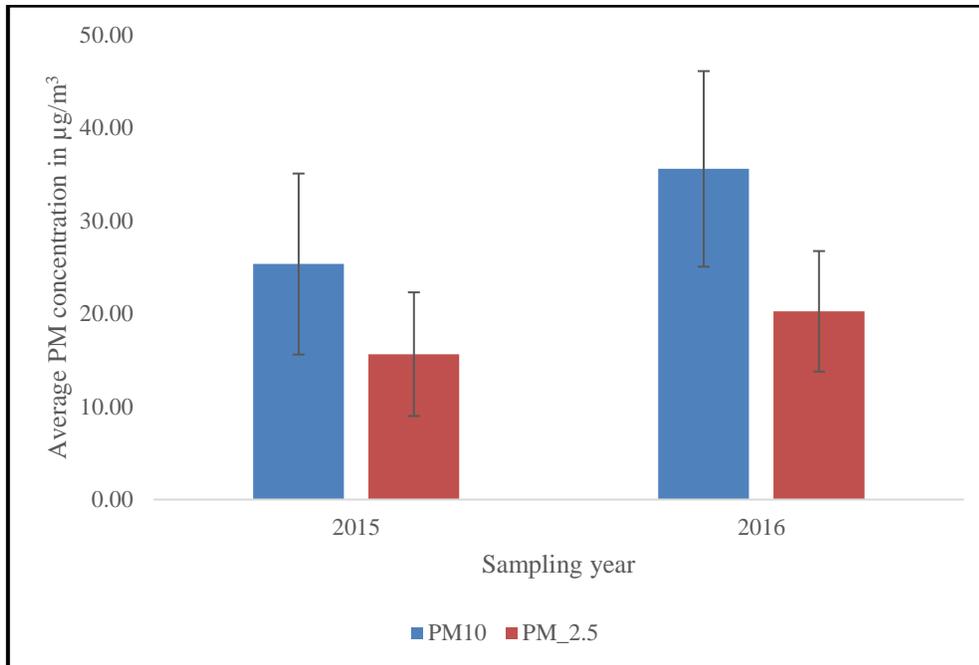


Figure 10. Yearly average PM concentrations at site 1.

Table 1. Stepwise regression analysis results of PM concentrations at site 1

Particulate matter type	Year of sampling	Stepwise regression model equations
PM ₁₀	2015 & 2016 combined	No variables were statistically significant
	2015	$PM_{10} = 28.516 - 79.55 \times \text{rainfall_in_mm}$ ($r^2 = 0.07$)
	2016	$PM_{10} = 46.978 + 1.4615 \times \text{vehicle_count} - 32.2796 \times \text{wind_speed} - 0.37429 \times \text{wind_direction} - 51.06820 \times \text{rainfall_in_mm}$ ($r^2 = 0.30$)
PM _{2.5}	2015 & 2016 combined	$PM_{2.5} = -0.75421 + 0.19184 \times \text{vehicle_count}$ ($r^2 = 0.16$)
	2015	$PM_{2.5} = 0.98252 + 0.02480 \times \text{wind_direction} + 63.485 \times \text{rainfall_in_mm}$ ($r^2 = 0.51$)
	2016	$PM_{2.5} = -11.33165 + 0.43686 \times \text{vehicle_count}$ ($r^2 = 0.38$)

Notes: - All variables here are significant at 0.15 level ($p=0.15$)

- r^2 values reported are model r^2 values

Based on 24-hour sampling period, the PM_{10} concentration value ranged from $7.55 \mu\text{g}/\text{m}^3$ to $60.5 \mu\text{g}/\text{m}^3$ in 2015 and from $0.79 \mu\text{g}/\text{m}^3$ to $261.45 \mu\text{g}/\text{m}^3$ in 2016. Similarly, the $PM_{2.5}$ concentration value ranged from $0.34 \mu\text{g}/\text{m}^3$ to $15.85 \mu\text{g}/\text{m}^3$ in 2015 and from $2.63 \mu\text{g}/\text{m}^3$ to $37.00 \mu\text{g}/\text{m}^3$ in 2016. Figure 10 shows the average PM_{10} concentrations in 2015 and 2016 were $25.33 \pm 9.74 \mu\text{g}/\text{m}^3$ and $35.56 \pm 20.25 \mu\text{g}/\text{m}^3$, respectively; and the average $PM_{2.5}$ concentrations in 2015 and 2016 were $15.64 \pm 6.65 \mu\text{g}/\text{m}^3$ and $20.25 \pm 6.48 \mu\text{g}/\text{m}^3$, respectively. Most of the time, the PM_{10} concentration was below the NAAQS value ($150 \mu\text{g}/\text{m}^3$). However, during June 28-30, 2016 sampling, the average PM_{10} concentration was $142.14 \pm 89.28 \mu\text{g}/\text{m}^3$ which exceeded the NAAQS threshold values. This may be attributed to the gravel road construction and ongoing well pad construction near site 1 (15th St). The average PM concentrations for 2016 were slightly higher than that of 2015 which might be due to drier weather and road construction/leveling activities. In site 1, $PM_{2.5}$ concentration value exceeded ($37 \mu\text{g}/\text{m}^3$) NAAQS reference value for $PM_{2.5}$ ($35 \mu\text{g}/\text{m}^3$ for 24-hour sampling period) for one instance (June 28-30, 2016) during the sampling time. Except for one or two incidents, the PM concentrations were below the NAAQS reference value despite having high traffic.

PM emissions from a road likely depend on road conditions (dry vs. wet, treated vs. un-treated), the number of vehicles, and weather conditions (precipitation, calm vs. windy), etc. The lower PM concentration in site #1 during June 24-26, 2015 was likely due to road treatment. The road (15th St) adjacent to site 1 was periodically treated with dust suppressants i.e., magnesium chloride. In addition, there was 2.88 mm of rainfall during that sampling period, which might also contribute to lower PM emissions. There was a significant drop in PM emissions during May 11-13, 2016, which may be attributed to freezing and thawing effect as well as lower traffic activities.

A stepwise regression analysis was conducted to find out the impact of different variables on PM emission. Statistical analysis revealed that, in 2015 sampling, the rainfall was poorly correlated ($r^2=0.07$) with PM_{10} concentrations; but, the combination of rainfall and wind direction had a better relationship ($r^2=0.51$) in the case of $PM_{2.5}$ concentration emission at a significance level of $p=0.15$. In 2016, PM_{10} concentrations were moderately correlated ($r^2 = 0.30$) with vehicle passing by, wind speed, wind direction, and rainfall. A similar or equally better correlation ($r^2 = 0.39$) was observed for the $PM_{2.5}$ concentrations.

Figure 11 shows the average PM concentrations (PM_{10} and $PM_{2.5}$) measured at site 2 with respect to the number of vehicles and the amount of rainfall during the corresponding sampling dates. Figure 12 shows the yearly average PM concentration at site 2. Table 2 shows the stepwise regression analysis of PM at site 2.

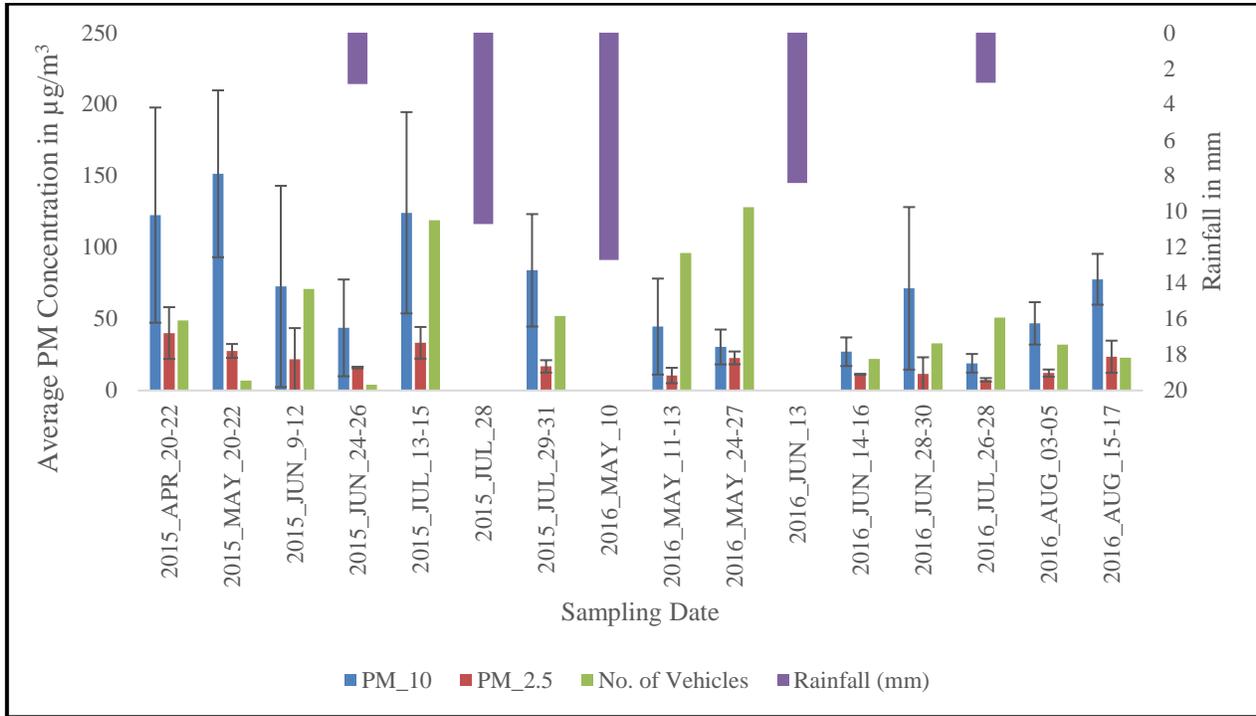


Figure 11. Average PM concentrations with respect to traffic and rainfall at site 2.

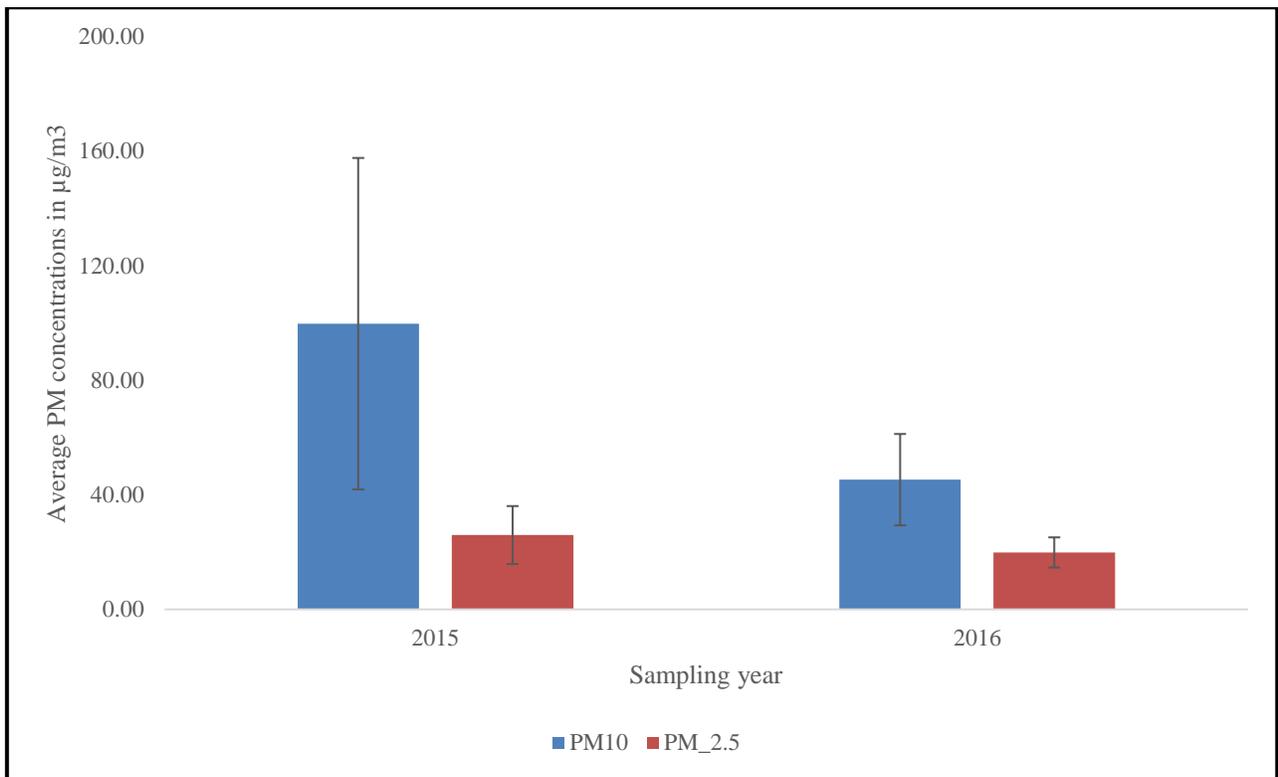


Figure 12. Yearly average PM concentrations in site 2.

Table 2. Stepwise regression analysis results of PM concentrations at site 2

Particulate matter type	Year of sampling	Stepwise regression model equations
PM ₁₀	2015 & 2016 combined	PM ₁₀ = 72.08904 - 51.12641 × rainfall_in_mm (<i>r</i> ² = 0.07)
	2015	PM ₁₀ = 99.74191 - 552.38530 × rainfall_in_mm (<i>r</i> ² = 0.10)
	2016	PM ₁₀ = 70.44775 - 2.63587 × wind_speed - 35.85478 × rainfall_in_mm (<i>r</i> ² = 0.20)
PM _{2.5}	2015 & 2016 combined	No variables were statistically significant
	2015	PM _{2.5} = -14.91731 + 0.50329 × vehicle_count + 0.11719 × wind_direction (<i>r</i> ² = 0.58)
	2016	No variables were statistically significant

Notes: - All variables here are significant at 0.15 level (p=0.15)

- *r*² values reported are model *r*² values

The pooled average PM₁₀ concentrations at site 2 were $70.42 \pm 38.37 \mu\text{g}/\text{m}^3$ and PM_{2.5} concentrations were $19.60 \pm 7.51 \mu\text{g}/\text{m}^3$ at standard pressure and temperature measured over a two-year sampling period. However, the PM₁₀ concentration over a 24-h sampling ranged from $1.91 \mu\text{g}/\text{m}^3$ to $253.60 \mu\text{g}/\text{m}^3$ in 2015 and from $5.17 \mu\text{g}/\text{m}^3$ to $179.66 \mu\text{g}/\text{m}^3$ in 2016, which is higher than the pooled average concentration. Similarly, PM_{2.5} concentration value ranged from $2.56 \mu\text{g}/\text{m}^3$ to $52.91 \mu\text{g}/\text{m}^3$ in 2015 and from $3.27 \mu\text{g}/\text{m}^3$ to $31.52 \mu\text{g}/\text{m}^3$ in 2016. Figure 12 shows that the average PM₁₀ concentrations in 2015 and 2016 were $99.74 \pm 57.88 \mu\text{g}/\text{m}^3$ and $45.29 \pm 15.95 \mu\text{g}/\text{m}^3$, respectively, and the average PM_{2.5} concentrations in 2015 and 2016 were $25.94 \pm 10.12 \mu\text{g}/\text{m}^3$ and $19.88 \pm 5.27 \mu\text{g}/\text{m}^3$, respectively. Same as site #1, the average PM₁₀ concentrations in site #2 were lower in 2016 than 2015. This may be attributed to lower traffic from decrease oil extraction activities in the sampling area.

In 2016, the average PM₁₀ concentrations ($199.32 \pm 36.13 \mu\text{g}/\text{m}^3$) and PM_{2.5} concentrations ($47.02 \pm 8.33 \mu\text{g}/\text{m}^3$) exceeded the NAAQS reference values (PM₁₀ = $150 \mu\text{g}/\text{m}^3$; PM_{2.5} = $35 \mu\text{g}/\text{m}^3$ for 24-hour sampling period). This was likely attributed to various factors i.e., high traffic on a loose gravel road and untreated road conditions. Also, traffic next to the sampling area likely contributed to higher PM concentration, except May 20-22, 2015 when gravel was applied to the road. For example, on May 20-22, 2015, the average PM₁₀ concentration was $151.4 \pm 58.32 \mu\text{g}/\text{m}^3$ that exceeded NAAQS PM₁₀ value. The lower PM concentrations during June 24-26, 2015 was likely due to lower traffic and 2.88 mm rainfall. During July 13-15, 2015, there were higher PM concentrations compared to the amount of traffic which may be attributed to the ongoing underground cable/pipe installation about 30 m to the south of the road, as well as drier road

conditions. Despite of having comparatively higher traffic count, the PM concentrations during May 11-13, 2016 were low likely due to the rainfall on May 10th (12.5 mm) and high wind speeds. A similar pattern was also observed during May 24-27, 2016 (2.8 mm rainfall on May 25th), June 14-16, 2016 (8.4 mm rainfall on June 13th) and July 26-28, 2016 (2.88 mm rainfall).

From stepwise regression analysis, in 2015, the PM₁₀ concentrations had weak correlation ($r^2 = 0.07$) with rainfall but PM_{2.5} concentrations seemed to have a better relationship ($r^2 = 0.58$) with vehicle count and wind direction ($p=0.15$). In 2016, the PM₁₀ concentrations had a weak correlation ($r^2 = 0.20$) with wind speed and rainfall, whereas PM_{2.5} had no association with other factors ($p=0.15$).

Mineralogical characterization of particulate matter

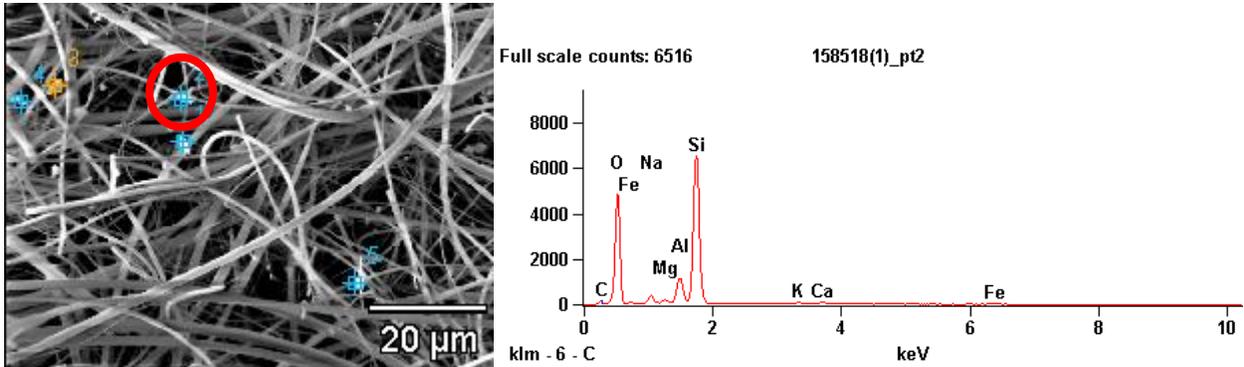
Based on elemental composition and morphology, 299 particles were analyzed using SEM-EDS. These particles were classified into three major groups: geogenic particles (derived from soil sediments, weathered rock surfaces), anthropogenic particles (particles derived from industrial and combustion activities), and biogenic particles (fungal hyphae with root outgrowth, organic plant fragments, living micro-organisms). Some of them are explained below:

Geogenic particles

Most of the analyzed particles were found to be geogenic particles. These particles with crustal origin include silicates of iron, magnesium, aluminum, calcium, quartz, Fe/Ti oxides, calcium particles, chloride particles, carbonate minerals etc.

Quartz (SiO₂) is one of the most common minerals found in on earth's surface as it is a significant component of many sedimentary, metamorphic, and igneous rocks. Quartz can occur in many different colors, habits, and forms. Quartz crystals can be prismatic and can also appear in massive form with no definable shape with no visible aggregate or crystals. The source of quartz can be of natural origins. Quartz is characterized by high content of oxygen (O) and silicon (Si) (Si + O > 90% by weight) summing up to 100% with an atomic ratio of 1 Si to 2 O.

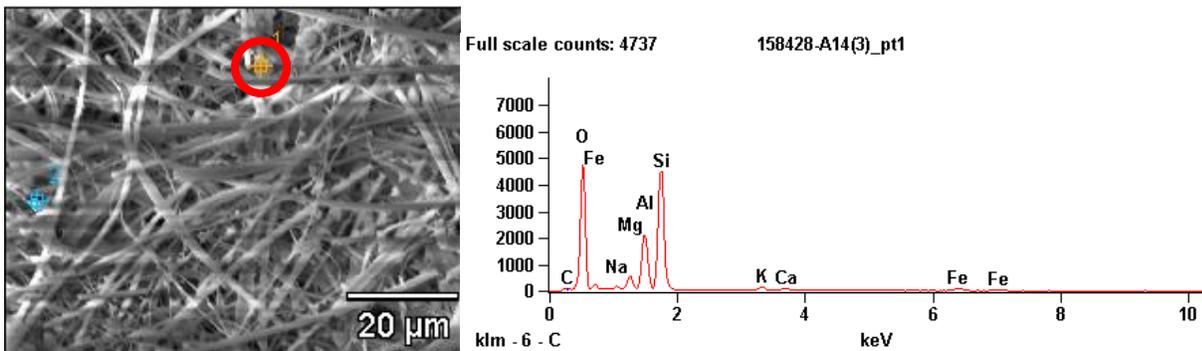
Non-quartz silicates particles are identified by high Si, aluminum (Al), O, and iron (Fe) content with variable content of sodium (Na), magnesium (Mg), potassium (K), calcium (Ca), titanium (Ti) with trace amounts of phosphorus (P) and sulfur (S), and sometimes carbon (C). Most particles in this group showed irregular, sub-spherical, and spherical morphology. Possible phases/minerals include feldspars, clays, oxides, carbonates, etc. Figure 13 shows possible identification of aluminosilicates group (Al₂SiO₅) containing O, Si, and Al with lesser amounts of Na, Mg, K, and Ca. It showed irregular morphology. Oxide minerals are identified by the high content of O and other elements like Fe, Al with a low amount of trace elements. They tend to have sub-spherical shape. Figure 14 shows an oxide mineral which has high Al and O content with a trace amount of Na, Mg, K, Ca, and Fe. It likely is aluminum oxide.



Weight	O	Na	Mg	Al	Si	K	Ca	Fe
158518(1)_pt2	50.27S	2.76	0.56	5.49	37.64	0.88	1.28	1.11

SEM ID Number	Mineral Group	Major Elements	Minor Elements	Morphology	Formulas from SEM data
158518(1)_pt2	Silicates	O, Si, Al	Na, Mg, K, Fe	Irregular	158 O, 6 Na, 1 Mg, 10 Al, 67 Si, 2 Ca, 1 Fe

Figure 13. Particulate matter identification from actual samples (Silicate minerals - aluminosilicates)



Weight %	O	Na	Mg	Al	K	Ca	Fe
158428-A14(3)_pt1	40.50S	2.35	6.36	31.36	3.02	2.42	13.98

SEM ID Number	Mineral Group	Major Element	Minor Element	Morphology	Formulas from SEM data
158428-A14(3)_	Oxides	O, Al	Na, Mg, K, Fe	Sub-spherica	42 O, 2 Na, 4 Mg, 19 Al, 1 K, 1 Ca, 4 Fe

Figure 14. Particulate matter identification from actual samples (Silicate minerals - oxides)

Anthropogenic Particles

Anthropogenic particles include carbonaceous and industrial particles. Among industrial particles, the dominant metalliferous particles contain Cr>40%, Mn>50% and Ni>10% by weight in combination with trace particles. Very few industrial particles were found in this study as the sampling sites were very far from industrial zones. Carbonaceous particles are significant as they contribute highly to the total mass of the particles. In Figure 15, soot was identified. It had high carbon content and low oxygen content. This type of particle can be produced from biomass and biofuel burning. Earlier studies show that this spherical particle can scatter and absorb light (Cong et al. 2008). Agricultural burning, tire residue, and waste incineration might be the origin of these particles.

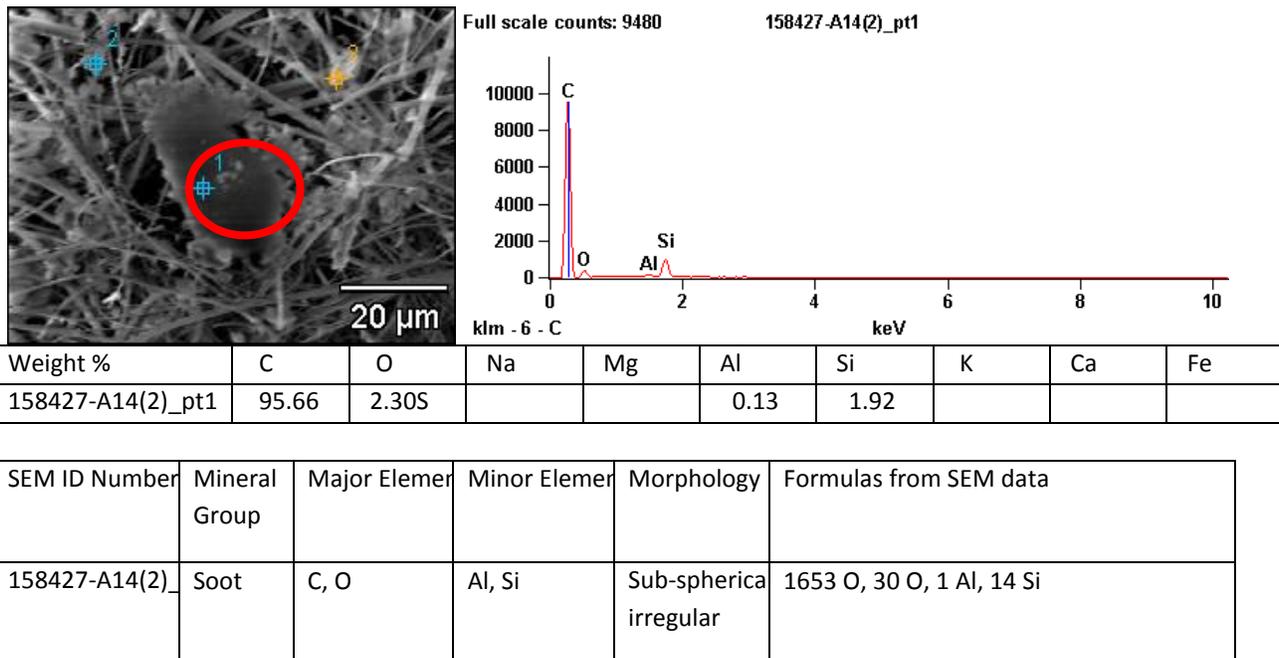
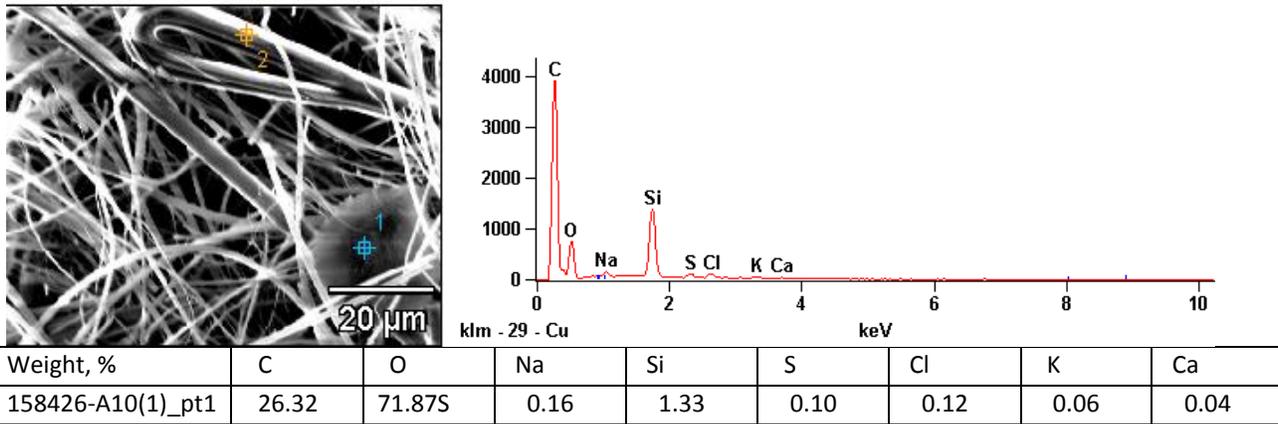


Figure 15. Particulate matter identification from actual samples (Anthropogenic minerals - soot)

Biogenic particles

Particles of biological origin were quantified by the method used by Matthias-Maser and Jaenicke (1994). Both dead and alive biogenic aerosols contain minor amounts of Na, Mg, K, P, Si, Cl, Al and Ca. These elements sum to approximately 10% of the whole weight of the particle. These elements are also essential trace elements present in plants (Artaxo & Hansson, 1995). The rule to identify such particles is: biological aerosols will have combined weight percentage of greater than 75% of carbon and oxygen, and phosphorus, potassium and chlorine will have weight percentage of between 1% and 10% (Coz et al., 2010). S, Si, Zn, and Ca are also tracers of biogenic materials. Figure 16 shows a round shaped outgrowth. It has a high carbon and oxygen content which sums up to more than 75% by weight with trace amounts of K, Na, Cl, and Ca. The silica content is probably from the filter fibers.



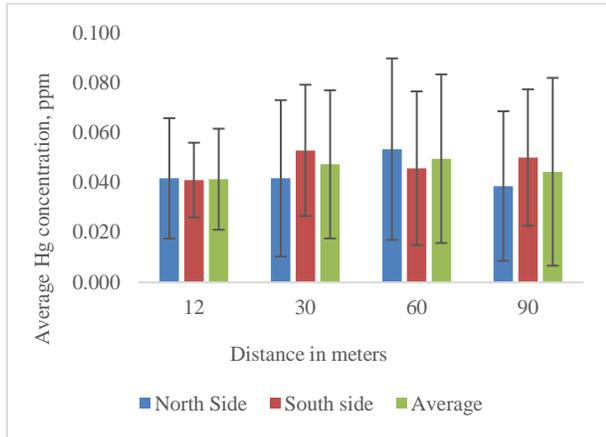
SEM Number	Mineral Group	Major Element	Minor Element	Morphology	Formulas from SEM data
158426-A10(1)_	Biological group	C, O	Si, Na, Cl, K, Ca	Round/spher	2195 C, 4500 O, 7 Na, 47 Si, 3 Cl, 2 K, 1 Ca

Figure 16. Particulate matter identification (Biological particles)

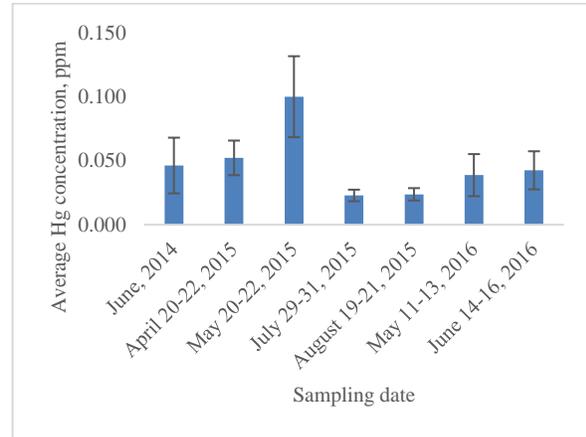
Such biological particles include microorganisms and fragments of all varieties of living matter like viruses, bacteria, fungal growth, spores, pollen, plant debris, etc. (Cong et al., 2008; Coz et al., 2010; Matthias-Maser & Jaenicke, 2000).

Elemental analysis of soil samples

The soil samples were analyzed to determine their elemental composition with regard to sixty chemical elements by ICP-MS. Selected metals of interest were chosen because of their potential impact on the local environment and, essentially, crops and human health. There were several studies conducted in early 1980s which depict the elemental compositions of metals and their reference values in the soil (Shacklette & Boerngen, 1984). In this study, concentrations of most of the metals were lower than the reference values. Additional data collected by the United States Geological Survey (USGS) Mineral Resources National Geochemical Survey (NGS) (USGS, 2003) (Sample ID: C – 250179, C – 237228, C-237239) and Smith et al. (2013) (Lab ID: C – 340224) were used to compare the measured values with these previously published values. Evaluation of the analytical data from this study showed few elements that appeared to be potentially influenced by dust from road traffic. However, some anomalies appeared to occur in the data from mercury (Hg), lead (Pb), and nickel (Ni). Thus, these elements were examined more closely. Figure 17 and 18 show the average mercury (Hg), and lead (Pb) concentrations with increasing distances from the center of the road and their concentrations with respect to sampling dates.



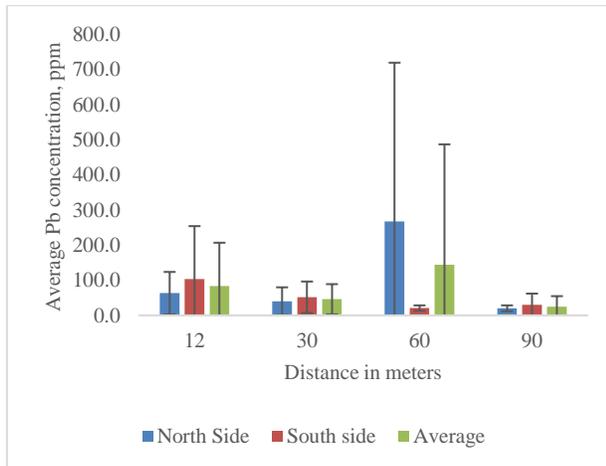
(a)



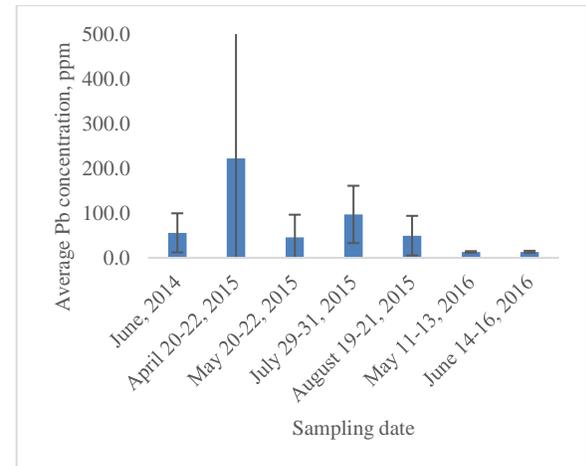
(b)

Figure 17. (a) Average mercury (Hg) concentrations in ppm in soil at varying distances from the road (n=8 at 12 m, n=6 at 30 m, 60 m, 90 m); (b) Average mercury (Hg) concentration in ppm with respect to the date of trip (n=8 for all sampling dates except, n=6 for April 20-22, 2015).

The pooled (over a three years period) average Hg concentration was 0.046 ± 0.029 ppm. The concentration of Hg varied from 0.020 to 0.10 ppm. The reference value from NGS was found to be 0.020 ppm and 0.07 ppm (Smith et al., 2013). The average Hg concentrations on the north side of the road were higher than that on the south side of the road. The mercury concentration is highest in the month of May, 2015 and then decreased significantly. There is a rise in Hg concentration in 2015, but the concentrations during 2014 and 2016 were low. It could be also due to disturbance of soil on the south side of the road as the underground cable/pipe installation activities were going on at that time.



(a)



(b)

Figure 18. (a) Average lead (Pb) concentrations in ppm in soil at varying distances from the road (N=8 at 12 m, N=6 at 30 m, 60 m, 90 m); (b) Average lead (Pb) concentration in ppm with respect to the date of trip (n=8 for all sampling dates except, n=6 for April 20-22, 2015).

The pooled average Pb concentration was 76.7 ± 168 ppm sampled over a period of three years. The reason of large error range is due to high Pb concentrations on April 20-22, 2015 sampling

date (222.3 ± 391.5 ppm), and on July 29-31, 2015 sampling date (97 ± 64.2 ppm). The Pb concentrations varied from 6.4 to 435.9 ppm. The reference value from NGS was found to be 8.3 ± 1.5 ppm and 15.2 ppm (Smith et al., 2013). The average Pb concentrations increased over distance to the 60m sampling point and then dropped at 90 m. The Pb concentrations, like Hg, were much higher in 2015 than that of 2014 and 2016's. The high Pb concentrations during the 2015 sampling period could cause health issues to human working in the area and the animals that are feeding off the site, if the soil is ingested. As the soil pH (5.92) was below 6.50, it could also become available to plants.

Conclusions

The primary objective of this project was to quantify particulate matter (PM₁₀, PM_{2.5}) emissions from unpaved roads (treated vs untreated) in well development area in the Western North Dakota. Airmetrics miniVOL™ Tactical Air Samplers (Springfield, OR, USA) were used to quantify PM₁₀, PM_{2.5}, TSP at selected locations. The pooled average PM₁₀ and PM_{2.5} concentrations were 30.84 ± 14.19 $\mu\text{g}/\text{m}^3$ and 14.08 ± 6.56 $\mu\text{g}/\text{m}^3$ from a periodically treated road (Site 1), respectively over a two-year sampling period. The PM₁₀ emissions at site 1 were found to be weakly correlated with rainfall in 2015 ($r^2 = 0.07$) and moderately correlated with vehicle count, wind speed, wind direction, and rainfall in 2016 ($r^2 = 0.30$) at $p=0.15$. Likewise, the PM_{2.5} emissions were strongly correlated with wind direction and rainfall in 2015 ($r^2 = 0.51$) and with vehicle count in 2016 ($r^2 = 0.38$). So, most of the time, the PM concentrations were high when the vehicle count was high and PM concentrations were low when there was a rainfall event. However, the average PM concentrations in 2015 were higher than 2016 but they were still below the NAAQS threshold values. In addition, the PM concentrations were low when magnesium chloride was applied on the road surface.

The pooled average PM₁₀ and PM_{2.5} concentrations (over a two-year sampling period) were found to be 70.42 ± 38.37 $\mu\text{g}/\text{m}^3$ and 19.60 ± 7.51 $\mu\text{g}/\text{m}^3$ from an untreated loose gravel road (Site 2), respectively. There were some instances when the PM concentrations exceeded NAAQS values which could be due to construction activities on road or high vehicle count or new gravel application on the road or due to the untreated road surface. The PM₁₀ concentrations were loosely correlated ($r^2 = 0.10$) with rainfall in 2015 and with wind speed and rainfall ($r^2 = 0.20$) in 2016. The PM_{2.5} concentrations were strongly correlated ($r^2 = 0.58$) with vehicle count and wind direction in 2015 and no correlation was found in 2016 ($p=0.15$). The PM concentrations in 2016 were lower than that of 2015 because of a decrease in oil rigging activities in the sampling area.

Elemental composition, and morphology of samples were analyzed by scanning electron microscopy energy dispersive spectroscopy (SEM/EDS) which revealed there is a wide range of minerals, biological aerosols, and little amount of anthropogenic particles in the area. 46% of the particles analyzed were quartz, and 36% of the particles were found to be other types of silicates which are basically constituents of road gravels in the sampling area. There were small amounts of biological particles (9%), and oxides (7%). Very limited amount of anthropogenic particles (soot, 1%) was found in the area. The relative amount of quartz was higher at site 1 than that of site 2 which could be due to accelerated weathering process from a high number of traffic. Quartz and oxides were predominant in PM_{2.5} samples too.

Soil samples were analyzed using inductively coupled plasma – mass spectroscopy (ICP-MS) to find out elemental compositions of metals present in the sampling area. To compare the measured value, elemental compositions of metals from three reference sites were compared with the United States Geological Survey (USGS) – National Geochemical Survey website and (Smith et al., 2013). It was found that the concentrations of most metal decreased with increasing distances from the center of the road to the north and south sides. Concentrations of the metals were higher in some cases which were likely due to increased oil drilling activities, higher traffic, disturbance of soil from underground cable installations, etc. The concentrations of most of the metals were higher in 2015 than that of 2014 and 2016, during which, traffic and oil activities were the highest. However, most of the metal concentrations were lower than the USGS reference values, thus road dust may not pose any concern on soil quality based on this study. However, additional long term studies are needed to evaluate the impact on soil and crop, as well as on human health and livestock welfare.

Acknowledgment

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Products

Under this project, Mr. Sumon Datta has completed his MS degree in Agricultural and Biosystems Engineering and title of his thesis is “Quantification and characterization of particulate matter generated from unpaved roads in the oil development area of western North Dakota”. Sumon has also presented preliminary research findings in the ASABE annual meeting (Datta, S., S. Rahman, M.S. Borhan, B. Saini-Eidukat, and L. Cihacek. 2016. Quantification and characterization of particulate matter generated from unpaved roads in the oil development area of western North Dakota. 2016 ASABE Annual International Meeting, Orlando, Florida, July 17-20, 2016).

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