ABSTRACT

Title of Thesis: UTILIZING RAMAN MICROSCOPY TO IDENTIFY SOURCES OF PM10 DOWNWIND OF AGRICULTURAL OPERATIONS

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Emission of particulate matter (PM) from animal feeding operations (AFOs) poses a potential threat to the health of human and livestock. Current efforts to characterize PM emissions from AFOs generally examine variations in mass concentration and particle size distributions over time and space, but these methods do not provide information on the sources of the PM. Raman microscopy was employed in an innovative manner to quantify the contributions of source materials to PM_{10} emitted from a large cattle feedlot. Raman spectra from potential source materials were first compiled to create a spectral library. Multivariate statistical analysis model was developed to identify the source of particles collected on PM_{10} sample filters. Cross validation of the model resulted in 99.76% correct classification of the model spectra. Source characterization results from samples collected over a two-day period indicate

that pen surface dominated in PM_{10} emission with unpaved road as the second biggest contributor.

UTILIZING RAMAN MICROSCOPY TO IDENTIFY SOURCES OF PM10 DOWNWIND OF AGRICULTURAL OPERATIONS

By

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CHAPTER 1: INTRODUCTION

1.1 BACKGROUND

1.1.1 PM DEFINITION

Particulate matter (PM) refers to tiny particles suspended in a gas or liquid. United States Environmental Protection Agency (US EPA) defines PM as “a complex mixture of extremely small particles and liquid droplets” (US EPA, 2011a).

PM is commonly categorized by particle size, which is simply the diameter of the particle. However, particles are usually geometrically irregular. For example, particles might have shapes of flake, fiber, hollow sphere, and aggregate. So diameter is hardly applicable for definition of particle size. In addition, even if the shapes are identical, particles might be extremely different in chemical compositions and therefore, have distinctive densities. As the shape and density can directly affect the behaviors of the particles in the atmosphere, definitions of particle size for particle with similar environmental behaviors are needed. The most widely used definition is the aerodynamic diameter. US EPA has a specific module for particles, and defines the aerodynamic diameter as “the diameter of a spherical particle having a density of 1 gm/cm^3 that has the same inertial properties in the gas as the particle of interest”. The aerodynamic diameter is not a true size and is useful for all particles including fibers and particle clusters (US EPA, 2010a).

Since particles of different sizes present different properties and environmental fate in the atmosphere, EPA defines four terms to divide particles into smaller categories for better air emission evaluation (US EPA, 2010b), as shown in Table 1-1.

Table 1-1: EPA Terminology for Particle Sizes

EPA Description	Particle Size (aerodynamic diameter d)
Supercoarse	$d > 10\ \mu m$
Coarse	$2.5\ \mu m < d \leq 10\ \mu m$
Fine	$0.1\ \mu m < d \leq 2.5\ \mu m$
Ultrafine	$d \leq 0.1\ \mu m$

PM is regulated and monitored using the above classification. Specifically, US EPA has defines two terms for PM concerns related to air pollutant, PM_{10} and $PM_{2.5}$. PM_{10} is defined as particulate matter with a diameter of 10 micrometers collected with 50% efficiency by a PM_{10} sampling collection device. However, the term PM_{10} is used to include all particles having an aerodynamic diameter of less than or equal to 10 micrometers for convenience (US EPA, 2010a). $PM_{2.5}$ is defined in the exactly same way but with the size of 2.5 micrometers. EPA particularly addresses PM_{10} and $PM_{2.5}$ because of their adverse effects on human health, which is discussed in later sections.

1.1.2 PM FORMATION

Knowing the sizes of the PM is critical to assess the impacts and transportation of particles in the atmosphere. The collection efficiency of pollution control equipment is dependent on the particle size. Also, samplers or measuring instruments usually have specific targeted particle sizes. Most of the time, the formation mechanisms of PM can lead to specific size range. By identifying and evaluating the mechanisms of particle formation, one can estimate the general size range.

PM can originate from a variety of natural sources. For example, sandstorms can drive tiny mineral dust into the air from deserts. Ocean waves yield numerous sea salt particles from powerful spray. Volcano eruptions send into the atmosphere a huge amount of ash, sulfur dioxide and other gases, which can further become aerosols through physical or chemical changes. Living vegetation, such as forests and grassland, is a major source of aerosols. Some plants can generate gases that can react with other matters in the air to form aerosols, and forest fires contribute a great deal of soot also classified as PM.

Anthropogenic formations of PM are of increased concern with respect to their severe impacts on air quality. EPA concludes four processes as the most important particle formation mechanisms in air pollution sources (US EPA, 2010c). The first one is physical attrition or mechanical dispersion. It describes situations where two surfaces rub together and generate small particles that are identical to the parent materials in compositions and densities. Examples are as grinding a metal rod on a grinding wheel and operation of stone crusher. This mechanism primarily produces particles with moderate to large sizes. The second mechanism is combustion particle burnout. In the combustion process, most of the organic compounds from the fuel are vaporized and oxidized in the hot furnace area, making fuel particles become smaller and reduce to the incombustible matter, or ash, and the slow burning char, which will also burn out eventually. The resulting particles of ash and char are primarily in the 1 to 100 micrometer range. The next mechanism is homogeneous and heterogeneous nucleation. In both cases, particles are produced through the conversion of vapor phase materials to particulate form. The nucleation occurs when the gas streams are cool down to a certain temperature when the dew points of the materials are reached. The homogeneous nucleation generates particles contain only on compound while the heterogeneous nucleation results in the accumulation of material on the surfaces of existing particles and produces particles that are comprised of two or more compounds. Organic compounds and inorganic metals or metal compounds are to main categories of materials that can nucleate in the gas streams. Example of this mechanism is municipal and medical waste incinerator. Particles generated from nucleation remain in the gas stream and go into the environment as it leaves the incinerator. Nucleation mechanism creates particles with the small size range of 0.1 to 1.0 micrometer. The last mechanism is droplet evaporation, which happens when some systems use solids-containing water recycled from wet scrubbers to cool hot gas streams. The suspended and dissolved solids in the water are released as fine particles when the water evaporates to dryness after it encounters the hot gas stream. The size of the particle generated by this mechanism has not been extensively studied and an estimate of 0.1 to 20 micrometers is provided.

US EPA identifies anthropogenic PM sources and provides a national database of air emission by source sector. There are 8 main sectors with recognized sources (US EPA, 2011b):

(1) Dust (unpaved road dust, construction dust, and paved road dust);

(2) Fuel Combustion (electric generation, residential, industrial boilers, and common/institutional);

(3) Agriculture (crops & livestock dust, and livestock waste);

(4) Industrial Processes (NEC, mining, storage and transfer, pulp & paper, ferrous metals, chemical manufacture, petroleum refineries, cement manufacture, non-ferrous metals, and oil & gas production);

(5) Mobile (non-road, on-road, commercial marine vessels, locomotive, and aircraft);

(6) Miscellaneous (waste disposal, commercial cooking, miscellaneous non-industrial NEC, bulk gasoline terminals, and gas stations);

(7) Fires (prescribed fires, and agricultural field burning);

(8) Solvent (industrial surface coating & use, graphic arts, degreasing, consumer & commercial use, dry cleaning, and non-industrial surface coating).

1.1.3 ADVERSE EFFECTS OF PM

PM can cause serious health problems because of their small sizes. Large particles can be filtered in the nose and throat and have no access into the body. When the size is small enough, typically below 10 μm, the particles are able to penetrate deeply into the lungs and cannot be removed by respiration (Monn et al., 1997; Wilson and Suh, 1997), resulting in serious health effects such as asthma, lung cancer, and cardiovascular issues. A growing body of evidences supports the relationship between PM levels in the ambient air and the detrimental impacts on human health. Neukirch et al. (1998) revealed consistent and significant associations between asthma attacks and symptoms and Paris winter air pollution, such as dioxide, nitrogen dioxide, and suspended particulates with an aerodynamic diameter close to 10 μm (Neukirch et al., 1998). Pope et al. (2002) found increase risk of lung cancer and cardiopulmonary mortality associated with augmented levels of fine particulate air pollution (Pope et al., 2002). McConnell et al. (1999) reported that risk of bronchitis for children increased with the elevation of PM10 level (McConnell et al., 1999). Exposure to PM pollution was also found to cause increased heart rate, decreased heart rate variability, and increased cardiac arrhythmias (Dockery, 2001).

Besides particle size, PM can be made of thousands of different chemicals. As previous discussion suggests, there are various anthropogenic sources of PM. These sources usually generate PM that are consisted of toxic compounds or materials and result in more acute health problems by human exposure. Perez et al. (2007) explored the relationship between PM10 and cell toxicity and linked the PM10 concentration with the inhibition of cell proliferation (Perez et al., 2007). A review focused on oxidative stress resulted from PM10 and how it affected the lung target cell by activating a number of redox-responsive signaling pathways, which were related to pulmonary inflammation and pathological change (Donaldson et al., 2003). BeruBe et al. (2007) linked transition metals in fine particles deposited in pulmonary system with respiratory health effects (BeruBe et al., 2007). Kleinman et al. (1995) compared the toxicity of fine particles that had fraction of ammonium sulfate and ammonium nitrate with suspended road dust and reported an order of ammonium nitrate, ammonium sulfate, and road dust with respect to the severity in damaging lung defense functions (Kleinman et al., 1995).

Furthermore, PM in the atmosphere can migrate and settle on different environmental media, such as water body and terrestrial land, affecting the original system by introducing the toxic chemicals. For example, acidic aerosols can result in acid rain and acidification of lakes or streams, damaging the vegetation and the nutrient balance in the water and the soil. When they encounter sunlight, fine PM can lead to haze that reduces the clarity and color of what we can see in the cities and scenic areas. Poor visibility in national parks and wilderness area is a concerned issue that EPA endeavors to monitor and improve (US EPA, 2011c).

1.1.4 PM EMISSION AND OPEN CATTLE FEEDLOTS

1.1.4.1 CATTLE FEEDLOTS IN US

US EPA defines Animal Feeding Operations (AFOs) as agricultural operations where animals are kept and raised in confined situations (US EPA, 2011d). A lot or facility has to meet two conditions to be an AFO: (1) animals have been, are, or will be stabled or confined and fed or maintained for a total of 45 days or more in any 12-month period and, (2) crops, vegetation, forage growth, or post-harvest residues are not sustained in the normal growing season over any portion of the lot or facility. Open cattle feedlot is one of the most common and important AFO sectors in the United States. The United States has the largest fed-cattle industry in the world. According to Agricultural Statistics Service (NASS), as of July 1st, 2011, all cattle and calves in the United States totaled 100 million head (USDA-NASS, 2011). Since Concentrated Animal Feeding Operations (CAFOs) are point sources for pollutants, EPA refers to the actual number of animals at the operation to define the size of a

CAFO from a regulation perspective: less than 300 head for small CAFOs, 300 to 999 head for medium CAFOs, and 1000 or more head for large CAFOs (US EPA, 2011e).

Based on the 2011 statistics (USDA NASS, 2011), three states ranked the top in the number of cattle raised in more than 1000 head capacity cattle feedlots (large CAFOs). They are Texas (2.95 million head), Kansas (2.32 million head), and Nebraska (2.21 million head). As typical states with leading cattle feeding industry, the number of large CAFOs has increased in all three states from the year 2003 to 2007, with Texas from 1400 to 1500, Nebraska from 950 to 1100, and Kansas from 630 to 800. The total increased of large CAFOs for the entire US was from 9790 to 10810, and the percentage of large CAFOs increased from 28.0% to 33.9% in the same period (USDA NASS, 2009). With the growth of cattle feeding industry, CAFOs in US present the tendency to become more concentrated.

Cattle feedlot operations are one of the three operations in the US beef industry, which are referred to as cow-calf operations, backgrounding, and finishing. The feedlot phase is corresponding to the final phase of the beef cattle production cycle, the so-called finishing. Normally, beef cattle of six-month old are sent to the feedlot for the finishing phase, which ends in about 150 to 180 days when the cattle on feed reach the slaughter weights (USDA NASS, 2009).

1.1.4.2 PM EMISSION FROM CATTLE FEEDLOT

EPA has reported that Animal Feeding Operations are sources of various pollutants to ambient air by emitting particulate and gaseous substances (US EPA, 2001). Gaseous emissions from cattle feedlots include hydrogen sulfide, ammonia, nitrous oxide, methane, carbon dioxide, and volatile organic compounds (VOCs).

These gaseous substances are believed to be harmful to human and the environment. Under anaerobic conditions, hydrogen sulfide and other reduced sulfur compounds can be produced by the decomposition of manure, which contains sulfur amino acids and inorganic sulfur compounds that are used as feed additives. Ammonia and nitrous oxide are produced through microbial decomposition of the organic nitrogen compounds in manure. Microbial degradation of organic matter under anaerobic conditions results in the production of methane and carbon dioxide, which can be also produced under aerobic conditions. The VOCs are generated as intermediate metabolites in the degradation of organic matter and can be further metabolized to simpler compounds (US EPA, 2001).

Since cattle feedlots are open operations that exposed to the outside environment, they have greater potential to emit PM to the ambient air environment than those with confined buildings. Sweeten et al. measured PM concentrations from three feedlots in Texas and reported that PM10 concentrations were 40% of the total suspended particulate (TSP) mean concentrations, which was 412 μg/m3 (Sweeten et al., 1988). Later in 1998, they measured TSP and PM10 downwind of three cattle feedlots in the Southern Great Plains and reported the mean concentrations of 700 μg/m3 and 285 μg/m3, respectively (Sweeten et al., 1998). Purdy et al. compared PM10 and PM2.5 concentrations between two small cities located in the Southern High Plains, and concluded that the feedlots increased the PM concentration in and around one of the cities that had more than 35 feedlots in and near it (Purdy et al., 2010). They reported higher PM concentrations downwind than upwind of the feedlots and higher PM concentrations in the summer than in the winter (Purdy et al., 2007). Razote et al. measured PM10 concentration at a large commercial feedlot in Kansas and reported the concentrations ranged from 35 to 195 μg/m3 (Razote, et al., 2007).

PM emissions from cattle feedlots are not only significant in concentrations, but they also have special properties when it comes to the bad effects on human health and the environment. With cattle involved, the PM compositions could be very unique and distinct from PM from urban or industrial sources. PM adsorbs odor and gases and carries bacteria, potentially being a transmitter of odor and diseases. Manure and urine from the cattle could mix with the pen soil and make the PM with more organic chemicals in composition and with bacterial, fugal, and endotoxin concentrations in them (Purdy et al., 2004; Woolums et al., 2001). As PM can directly influence the health of workers at the feedlots, they were found to be dangerous to cattle as well. Macvean et al. associated the incidence of pneumonia in the studied cattle group with the concentration of particles 2.0 to 3.3 μm in diameter (Macvean et al., 1986). In addition, if the dust emission is extremely severe, it might generate safety problems on adjacent highways by reducing the visibility.

1.1.4.3 PM SOURCES IN CATTLE FEEDLOT

Sources of particulate matter emissions from AFOs include feed, bedding materials, dry manure, unpaved soil surface, animal dander, and poultry feathers (US EPA, 2001). Different sources may have different and variable contributions to the PM emission and are subjective to three impact factors. First of all, the type of animal being raised; secondly, the design of the confinement facility being utilized; and thirdly, the method of manure handling (US EPA, 2001). For AFOs, these factors apparently are interrelated and applied on specific situations. Specifically, large open cattle feedlots usually raise cattle in a highly concentrated pattern and without confinement buildings. The pen surface and unpaved roads are the general terrestrial components at the feedlot and they are the major sources of PM emission. Feed mills, operating vehicles, and wind erosion are also potential contributors. These sources and the possible emission mechanisms are all interrelated.

The pen surface of the open cattle feedlots is composed mainly of manure and soil. Manure is accumulated on the pen surface and they contribute significant PM emission. Therefore the amount of manure may directly infect the concentration of PM. The number of cattle in the confinement and the method of manure handling are two factors that can determine the amount of manure. The more concentrated the feedlot is, the more manure is accumulated in a given time. Cattle feedlots usually have stable schedule for manure harvesting or pen cleaning. The higher the frequency of harvesting, the thinner manure layer will be. The amount of source obviously controls the amount of PM that can be emitted. The cattle being confined perform all activities on the pen surface through out the raising cycle. The dry layer or mixture of manure and soil can be trampled or crushed to smaller sizes and made easier to emitted when the cattle walk or run on the pen surface. Cattle activities, such as walking and running, directly cause PM to rise from pen surface and get into the air. The more active the cattle are, the more PM emission will be. Auvermann et al. observed that cattle activities or movement increased during the early evening and it coincided with the reported PM emission concentration peaks at this particular period (Auvermann et al., 2006).

Besides cattle activities, the wind is another factor that leads to PM emission. Since open cattle feedlots are naturally ventilated, manure and mixture of pen surface materials are all subjective to impacts of the wind. On one hand, wind possesses great momentum that could stir up the PM from pen surface. The higher the wind speed, the more potential there is for PM emission. On the other hand, high wind speed can accelerate the evaporation of moisture content from pen surface materials, and result in erosion especially with strong wind blow and shifts.

The moisture content of the pen surface materials can prevent PM emission by making PM particles congregate and increasing the weights of possible emitted particulate, hindering their transportation in ambient air. In one study, researchers compared the potential for PM emission from cattle feedlot soil and surface samples under a variety of environmental conditions. They reported decreasing PM emission potential with increasing moisture content in all the samples (Miller and Woodbury, 2003). As highly ventilating condition can increase the rate of evaporation of moisture content, high temperature can also intensify the drying process of pen surface materials, resulting higher PM emission potential. Contrastingly, rainfall can contribute to the moisture content and cool down the surrounding environment. In addition, rainfall can effectively wash out the air and send the emitted PM back onto the pen surface. Cattle urine serves as a direct source of moisture content to hamper PM emission. Water application system, such as water-sprinklers, is used in order to reduce the concentrations of PM (Razote et al., 2007). Applied water to the surface of cattle feedlots is effective for controlling PM emission, but a cost-effective method is needed for operations.

Roads or paths at the cattle feedlots are made for operating vehicles. Unlike the pen surface, unpaved roads surface consisted of materials that are less organic, such as sand and crushed rock. Therefore they contribute very high dust emission, especially when the humidity is low, the wind speed is high, or the vehicles are traveling on. PM might be fraction of the emitted dust, but the size distribution is not well known.

Feed mills are usually located at the cattle feedlots for feed storage and processing to meet the huge amount of feed requirement for CAFOs. Feeds are transported to the feedlots and usually piled up in the open air for convenience of operation. Some of the feeds are low in moisture content, such as hay and dry corn kernel. Under hot weather or high wind speed condition, they can emit feed dust. Feed processing, for example, hay grinding, grain unloading, feed mixing and dispensing, can generate feed dust at all sizes. Even though feed dust emission is observed to be significant, the PM fraction, especially PM10 fraction, needs to be further studied to determine.

Motor machines at the cattle feedlots, including vehicles for transportation and motor machines for feed processing, can also cause PM emission. Operating vehicles travel on the unpaved road, for example, workers driving cars or feed delivering trucks unloading the feed to troughs at different pens, resulting large road dust emission. Moreover, vehicles and the motor machines can generate all kinds of fuel and diesel exhaust, which are common PM in urban area (Sadezky et al., 2005).

1.1.5 AIR QUALITY REGULATIONS ON PM

1.1.5.1 EPA REGULATIONS ON PM

Under the Clean Air Act (CAA), US EPA is required to set National Ambient Air Quality Standards (NAAQS) for six criteria pollutants, which are carbon monoxide (CO), lead (Pb), nitrogen dioxide (NO2), ozone (O3), particulate matter (PM), and sulfur dioxide (SO2). These six pollutants are considered detrimental to human health and the environment, with numerous and diverse sources identified or being studied. For PM pollution, the Clean Air Act established two types of national air quality standard. Primary standards contain limits that are set to protect public health. Special populations that are sensitive to particle pollutions, including people with heart or lung diseases, children, and the elderly, are included as protected target of public health. Secondary standards are aiming at protecting public welfare by setting specific limits. The protection includes prevention of visibility impairment and the reduction of damage to animals, natural environments, crops, vegetation, and buildings (US EPA, 2011f).

EPA categorizes the particle pollution as two types. The first one is “inhalable course particles”, which are larger than 2.5 μm and smaller than 10 μm in aerodynamic diameter. The other one is “fine particles” with aerodynamic diameters of 2.5 μm or less. EPA only regulates these two types of particles because they are extremely small in size that they can get deeply into the airways and alveoli of lungs, resulting serious health problems such as airways irritation, breathing difficulty, lung dysfunction, chronic bronchitis, asthma, heart attacks, irregular heartbeat, and even premature death. Particles larger than 10 μm are not regulated (US EPA, 2011g).

While EPA has the responsibility to issue NAAQS for PM pollutions, the CAA also requires EPA to conduct a regularly scheduled review of its NAAQS every five years (US EPA, 2011h). The purposes are to make sure public health and welfare are sufficiently protected and to provide the best available knowledge regarding PM pollutants. It takes several years for EPA to perform the review process, which includes a “integrated science assessment” to review the most recent science about PM pollution and its effect on public health and the environment, and the review of a staff “policy assessment document” that provides conclusions on the current standard and possible alternation to the standards from the staff to the Administrator (US EPA, 2011h). EPA has to issue a proposal by the end of the review. The proposal may recommend either changing any available standards or retaining the current ones. A proposal is anticipated in 2011 by EPA on PM NAAQS.

1.1.5.2 PM STANDARDS

EPA started to regulate particle pollution from 1971 for PM10 and PM2.5. Standard limits are set for both primary and secondary standards. Over the years, EPA conducted researches and review to learn more about PM behaviors and environmental impact. As more scientific research and monitoring were conducted on diverse sources of PM, EPA changed the standards to reflect the best knowledge on PM pollution. Table 1-2 summarizes the NAAQS changes for PM.

Table 1-2: Summary of National Ambient Air Quality Standards for Particulate Matter 1971-2006 (US EPA, 2008).

Year	Indicator	Averaging Time	Level*	Form
1971	Total Suspended Particulate (TSP)	24-h	260 µg/m^3 (primary) 150 µg/m^3 (secondary)	Not to be exceeded more than once per year
		Annual	75 µg/m^3	Annual average
1987	PM_{10}	24-h	150 µg/m^3	Not to be exceeded more than once per year over a 3-year period
		Annual	50 µg/m^3	Annual arithmetic mean, averaged over 3 years
1997	$PM_{2.5}$	24-h	65 µg/m^3	98th percentile, averaged over 3 years
		Annual	15 µg/m^3	Annual arithmetic mean, averaged over 3 years
	PM_{10}	24-h	150 µg/m^3	Not to be exceeded more than once per year over a 3-year period
		Annual	50 µg/m^3	Annual arithmetic mean, averaged over 3 years
2006	$PM_{2.5}$	24-h	35 µg/m^3	98th percentile, averaged over 3 years
		Annual	15 µg/m^3	Annual arithmetic mean, averaged over 3 years
	PM_{10}	24-h	150 µg/m^3	Not to be exceeded more than once per year over a 3-year period

*when not specified, primary and secondary standards are the same.

In 1987, EPA made significant revisions to the initial standards promulgated in 1979, choosing PM_{10} as indicator for particles instead of total suspended particulate (TSP). In order to address the consideration of serious health effects that were associated with short-term and long-term exposure to PM pollution, EPA made two averaging limits with time of 24-hour and one year, respectively. The NAAQS 24-h standard of PM_{10} has been used since 1987 to date as 150 $\mu g/m^3$. It remains unknown that whether this standard will be changed in the anticipating proposal EPA has to issue in 2011. However, the PM standards were revised to be more and more stringent by EPA, who added the limits for $PM_{2.5}$ in 1997 and reduced the tolerant levels for both primary and secondary standards in 2006. Also, the secondary standards were revised to be identical to the primary standards from 1987, indicating that EPA modified the standards for public welfare and environment to the same level of the standards for human health.

1.1.5.3 PM REGULATIONS AND CATTLE FEEDLOTS

Every time EPA sets a new NAAQS or revises an existing standard, the CAA also requires EPA to designate areas as three types. The first one is “nonattainment areas”, meaning areas with air quality that are not meeting the new NAAQS according to the collected data from air quality monitors. The second one is “unclassifiable/attainment areas”, which meet the standard or are expected to meet the standard even if there is no monitoring data. The last one is “unclassifiable areas”, which means areas that cannot be classified due to the lack of data (US EPA, 2011i).

Although it is the responsibility of EPA to regulate PM emission and designate the nonattainment areas, the Clean Air Act also requires that all states work with the EPA to from a federal-state partnership in order to protect and improve the nation’s air quality (US EPA, 2011h). Under the CAA, EPA requires all state environment agencies to develop state implementation plans. The state environment agencies are expected to make plans on how to reduce the air pollution in the nonattainment area to meet NAAQS. In addition to implementing and ensuring NAAQS are achieved, states may create regulation laws to address issues that federal regulation has not included, or modify the existing regulation to make standards that are even more stringent than NAAQS (NRC, 2003). For Kansas, the state environment agency is the Kansas Department of Health and Environment (KDHE).

Even though EPA establishes specific standards for PM10 and PM2.5 pollution in the ambient air, these limits do not require emission control for any particular industry, including agriculture. Instead, it is every state that regulates and develops control plans for PM pollution basing on the most interests of the area to meet the standards. Most states endeavor to reduce PM10 from industrial sources, but there is no requirement for agriculture operations, including cattle feedlots, to implement specific plans for PM10 emission abatement (US EPA, 2011h). The reason for the lack of regulating actions on PM10 emission from cattle feedlots might be that the scientific researches and monitoring data are insufficient to fully characterize the emission level, sources distribution, and factors that impact PM pollution. Therefore it is difficult to provide feasible solutions for control implementations (NRC, 2003).

The state of Kansas promulgates its own Air Quality Regulations to ensure NAAQS is properly implemented (KDHE, 2011). The Kansas Air Quality Regulations require the owner or operator to be issued a permit for approval before they can start actual construction or modification. Information on the net emissions increase happening at the time that the permitted activity is completed is required to be provided in the application for the permit (KDHE, 2011). Although cattle feedlots are not categorized as major pollutant sources by the State of Kansas, they are not in the fugitive emission exemption list, either (KDHE, 2011). KDHE also issues Design Standards for Confined Feeding Facilities, which only regulate on the waste discharge but not on PM emission (KDHE, 2006).

Even though there is no specific regulation on PM emissions from open cattle feedlots, the concerns is becoming more important from public and EPA because the ongoing researches reported significant PM emissions (Bonifacio et al., 2011; Guo et al., 2009; Guo et al., 2011). It could be expected that regulation standards will eventually be established for emission abatement and protection of public health. In order to make that happen, more extensive researches and monitoring data are needed for the agencies to set proper standards that can effectively control PM pollution.

1.2 RESEARCH ON PM FROM CATTLE FEEDLOTS

A number of studies have been conduced to investigate the sources and environmental fate of PM from cattle feedlots. Compared with those occurring in natural environment, PM emissions from anthropogenic sources contain materials or chemicals that are detrimental to human body, with the potential to induce chronic or acute disease symptoms. Most of the researches have been focusing on anthropogenic sources in the urban or industrial area where large population are residing.

Harmful effects as well as the lack of regulations on PM emissions all call for a better understanding of PM emission characteristics. More and more scientists start to focus on research of PM from cattle feedlots. However, the existing studies have concentrated on the development of methodologies and instrumentation to quantify PM mass concentrations and size distribution (Guo et al., 2009; Guo et al., 2011; Sweeten et al., 1988; Sweeten et al., 1998). While they provided very useful data on PM emission levels and suggestion to improve the sampler for better measurement, none of them address the chemical composition of PM particles and quantification of PM contribution from potential sources.

Information on these two issues can offer insightful perspective when it comes to characterize PM from cattle feedlots. For one thing, chemical composition of PM can be a direct indicator of potential toxins or adverse materials to human and cattle health. Furthermore, identified chemicals can also be used as markers to trace the sources of the particles. Quantification of PM contribution from different sources can serve as solid scientific data, which law makers can rely on to set more effective standards and require specific abatement actions to better control PM from cattle feedlots. However, very limited information is currently available regarding the source apportionment of PM10. Since the means to collect PM10 for this particular purpose and corresponding analytical methods have not yet been well studied, it is very challenging to approach this task. But still, there are a few studies trying to find feasible solution.

Rogge et al. (2006) tried to identify specific molecular marker compounds for potential sources profiles of fugitive dust from cattle feedlots (Rogge et al., 2006). They collected surface soil samples from feedlots at the San Joaquin Valley in California and employed gas chromatography-mass spectrometry (GC-MS) for chemical characterization and quantification. Although they quantified more than 100 organic compounds and reported that the stearic (C18) and palmitic (C16) ratio (C18/C16) was unique and could be used in source apportionment studies, they did not go further to analyze real PM emission. They did not provide any information on how to sample the PM from the ambient air, and gave no solid evidence that the analytical procedure involving complicated solvent extraction could be applied to the PM sample collected in the particular manner. Furthermore, the marker compounds were exclusive organic and the analytical procedure was designed to detect the organic fractions of the samples. It might fail to identify the inorganic part of the sources and the ambient PM.

Also at the San Joaquin Valley, another study tried to construct PM10 chemical source profiles for different geological dust, including those from the feedlot surfaces (Chow et al., 2003). They conducted a systematic surface material sampling from 37 locations and the samples were dried, sieved, re-suspended, and sampled through a PM10 inlet on to Teflon-membrane and quartz-fiber filters. The analytical process was complex. Teflon-membrane filters were analyzed by high-sensitivity X-ray fluorescence for 40 metal elements. Half of the quartz filters were analyzed by ion chromatography for chloride, nitrate, and sulfate, by automated colorimetry for ammonium, and by atomic absorption spectrophotometry for Na+ and K+. The other half of the quartz filters were analyzed by the IMPROVE thermal/optical reflectance protocol for eight carbon fractions. Six source types of source profiles were reported based on the composition features. This study shed a light on a variety of possible analytical approaches for chemical characterization of

PM sources. Like the previous discussed study, this research did not address any PM sample. It only focused on the construction of source profiles, and provided no information on ambient PM sampling and analytical procedure that could be coupled with the developed source profiles to classify and quantify PM sources.

Lange et al. (2009) employed neutron activation analysis to measure concentrations of 30 elements in filtered air particulates in the hope of estimating the fraction of PM from different sources (Lange et al., 2009). Even though they reported a successfully implemented method and the results of PM fraction, there were issues with the study. First of all, neutron activation analysis is not a common analytical method and includes complicated sample treatment, such as irradiation. Secondly, like most of the analytical methods, neutron activation analysis is sample-destructive since it required the removal of the PM from the filter media for instrument analysis. Thirdly, they incorporated multivariate statistical analysis combined with EPA’s Chemical Mass Balance (CMB) model, EPA-CMBv8.2, to quantify the fraction. The CMB model is a receptor model designed as a regulatory planning tool to address source apportionment issue for air quality problems. However, there are some drawbacks with this method.

On one hand, CMB model requires specific source profiles. The measured chemical and physical characteristics of the sources have to be distinguishable and well defined (US EPA, 2004). The characteristics measurement usually involves chemical characterization by analytical instruments, such as GC-MS, ion chromatography, and infrared spectroscopy. Since the sources are usually extremely heterogeneous, to fully characterize the chemical composition of sources requires different methods for different chemicals. The process ends up being complicated and intensive like the study from Chow et al (2003). In addition, the chemical characterization is of little research interest if the sources are abundant and common in the environment. On the other hand, CMB model has some critical issues that might lead to erroneous results. The issues include flaws resulted from certain file related operation, alteration occurring during the input of source information, lack of files for some tests, calculation that dose not agree with formula of theory provided by the protocol, and so on (Schauer et al., 2005).

Many researches on source apportionment use EPA's CMB model to investigate sources other than feedlot (Chan et al., 1999; Chow et al., 1992; Lee et al., 2008; Maykut et al., 2003; Viana et al., 2008; Watson et al., 1994; Zheng et al., 2002). Although they provided great values on exploring the feasible approaches for source analysis at feedlot, they were rather complicated in the methodology. No existing standard method is established regarding PM source fraction quantification for feedlot so far, and a simpler and more direct approach is needed.

1.3 SCOPE OF WORK AND OBJECTIVES

The current challenges for quantification of source contribution to PM10 emission from cattle feedlots are (1) lack of related standard method and data; (2) finding a cost-effective analytical procedure for source identification of PM. Raman microscopy is proposed for investigation of feasibility to solve the problems.

Raman microscopy is a powerful technique for chemical analysis. Combined with an optical microscope, Raman spectroscopy can be used to obtain spectral information from a very small sample, and therefore has the potential to analyze PM particles. In fact, scientists have used Raman spectroscopy to collect spectra from ambient air particles, including carbonaceous PM, diesel soot, humic-like substances, and inorganic compounds aerosols (Escribano et al., 2001; Ivleva et al., 2007; Sadezky et al., 2005; Sze et al., 2001). Hiranuma et al. used Raman microscopy for the chemical composition analysis of PM10 from an open cattle feedlot, indicating a promising procedure for chemical characterization of targeted PM (Hiranuma et al., 2011). However, Hiranuma et al. only employed Raman microscopy to analyze 10 samples and they did not address the source identification or quantification of the PM at all.

The reasons for Raman microscopy are as follows: (1) Raman spectroscopy is a commonly used technique in chemistry, providing possibility for chemical characterization of PM; (2) it is non-destructive technique; (3) it requires simple or no sample treatment.

The main goal of this research is to develop a feasible method for quantification of source contribution to PM10 from cattle feedlots. With the method successfully implemented, samples are analyzed to characterize the source contribution to PM10 at a typical commercial feedlot. The objectives of this study are:

(1) Develop a method to identify the sources of PM10 sampled on the filters;

(2) Develop a method to analyze the filters for quantification of the source fractions.

(3) Characterize PM10 emission from identified sources at the feedlot.

Our objectives are achieved by accomplishing the following tasks:

(1) Collect sufficient Raman spectra from potential source materials to build up a library for reference.

(2) Identify and designate Unique Raman shifts from spectra as markers for distinguishing sources.

(3) Establish a method on identifying the source of an unknown spectrum by comparing it with the library reference.

(4) Develop a statistical method on justifying the number of particles selected to represent one filter sample.

(5) Analyze filter samples to estimate PM emission fractions.

CHAPTER 2: MATERIALS AND METHODS

2.1 SITE DESCRIPTION: FEEDLOT IN KANSAS

2.1.1 ONGOING RESEARCH AT THE FEEDLOT

To comprehensively address the open feedlot emission issue, a series of intensive field sampling campaigns have been conducted under different meteorological conditions at a large commercial open cattle feedlot in Kansas. Conducted by Kansas State University and the United States Department of Agriculture – Agricultural Research Service (USDA - ARS), the program is dedicated to simultaneous measurements of the concentrations and emission fluxes of particulate matter (TSP, PM_{10}, and $PM_{2.5}$), selected volatile organic compounds (phenols and indoles), and greenhouse gases (CO_2, CH_4, and N_2O) from the feedlot. Anther major objective is to characterize the chemical composition of PM and investigate the source apportionment. The program is also seeking to package all the measured datasets for database construction, so that they can be peer-reviewed and used as field data reference for emission model validation.

2.1.2 SITE DESCRIPTION

Surrounded by agricultural fields, the feedlot is located at Kansas with a total area of approximately 850000 m^2 and a capacity of 30,000 head of cattle. Unpaved roads encircle and go across the feedlot in a gird pattern and make up around 25% of the total area. Feed trucks deliver feed to the pens three times a day from a feed mill, which is located at the southwest corner of the feedlot. The feed is processed and mixed continuously, and is loaded by an overhead truck loader outside the mill. The soil at the feedlot is generally sandy soil. Manure scraping is carried out two or three times a year, and manure is harvested at least once a year from every pen. Annual average precipitation is approximately 488 mm (2010) and prevailing wind directions were south-southeast in summer and north-northwest in winter. Averaged wind speed was 16 kph through out the year of 2010. The producer utilizes water sprinkling of the pens for dust control. A diagram of the feedlot is shown in Figure 2-1.

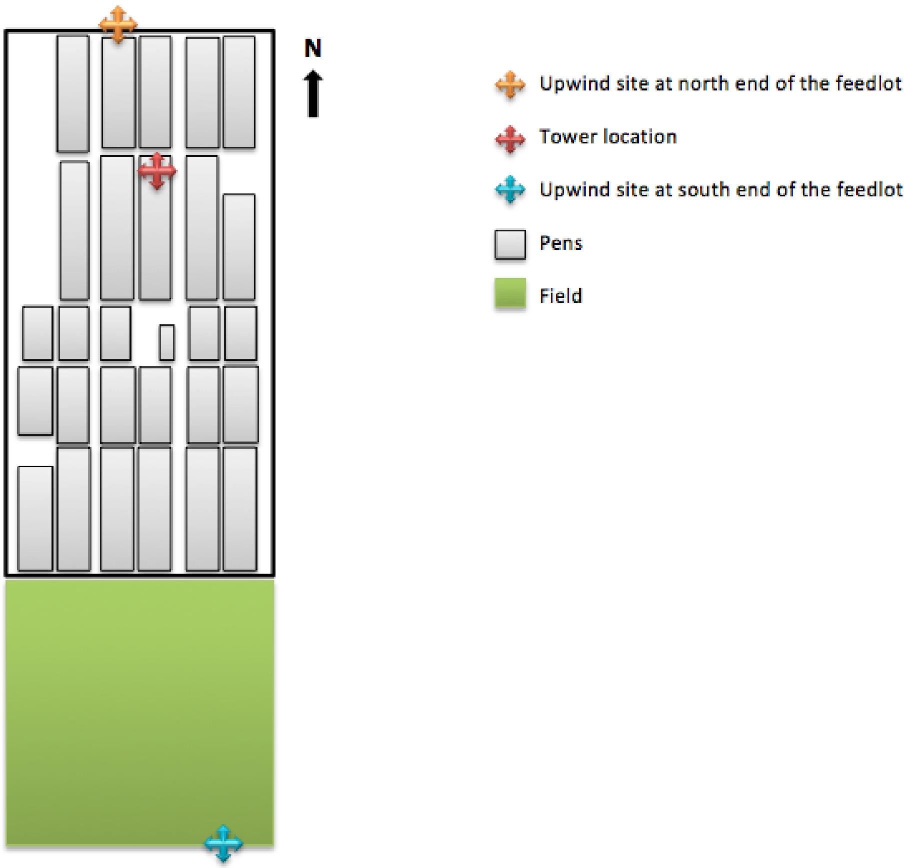

Figure 2-1. Schematic diagram of the cattle feedlot in Kansas.

2.2 PM SAMPLING

2.2.1 SAMPLING METHODS

PM10 is the targeted PM fraction we are focusing on in this study. Mass concentration measurement of PM10 is one of the major components of the sampling campaign conducted at the feedlot. The United States Environmental Protection Agency (US EPA) makes the Federal Reference Method (FRM) and Federal Equivalent Method (FEM) for PM10 measurement and monitoring. The FRM provides for the measurement of the mass concentration of PM10 in ambient air over a 24-hour period for purposes of determining attainment and maintenance of the primary and secondary national ambient air quality standards (US EPA, 2010d). Ambient air is drawn at a constant flow rate into a well-designed inlet which separate the suspended particulate matter by the different inertial of particles of various sizes and let only PM10 fraction pass through. The separated PM10 is collected on a filter that is weighed before and after use to determine the net mass gain. The mass concentration is then determined by dividing the net weight gain by the volume of air sampled (US EPA, 2010d). The FEM has the same principle for sampling, but it provide direct PM mass measurement for near real-time continuous data collection (Guo et al., 2009).

2.2.1.1 SAMPLERS

This study employs the FRM for PM_{10} collection, even though mass concentration is not our focus. Low-volume PM_{10} samplers (2100 Mini-Partisol, Thermo Fisher Scientific, Franklin, Massachusetts) are used. During the measurement, the samplers draw ambient air at a constant volumetric flow rate of 5 L/min, controlled by a temperature and pressure compensated mass flow control scheme (Rupprecht &Patashnick Co., Inc, 2004). A low-volume PM10 sampler is shown in Figure 2-2.

Figure 2-2. A low-volume PM_{10} sampler.

2.2.1.2 PTFE FILTER

The low-volume PM_{10} samplers use polytetrafluoroethylene (PTFE) filters (Whatman Inc., Clifton, New Jersey) for PM_{10} collection. The membranes are manufactured under clean room conditions. The filter media is PTFE with a diameter of 46.2 mm and thickness of 40 µm. The filter media is encircled by a polypropylene support ring.

2.2.2 SAMPLING LOCATIONS

PM_{10} samples are collected at an upwind station and at a station on the feedlot property. The station on the feedlot property is within one of the confined pens in the center of the feedlot. This location is designed to serve as downwind sampling station to monitor the PM_{10} from the feedlot. Since the wind direction shift is beyond control, setting the sampling station in the middle of the feedlot ensure it is always in the PM_{10} emission plume regardless of the wind direction. This station is actually a scaffolding tower that is consisted of 4 height levels. The heights of the levels are 1.83 m, 3.75 m, 5.27 m, and 7.62 m from the pen surface. A low-volume PM_{10} sampler is placed at each level in order to investigate the relationship between the PM_{10} emission and the height. The scaffolding tower equipped with samplers is shown in Figure 2-3, and its location is shown in Figure 2-1.

Figure 2-3. The scaffolding tower for PM_{10} sampling.

There are two upwind stations. One was located on the north edge of the feedlot with 5 m to the closest pen. The other one is 880 m from the south of the feedlot. During the sampling period, one of the stations is selected base on the wind direction at that specific period to serve as upwind measurement. For the upwind stations, low-volume PM_{10} samplers are set 2-3 m above the ground. The locations of the upwind stations are shown in Figure 2-1 and the south upwind station is shown in Figure 2-4.

Figure 2-4. South upwind station for PM_{10} sampling.

2.2.3 SAMPLING PERIODS

The sampling campaigns has been conducted once a month for the following time: May, June, July, and November 2010; March, May, June, and July 2011. The campaigns were coordinated by Kansas State University and United States Department of Agriculture - Agricultural Research Service. An intensive 5-day continuous sampling was performed for each of those months. The whole 5-day period was broken down to shorter sampling runs. A run lasts usually 2-h if in the daytime, and 12-h if in the evening. A regular sampling schedule for one day is comprised of 7 runs. There are 6 runs in the daytime: 6 am - 8 am, 8 am - 10 am, 10 am - 12 pm, 12 pm - 2 pm, 2 pm - 4 pm, and 4 pm - 6 pm. The last run starts from 6 pm to 6 am in the next morning for overnight sampling. In cases of low concentration, such as raining events, the duration of runs was extended to collect more PM_{10} for mass measurement. The extension may vary from 4 to 24 hours and are depend on the weather conditions at the sampling period. For each run we used one clean PTFE filter per sampler.

2.3 SOURCE MATERIALS SAMPLING

Previous research conducted at this particular feedlot provided qualitative observations and indicated animal activity as the primary mechanism for PM10 emission (Razote, et al., 2007). The manure accumulated on the pen surface was trampled and grounded by the cattle movements into small particles, which could subsequently emit to the atmosphere particularly in dry condition. The unpaved roads and paths contribute heavy dust emission especially when the vehicles are operating on the road or the wind is strong. Feed processing in the open air, such as hay grinding, grain unloading, and fedd mixing, can produce feed dust at all sizes. Unpaved roads, pen surface, and feed are identified as potential sources of PM10 emission, and materials from the three sources were collected directly from the feedlot.

2.3.1 ROAD DUST

The roads that encompass the rectangle-shape feedlot were chosen to take the source materials from. From each side of the feedlot, a spot located approximately at the center of the road was selected, and a line was drawn across the road. Surface material of about 1 kg was then collected using a scoop along the line. The four samples were mixed together after collection and stored under room temperature.

2.3.2 PEN SURFACE

Fresh manure was collected from the pen surface for moisture content measurement. About 0.5 kg manure was sampled by a scoop and stored in a sealed plastic bag. After the measurement, the manure was used as source material from the pen surface.

2.3.3 FEED

Feeds were piled up outside the feed mill in large amounts. There are three types of feeds at the time of sampling. For every kind of feed, three independent samples were collected and then mixed and sealed in a plastic bag. These feeds were subsequently stored in the refrigerator under 5 ℃. Special attention was paid to collecting all available components for every feed material.

2.4 RAMAN MICROSCOPIC ANALYSIS

2.4.1 RAMAN INSTRUMENT

The Raman equipment used in this study is a Horiba Jobin Yvon LabRAM Aramis Raman spectrophotometer (HORIBA, Ltd., Tokyo, Japan). An Olympus BX41 microscope is implemented in the spectrometer to make microscopic observation of small-volume samples available. The microscope contains three objectives that have the magnification of 10×, 50×, and 100×, respectively. The instrument uses a Synapse charge-coupled device detector (HORIBA, Ltd., Tokyo, Japan). A helium-neon laser was used for excitation at 632.8 nm. The Raman apparatus was equipped with a motorized table that allowed fine movement in the x, y, and z directions by manual adjustment.

Before collecting the spectra for this study, a large amount of spectra (about 1000) were collected from both the source materials and particles on PTFE filters for test purpose, using different configurations set by the software LabSpec (HORIBA Ltd., Tokyo, Japan) incorporated in the instrument system. The tests included consideration of signal sensitivity to sample and time consumption. A set of configurations was then determined to use for all measurements to keep the spectra collection in a consistent manner while collected spectra were good for use.

Using LabSpec, all spectra were recorded over the range of 200 to 3500 cm^{-1} where all the observed sharp peaks showed, and then saved as ".spc" format. Because the spectra were treated as vectors in this study, a spectrograph grating of 1200 was set to achieve a resolution of 0.75 cm^{-1} for each spectrum, meaning the distance between two data points in the spectra was 0.75 cm^{-1} over the range of 200 to 3500 cm^{-1}. Lower values of grating result in low-resolution spectra that might contain insufficient variables for each spectrum while higher values took more time for the spectrum acquisition. Longer exposure time could lead to stronger signal from samples, and increasing the number of scans could decrease random baseline noise. Therefore, exposure time of 2 s, Real Time Display (RTD) exposure time of 1 s, and accumulation number of 10 were set to ensure a satisfied signal to noise ratio in a acceptable collection time.

2.4.2 SPECTRA COLLECTION

The Raman spectrometer was used to collect spectra from two major sample sets: the source materials and the particles on the PTFE filters from the low-volume PM_{10} samplers. All the samples were observed under the 50× objective.

2.4.2.1 SPECTRA COLLECTION FROM SOURCE MATERIALS

Collected source materials were processed to fine particles before the Raman measurement. Road dust was sufficiently mixed and sieved to the size of PM_{10}. Manure was dried at 105 ℃ for 12 to 16 h before being grounded and sieved to the same size. Every feed was mixed well and grinded to fine powder without sieving. For every processed material, a small amount fraction of the powder was placed on a clean PTFE filter to create a same background as the ambient PM_{10} trapped on PTFE filters. Subsequently, the filter was attached to a glass slide, which was fixed on the motorized table for microscopic observation. Raman spectra were recorded on a single particle basis. For road dust and manure, particles with diameter of 5 to 10 μm were selected for Raman spectrum acquisition, while particles with diameter of 5 to 20 μm were selected for feed materials.

2.4.2.2 SPECTRA COLLECTION FROM PM ON FILTER SAMPLES

Filter samples from the low-volume PM_{10} samplers were retained for Raman analysis after the mass net gain was measured for mass concentration calculation. Filter samples from sample periods of interest were chosen for source apportionment analysis. Selected filter was attached to a glass slide, which was then fixed on the motorized table.

Only particles with diameter of 5 to 10 μm were selected for spectrum collection on a single particle basis. Since the number of the PM_{10} particles on the filters was very large, it is unlikely to analyze every single one. Instead, a certain number of particles would be selected to represent the distribution of the PM_{10} on the whole filter. The number should be achievable considering the time consumption Raman analysis required. In this study, 30 particles were selected from every filter sample analyzed. The effectiveness of this amount for estimating the distribution would be discussed using the statistical method described in the last section of this chapter.

2.5 DATA ANALYSIS

2.5.1 SPECTRA TREATMENT

2.5.1.1 DESPIKING

The Raman apparatus uses a charge-coupled devices (CCD) detector, which can result in several noise sources. In this study we are more concerned about the spikes that might be occurring in the spectra. The spikes are sharp lines displayed in the spectra with a very small full width at half of maximum (up to 1 cm-1). The reason for the present of spikes is that CCD detectors are sensitive to cosmic rays. The cosmic ray events occurs when some particles, such as muons and other ionizing particles, provoke a charge that can reach up to several thousand electrons to a single element or over several adjacent elements of the CCD detector (Ehrentreich and Summchen, 2001; Hill and Rogalla, 1992).

The spiked observed in the spectra collection process will be removed for spectra calibration (Schut et al., 2002). In this study, spikes were removed using the tool called “remove spike” in LabSpec. The spike correction was conducted right after the spectrum acquisition, or whenever a spike was identified in collected spectra later on.

2.5.1.2 SPECTRA INTERPRETATION

Since Raman spectroscopy is capable of chemical characterization, attempts were made to investigate for the feasibility of interpreting chemical compositions from collected spectra. However, there was little research interest in the chemical characterization of spectra from source materials because they are well-known materials at the feedlot. More importantly, chemical composition was not necessary in the task of identification and quantification of sources in this work. Therefore, spectra interpretation regarding the chemical characterization was secondary and could be attempted if demand occurred, such as exploring a particle belonging to none of the identified sources.

In case of spectra interpretation, spectra would be first treated by baseline correction to subtract the background signal, in the hope of enhancing the Raman feature (Schut et al., 2002). This operation was performed in LabSpec with the functionality of “Baseline”. Parameters for the correction were set to meet the best interest of the targeted spectrum.

2.5.2 MULTIVARIATE STATISTICAL ANALYSIS

Raman spectra provide useful information regarding the material being analyzed by exhibiting the Raman shifts, or displayed as peaks, which are specific to chemical bonds and the structure of molecules. However, for large data set of spectra, visual observation was not practical for data treatment and processing.

As a matter of fact, each spectrum is a locus in a two-dimensional Euclidean space with intensity corresponding to a continuous frequency. Therefore, spectrum can be treated as a vector, with the frequency data point as variables that have specific values of intensity of the signal. In this study, all spectra were collected over the range of 200 to 3500 cm-1 with a resolution of 0.75 cm-1 using LabSpec. So each spectrum is treated as a multivariate observation of 4382 dimensions. Chemometric methods were employed to serve the purpose of categorizing unknown observations to one of the classes of well-known observations. In fact, chemometric methods were widely used and reported to be extremely effective for discrimination and classification of Raman spectrum data (Brody et al., 2001; Paradkar et al., 2002; Schut et al., 2002; Vandenabeele and Moens, 2003).

2.5.2.1 PRE-PROCESSING

The purposes of pre-processing were as following:

(1) Extracting the spectrum characteristic mathematically. Raman peaks in the spectra were frequency specific, which reflect the uniqueness of the spectra.

(2) Normalize all the spectra to a comparable level. Spectra were different in two ways. One is the special frequency at which the peaks show; the other is the intensity of the peaks. Two spectra recorded from the same material exhibit peaks at the same frequency, but the difference in intensity might be 100 times.

In this study, every spectrum was pre-processed before the application of any further analysis. The pre-processing was performed in the PLS toolbox 6.2 (Eigenvector Research, Inc., Wenatchee, Washington) that running in MATLAB 7 (The MathWorks, Inc., Natick, Massachusetts) environment.

The process was comprised of three steps. The first step was to perform the first order derivative. Taking the first order derivative of the spectra would preserve the uniqueness of the peak and at the same time minimize the effect of non-peak area. The following parameters were set in the tool box: Savitsky-Golay algorithm; filter width: 15; polynomial order: 2; derivative order: 1.

The second step was to normalize the data. Standard normal variate (SNV) scaling (scaling offset: 0) was used to remove multiplicative effect. The observation was processed to have zero mean and units of standard deviation:

$$I'_j = \frac{I_j - \mu}{\sigma} \qquad \text{Eq. 2-1}$$

where I'_i = the processed intensity; I_i = the original intensity; μ = the average intensity; σ = the standard deviation;

In the last step, two regions of the spectrum, 250 to 1800 cm^{-1} and 2600 to 3400 cm^{-1}, were kept and combined to represent the spectrum. The two regions were where Raman shifts are usually interpreted, and in this study, were the regions where spectra from source materials exhibited unique peaks. This step was coded in MATLAB when spectra were read as input for data analysis.

2.5.2.2 PRINCIPAL COMPONENT ANALYSIS

The observations are 4382 dimensional, which is a huge number of variables, and there was actually a lot of redundant information in one spectrum, especially those non-peak areas. It is desirable to reduce the number of variables. In addition, some statistical analysis requires less number of variables (Vandenabeele and Moens, 2003), such as linear discriminant analysis, which we would employ later on. Therefore, it is also practical to extract only useful information from the data.

Principal component analysis (PCA) is recommended to perform on a set of data prior to performing any other kinds of multivariate analyses (Johnson, 1998a). For a set of data that are n-dimensional, PCA creates a new n-dimensional space that each dimension, or axis, is orthogonal to the others. These new axes are called principal component axes and they are uncorrelated. The principal components (PCs) are in a decreasing order of importance in the sense that the first PC accounts for the maximal variance in the data set, and each succeeding PC accounts for as much of the remaining variance as is possible (Johnson, 1998a). Therefore, the first few PCs might have captured most of the variance over the data and can be select as new variables. The values in PCA space for the variables are called PC scores. The loadings are a matrix of weight used to transform the original data to scores.

For spectra data, PCA was expected to screen the difference between peaks positions, or shapes. The difference would be retained and reflected in PC space as scores. It was expected that the first few PCs could capture most (i.e. >90%) variance and be used for subsequent analyses. In this study, PCA was used prior to both cluster analysis and linear discriminant analysis independently. The implementation of PCA was in MATLAB environment using the commend “[COEFF, SCORE] = princomp (X)”. The complete file for running the coded program is in Appendix I.

2.5.2.3 CLUSTER ANALYSIS

The performance of cluster analysis (CA) is actually a process of measuring the similarity and dissimilarity between individual observations or between clusters of observations. The purpose is to group the observations in the sample according to their similarity. It is an unsupervised classification method because knowledge of the possibly existing classes is unknown prior to the analysis. There are two types of clustering methods: nonhierarchical clustering and hierarchical clustering (Johnson, 1998b). Hierarchical clustering was used for this work.

There are many clustering methods with different algorithms available for hierarchical clustering. In this study, Ward’s minimum variance method was applied. This method defines the distance between two clusters as the square of the distance between the cluster means divided by the sum of the reciprocals of the number of points within each cluster (Johnson, 1998b).

Hierarchical cluster analysis was used to investigate the possible groups present within one set of data of a particular source material. Since the materials were all heterogeneous, it was anticipated that one material was consisted of several groups. The implementation of CA is performed in MATLAB using the PLS toolbox. The Ward’s method was selected for all the source data.

2.5.2.4 LINEAR DISCRIMINANT ANALYSIS

Unlike cluster analysis, linear discriminant analysis (LDA) is a supervised classification method. It requires a data set of well-known classes available before the analysis. This data set is also called training group and it will be used to make rules for classification of unknown observations. LDA is designed to create linear functions, which can best separate the classes in the training group. The linear functions are found by maximizing the ratio of the between-group variance to the within-group variance (Vandenabeele and Moens, 2003). The criterion of observations being one of the classes is made and compared to when an unknown observation is projected to that function and determined which class it belongs to.

In this work, spectra from PM10 sampled from ambient air were treated as unknown observations and put into LDA with the training group consisted of spectra from identified source materials. In this manner, unknown particle could be categorized to be from one of the sources. LDA was implemented in MATLAB using the command “[class, err] = classify (…)”. The complete file for running the coded program is in Appendix I.

2.5.2.5 STATISTICAL MODEL

A statistical model was built for analysis of the pre-processed spectra data. This model is consisted of two parts with applications of principal component analysis, hierarchical cluster analysis, and linear discriminant analysis. The model served to classify spectra of PM_{10} collected from ambient air to one of the identified sources at the feedlot, or to unidentified sources.

The first part was the training group construction. The source materials was treated by the following procedure on a one-by-one basis:

(1-1) Collect about 200 spectra from material of one source.

(1-2) Eliminate the obvious outliers by visual inspection. The outliers were those exhibiting large distinction from the majority of the spectra.

(1-3) Pre-process the remaining spectra.

(1-4) Perform principle component analysis on the pre-processed data.

(1-5) Retain the first few principal components that capture more than 90% variance for cluster analysis.

(1-6) Apply hierarchical cluster analysis with scores of the retained PCs as input.

(1-7) Investigate the possible classification resulted from the CA. PCA and visual inspection may help.

(1-8) Designate every spectrum as one class (in case of one class), or as one of the classes (in case of more than one class) identified by CA.

Repeated this procedure for every source material. Eventually, every spectrum was designated to a specific class. All of the spectra were then combined to one data set, which was the constructed training group with every spectrum well known by its class. This ended the first part of the model.

The second part was classification of unknown spectra. Spectra recorded from PM_{10} were classified by the following procedure:

(2-1) Classify the spectra as from unidentified source if they are obviously different from any class in the training group, and this completes the classification. If not the case, proceed to the next step.

(2-2) Perform principle component analysis for on training group (pre-processed spectra).

(2-3) Select the first few PCs that capture more than 90% variance (preferable more than 95%).

(2-4) Retain the loadings for the selected PCs.

(2-5) Multiply the unknown spectra by the loadings to get scores on PC space.

(2-6) Apply linear discriminant analysis with the training group on the scores for the classification.

This completed the procedure for classification of unknown spectra.

Instead of giving an indication, LDA classified the spectrum that in fact belonged to none of the classes in the training group as one of them. Therefore visual inspection was applied to address this in case of the particle came from an unknown source. Using the model for classification of an unknown spectrum, the result could only be either of the two cases: it is an observation belonged to one of the identified sources, or it is an observation belonged to unknown source. No further classification was provided for unknown sources in this study.

2.5.3 STATISTICAL JUSTIFICATION

Since only 30 particles were selected to estimate the distribution of particles types for one filter, we needed to justify 30 was statistically sufficient or not to represent the distribution on the entire filter. It was also possible that a number less than 30 was enough. This problem was addressed by simulation.

Data collected from each of several filters across a 2-day period was analyzed in the simulation process. Particles were classified into 4 categories, which were ‘Road Dust’, ‘Pen Surface’, ‘Feeds’, and ‘Unidentified’. The observed distribution of the 30 particles was assumed to represent the true particle distribution for that filter. For each filter, the 30 particles were sampled, one at a time, replacing the sampled particle before sampling the next one. This resampling procedure was conducted using several sample sizes, such as 10, 15, 20, and 25. A large number of samples (e.g. 200 or more) were taken from the 30 particles for a particular filter. The particle distribution of each sample was statistically compared to the ‘true’ particle distribution observed for the 30 particles processed for that filter.

A method of proportion difference was used to test if the particle distribution calculated from a sample of a given number of particles was statistically distinguishable from the ‘true’ particle distribution observed for the 30 particles processed for that filter. For each sample, the proportion of each particle type was calculated. Then, for each particle type, the difference between the proportion of that particle type in the sample and in the ‘true’ distribution was calculated. A largest acceptable difference (δ) was specified and the absolute proportion difference for the 4 particle types was compared to δ. If any of the 4 particle types exhibited a larger proportion difference between the sample and ‘true’, the current sample was labeled as being statistically distinguishable from the ‘true’ particle distribution. For example, if δ was specified as 2.5%, the proportion of a particle type in the sample could be

2.5% below or 2.5% above the proportion of that particle type observed in the ‘true’ distribution, and that specific sample was counted as having a particle distribution not statistically distinguishable from the ‘true’ particle type distribution. The sample and ‘true’ particle type distributions were calculated using SAS PROC FREQ (SAS Institute Inc., Cary, North Carolina) and the observed counts of each particle type.

For each sample size, the number of the samples for which the sample particle distribution was statistically indistinguishable from the ‘true’ particle distribution was an estimate of the statistical power for particle distributions based on samples of that size. The smallest sample size that produces a satisfactory statistical power for being indistinguishable from the ‘true’ particle distribution will be the minimum number of particles recommended for processing from each filter.

CHAPTER 3: UTILIZING RAMAN MICROSCOPY TO IDENTIFY SOURCES OF PM10 DOWNWIND OF AGRICULTURAL OPERATIONS

PAPER TO BE SUBMITTED TO ATMOSPHERIC ENVIRONMENT

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ABSTRACT

Emission of particulate matter (PM) from animal feeding operations (AFOs) poses a potential threat to the health of human and livestock. Current efforts to characterize PM emissions from AFOs generally examine variations in mass concentration and particle size distributions over time and space, but these methods do not provide information on the sources of the PM captured. Raman microscopy was employed in an innovative manner to quantify the contributions of source materials to PM_{10} emitted from a large cattle feedlot. Raman spectra from potential source materials (dust from unpaved roads, manure from pen surface, and cattle feeds) were first compiled to create a spectral library. Cluster analysis was used to classify the source library spectra into specific groups, and multivariate statistical analysis method was developed to identify the source of particles collected on PM_{10} sample filters. Cross validation of the model resulted in 99.76% correct classification of the model spectra. Source characterization results from samples collected at the cattle feedlot over a two-day period indicate that materials from the cattle pen surface contributed an average of 78% of the total PM_{10} particles, and unpaved roads accounted for an average of 19%. The proposed method exhibited potential to accurately estimate the fractions of PM_{10} sources at different conditions.

KEYWORDS

Particulate matter, Raman microscopy, multivariate statistical analysis, agriculture, source apportionment

3.1 INTRODUCTION

Activities related to agricultural production inherently generate gaseous and particulate emissions to the atmosphere. Large animal feeding operations (AFOs) can emit significant quantities of pollutants to the atmosphere such as ammonia, hydrogen sulfide, volatile organic compounds including odorous gases, along with fugitive dust (Blunden and Aneja, 2008; Cambra-López et al., 2010; Howard et al., 2010; Trabue et al., 2011). Fugitive dust contains particulate matter (PM) of different size classes. Particles of an aerodynamic diameter of <10 µm are often classified as PM10. Inhalable course particles are generally classified as between 10 and 2.5 µm, PM10-2.5, and fine particles are less than 2.5 µm (PM2.5). Decades of research has shown that exposure to particulate pollution can lead to health problems such as asthma, lung cancer, and cardiovascular issue (Knaapen et al., 2004; Li et al., 2008; McEntee and Ogneva-himmelberger, 2008; Pope et al., 2002; Riediker et al., 2004; Yeatts et al., 2007). PM generated from AFOs carries bacterial, fugal, and endotoxin, and may cause various respiratory problems in livestock as well as humans (Dungan et al., 2011; Macvean et al., 1986; Purdy et al., 2004). Dust and odor emissions generally have the greatest impact on local air quality while other pollutants like ammonia and reactive volatile organic compounds can influence regional air quality (National Research Council, 2003).

Results from emissions measurements of multiple air pollutants, including PM, from AFOs are now becoming available from the U.S. EPA National Air Emissions Monitoring Study of approximately 20 different AFOs over 2 years (US EPA, 2011j). A number of recent studies have also found significant PM10 emission from AFOs (Bunton et al., 2007; Cai et al., 2006; Cambra-Lopez et al., 2010; Fabbri et al., 2007; Guo et al., 2011; Purdy et al., 2010; Redwine et al., 2002). Concerns over emissions from these large animal operations may lead to increased state or federal regulations for producers. While the Natural Resources Conservation Service has already developed a number of conservation practices that farmers can use to reduce negative impacts on air quality (NRCS, 2011), it is likely new practices will be required and improvements in existing practices will be needed. A number of studies have concentrated on the development of methodologies and instrumentation to quantify PM concentrations and particle size distributions at AFOs (Bonifacio et al., 2011; Buser et al., 2007; Buser et al., 2008; Guo et al., 2009; Wanjura et al., 2005). However, little information is currently available on PM emission source apportionment, which is needed to improve environmental and agronomic practices for emissions control and management.

In the San Joaquin Valley Fugitive Dust Characterization Study, surface soil samples were collected and analyzed by gas chromatography-mass spectrometry (GC-MS) to identify distinctive molecular marker compounds (Rogge et al., 2006). In another study in San Joaquin Valley, six types of geological dust, including those from feedlot surface, were collected and chemically analyzed by X-ray fluorescence, ion chromatography, automated colorimetry, atomic absorption spectrophotometry, and thermal analysis (Chow et al., 2003). Both studies focused only on the construction of PM source profiles, but they did not address analysis of PM from ambient air.

No standard methods exist to quantify the distribution of sources in downwind PM10 samples. Lange et al. (2009) proposed a method using neutron activation analysis results combined with multivariate statistical analyses and EPA's Chemical Mass Balance model to estimate the fraction of PM from a cattle feedlot. The method involved complicated sample pre-treatment and was destructive to samples because PM was removed from filters used for sampling.

Raman microscopy is a powerful technique for chemical analysis. Combined with an optical microscope, Raman can be used to obtain spectral information from a very small sample, and therefore has the potential to analyze single atmospheric particles. Scientists have used Raman to collect spectra from ambient air particles, including carbonaceous PM, diesel soot, humic-like substances, and inorganic compounds aerosols (Escribano et al., 2001; Ivleva et al., 2007; Sadezky et al., 2005; Sze et al., 2001). Hiranuma et al. (2011) utilized Raman microscopy to characterize the chemical composition of particles emitted from an open cattle feedlot, indicating its use in the present study (Hiranuma et al., 2011).

In this project, a series of intensive field air sampling campaigns have been conducted under different meteorological conditions at a large commercial cattle feedlot in Kansas. The project is designed to develop accurate and simultaneous emission data of PM, selected volatile organic compounds, and greenhouse gases for a large cattle feedlot. Previous research findings at this site have provided qualitative observations and indicated animal activity as the primary mechanism for PM emission from the cattle feedlot (Razote, et al., 2007). The unpaved roads within and around the facility and outdoor feed processing are other potential sources of dust.

The objective of this portion of the larger project was to develop a method to accurately determine the source profile of PM10 particles emitted from a cattle feedlot. A Raman spectral library of potential source materials was collected, and a multivariate statistical analysis method was developed to identify the source of particles collected on PM10 sample filters. Source profile results are presented from PM10 sample filters collected approximately every 2 hours over a hot, dry, windy 2-day period in July 2011 and are compared with results from samples collected in March 2011 after a rain event. Results suggest this approach could be a useful tool for determining the strength of different PM sources from AFOs or other agricultural operations under different environmental conditions or under different management practices.

3.2 MATERIALS AND METHODS

3.2.1 PM10 AND SOURCE MATERIALS SAMPLING

Surrounded by agricultural fields, the feedlot is located at Kansas with a total area of approximately 850000 m^2 and a capacity of 30,000 head of cattle. Unpaved roads encircle and go across the feedlot in a grid pattern and make up around 25% of the total area. Feed trucks deliver feed to the pens three times a day from a feed mill, which is located at the southwest corner of the feedlot. The feed is processed and mixed continuously, and is loaded by an overhead truck loader outside the mill. The soil at the feedlot is generally sandy soil. Manure scraping is carried out two or three times a year, and manure is harvested at least once a year from every pen. Annual average precipitation is approximately 488 mm (2010) and prevailing wind directions were south-southeast in summer and north-northwest in winter. Averaged wind speed was 16 kph throughout the year of 2010. The producer utilizes water sprinkling of the pens for dust control.

Intensive 5-day sampling campaigns were conducted monthly from May 2010 to July 2010, and then during November 2010, March 2011, and finally May 2011 to July 2011. For each day of the campaign, 2-h PM samples were collected from 6 am to 6 pm and then over 12 h from 6 pm to 6 am. In cases of low concentration, such as raining events, the duration was extended to 4 to 24 h to increase PM_{10} mass on the filters. Samples were collected at an upwind station and at a station on the feedlot property to ensure samples were always collected in the plume despite the wind direction. The sampling tower within the feedlot consisted of 4 levels with heights of 1.83 m, 3.75 m, 5.27 m, and 7.62 m, respectively. At each level, a low-volume PM_{10} sampler (2100 Mini-Partisol, Thermo fisher Scientific, Franklin, Massachusetts) was used to collect particles through a PM10 size-selective inlet. The same type of samplers was set up at two upwind sites. One was located on the north edge of the feedlot within 5 m of the closest pen. The other was 880 m from the south of the feedlot. Samples for upwind were selected depending on the wind direction. PTFE filters (Whatman Inc., Clifton, New Jersey) with diameter of 46.2 mm were used in the samplers for mass concentration measurements. These filters were used for Raman microscopic analysis in the present study after mass concentration measurement.

Materials from potential sources were collected directly from the feedlot at the time of air sampling in order to build up a library for PM_{10} sources. The collected materials were manure from the pen surface, road dust from the unpaved road surface, and three different kinds of feeds piled outside the feed mill.

3.2.2 RAMAN MICROSCOPY AND SPECTRUM COLLECTION

A Horiba Jobin Yvon LabRAM Aramis Raman spectrophotometer (HORIBA, Ltd., Tokyo, Japan) equipped with an Olympus BX41 microscope and a charge-coupled device detector was used to collect spectra from single PM_{10} particles on the filters and from source materials. PM_{10} particles were observed under the 50× objective and particles with diameter of 5 to 10 μm were selected for analysis. A helium-neon laser was used for excitation at 632.8 nm. For all measurements, a spectrograph grating of 1200, exposure time of 2 s, Real Time Display (RTD) exposure time of 1s, and an accumulation number of 10 were used. All spectra were recorded over the range of 200 to 3500 cm^{-1} with a resolution of 0.75 cm^{-1} using LabSpec (HORIBA Ltd., Tokyo, Japan).

Collected sources materials were processed to fine particles and subsequently placed on clean PTFE filters for Raman measurement. Manure was dried at 105 ℃ for 12 to 16 h before being grounded and sieved to PM10 size. Road dust was also sieved to the same size. Each feed was mixed well and grinded to fine powder without sieving. Every processed material was observed under the 50×objective. Particles with diameter of 5 to 10 μm were selected from manure and road dust particles for spectra acquisition. For feed materials, the size range was 5 to 20 μm.

3.2.3 SPECTRUM DATA ANALYSIS

Chemometric methods were reported to be effective for discrimination and classification of Raman spectrum data in different disciplines from agriculture to medicine (Brody et al., 2001; Paradkar et al., 2002; Schut et al., 2002; Vandenabeele and Moens, 2003). Three multivariate statistical analyses were employed and combined to serve the purpose of classifications of spectra in this study. Principle component analysis (PCA) was performed as a data extraction method to reduce the number of variables for spectral data. Cluster analysis (CA) was used for investigation of possible classes present within one source material. Linear discriminant analysis (LDA) was applied to classify an unknown spectrum to one of the well-defined classes, or to unidentified sources.

All the spectra were despiked using LabSpec software. Before any statistical analysis, every spectrum was pre-processed in the PLS toolbox 6.2 (Eigenvector Research, Inc., Wenatchee, Washington) in MATLAB 7 (The MathWorks, Inc., Natick, Massachusetts) environment for differentiation and normalization. Hierarchical cluster analysis was performed using PLS toolbox with Ward’s method (Johnson, 1998b) as algorithm. Principal Component Analysis and Linear Discriminant Analysis were coded in MATLAB.

After taking the first derivative (Savitsky-Golay algorithm, filter width: 15, polynomial order: 2, derivative order: 1), each spectrum was normalized by Standard normal variate (SNV) scaling (scaling offset: 0) to remove multiplicative effect. Subsequently, two regions of the spectrum, 250 to 1800 cm-1 and 2600 to 3400 cm-1, were kept and combined to represent the spectrum. This procedure was called pre-processing and it was applied before the performance of any multivariate statistical analyses in the present study.

3.2.4 FILTER SAMPLES ANALYSIS

Particles on the filter samples were selected and classified on a one-by-one basis in the hope of quantifying the source contribution to the PM emission from the feedlot. It is not practical to collect spectrum from every single particle on the PTFE filters due to the large number of the particles. Instead, a certain small number of particles were selected for analysis. Simulation was performed to justify the selected number was statistically sufficient for estimation of PM distribution on a filter.

The observed distribution of the selected particles was assumed to represent the ‘true’ particle distribution for that filter. For every filter, the selected particles were resampled, one at a time, replacing the sampled particle before sampling the next one. This resampling procedure was conducted using several sample sizes smaller than the number of selected particles. A large number of samples were taken from the particles with the particular sample size chosen. The particle distribution of each sample was statistically compared to the ‘true’ particle distribution for that filter. The comparison was conducted using a method of proportion difference. For each sample, the difference between the proportion of each particle type in the sample and in the ‘true’ distribution was calculated. A largest acceptable difference (δ) was specified and the absolute proportion difference for the each particle type was compared to δ. If any of the particle types exhibited an absolute proportion difference larger than δ between the sample and ‘true’, the current sample was labeled as being statistically distinguishable from the ‘true’ particle distribution.

For each sample size, the number of the samples for which the sample particle distribution was statistically indistinguishable from the ‘true’ particle distribution was an estimate of the statistical power for particle distributions based on samples of that size. The smallest sample size that produces a satisfactory statistical power for being indistinguishable from the ‘true’ particle distribution will be the minimum number of particles recommended for processing from each filter. The simulation was performed using SAS PROC FREQ (SAS Institute, Inc., Cary, North Carolina).

3.3 RESULTS AND DISCUSSION

3.3.1 RAMAN SPECTRA OF SOURCE MATERIALS

Five source materials were collected from the feedlot and designated as Road Dust, Pen Surface, Feed 1, Feed 2, and Feed 3. For each of these five materials 210 Raman spectra were measured. Obvious outliers and spectra representing other materials were removed from further analysis by visual inspection. Observation of multiple types of spectra occurred within one material group was due to the heterogeneous nature of the source materials.

Cluster analysis was used to identify possible classes within each group of source spectra. Initially, principle component analysis was performed on pre-processed to reduce the number of variables. For the 198 spectra from Road Dust group, PCA was applied and 93.6% of the variance was captured in the first 6 PCs, which were retained for cluster analysis. Hierarchical cluster analysis was performed with the scores on the 6 PCs of the 198 spectra as input. Figure 3-1 shows the dendrogram from cluster analysis and three clusters (as colored in red, green, and blue) can be distinguished with large distance values between each other. Visual observation also suggested that there were three types of spectra within Road Dust group with unique sharp Raman peaks at specific wavenumbers (Figure 3-3). Three classes were designated as Road Dust I with Raman peak at 1081 cm-1, Road Dust II with peak at 458 cm-1, and Road Dust III with peaks at 471 cm-1 and 507 cm-1. Every spectrum from the Road Dust group was then categorized as one of these three types.

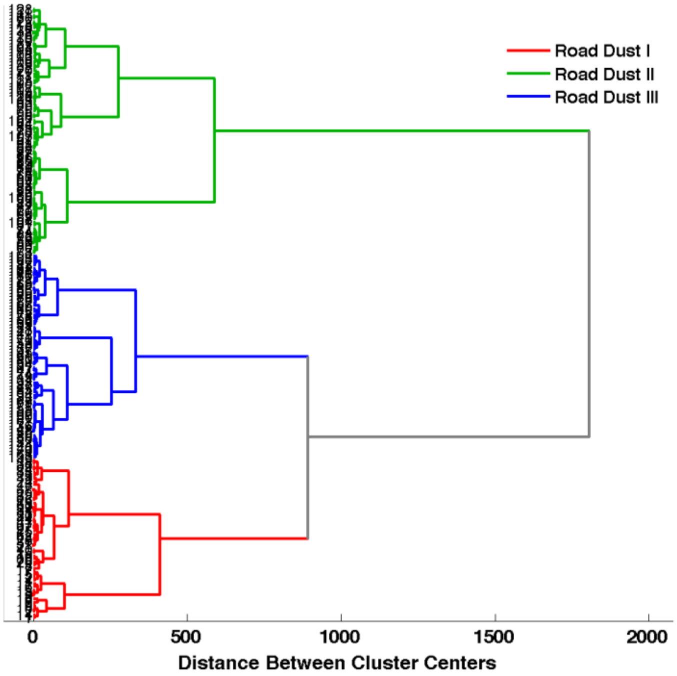

Figure 3-1: Dendrogram resulting from the hierarchical cluster analysis of 198 Raman spectra of road dust material. Three different clusters with large distances between each other are colored in red, green, and blue.

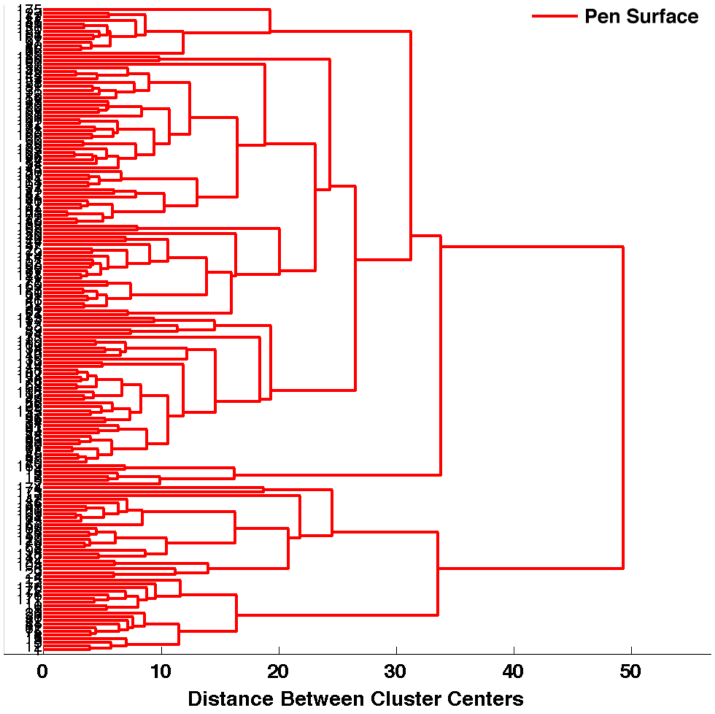

Figure 3-2: Dendrogram resulting from the hierarchical cluster analysis of 175 Raman spectra of pen surface material. No distinct clusters separated from each other.

The PCA-CA process was performed on the other source materials to identify and designate specific classes for the spectra. In PCA on each of the source material, the first few PCs that accounted more than 90% variance were selected for cluster analysis. For the pen surface material, the first 15 PCs only accounted for 44% of the total variance and cluster analysis with scores of the 15 PCs yielded a poorly separated clusters as shown in Figure 3-2. Furthermore, visual observation found no distinct difference between the 175 spectra. These all suggested that there were no different classes within the pen surface. For feed 1 and feed 2 materials, two classes were found within each of the groups, while feed 3 showed no classification as pen surface material. Therefore, 9 classes were identified and every spectrum from source materials was designated to a specific class. Typical spectra from these 9 classes are shown in Figure 3-3.

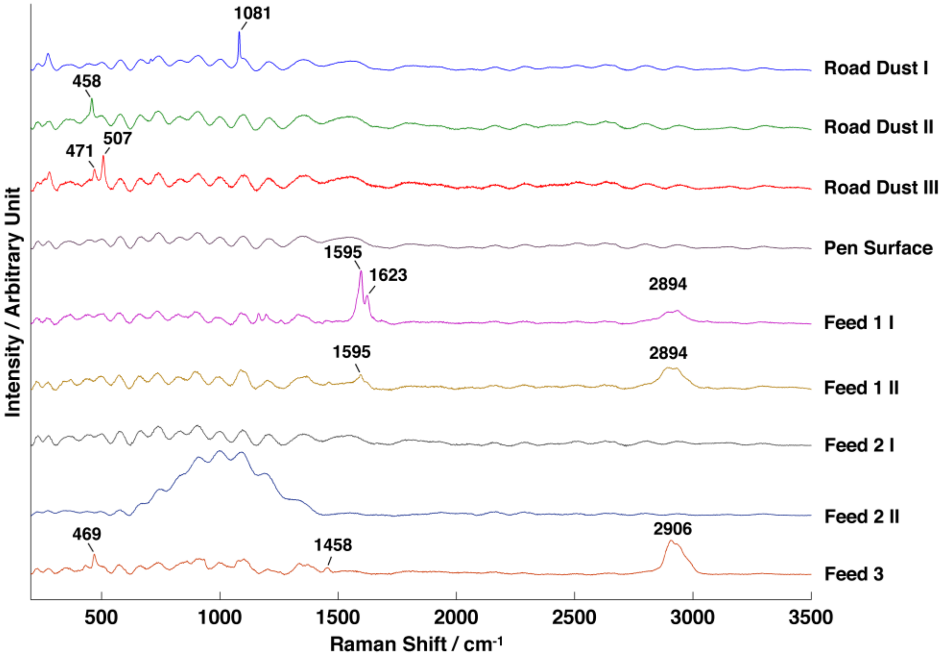

Figure 3-3: Raman spectra of all designated classes from identified source materials. Baseline correction is performed to enhance the Raman feature. Markers for different classes are labeled.

PCA and visual inspection indicated that two classes, Pen Surface and Feed 2 I, were identical in Raman spectra. The reason for this observation might be that the manure material contained the undigested Feed 2 I. Since we know that manure is far more abundant on the feedlot surface than any one type of feed, Feed 2 I was excluded from further analysis. Except for these two classes, unique peaks or region were observed for all the other classes and were designated as markers. Designated markers and their Raman assignment are summarized in Table 3-1.

Table 3-1: Markers for different source classes and Raman assignment.

Source Classes	**Markers as Raman Shift / cm^{-1}**	**Compounds**
Road Dust I	1081	Calcium carbonate[a]
Road Dust II	458	Quartz[b]
Road Dust III	471 507	Si-O-Si or Si-O-Al bend/stretch[c]
Pen	-	-
Feed 1 I	1595 1623 2894	Lignin[d]
Feed 1 II	1595 2894	Lignin[d]
Feed 2 I	-	-
Feed 2 II	~700 to ~1300	-
Feed 3	469 1458 2906	Skeletal modes of pyranose ring[e,f] CH_2 bending[e] C-H stretching[e]

[a] on the basis of Hiranuma et al. (2011)
[b] on the basis of Hope et al. (2001)
[c] on the basis of Mernagh (1991)
[d] on the basis of Kihara et al. (2002)
[e] on the basis of Kizil et al. (2002)
[f] on the basis of Cael et al. (1973)

3.3.2 CLASSIFICATION OF UNKNOWN SPECTRA

Linear discriminant analysis (LDA) served to classify unknown spectra with respect to the identified sources as a supervised classification method. LDA method was accomplished using a training group comprised of all the source material spectra classified in the PCA-CA process. The resulting training group was consisted of 899 spectra from 8 classes (with Feed 2 I excluded since it could not be distinguished from Pen Surface and was insignificant).

PCA was performed again on all the pre-processed spectra in the training group and the first 11 PCs were selected, representing 95.02% of the total variance in the training group data set. The scores on the 11 PCs were retained as input for the LDA. The projections of the training group spectra in selected linear discriminant (LD) spaces are shown in Figure 3-4 (Figure 3-5 shows 3-D views). Spectra for every class assembled and, except for Pen Surface class, separated from all the other classes in the figure. It could be concluded that spectra for Pen Surface class also gather at a unique space and thus all the 8 classes could be clearly distinguished. The performance of LDA in MATLAB returned an estimate error rate of 0.0024 from internal validation, which means the correct classifications of the training group spectra was 99.76%.

To identify the class of an unknown spectrum with LDA, it was pre-processed and transformed by the loadings from the PCA for the training group and the scores on the first 11 PCs were kept as input to the LDA. The LDA was performed using the *'classify'* commend in MATLAB with linear as *'type'* and equal prior probabilities.

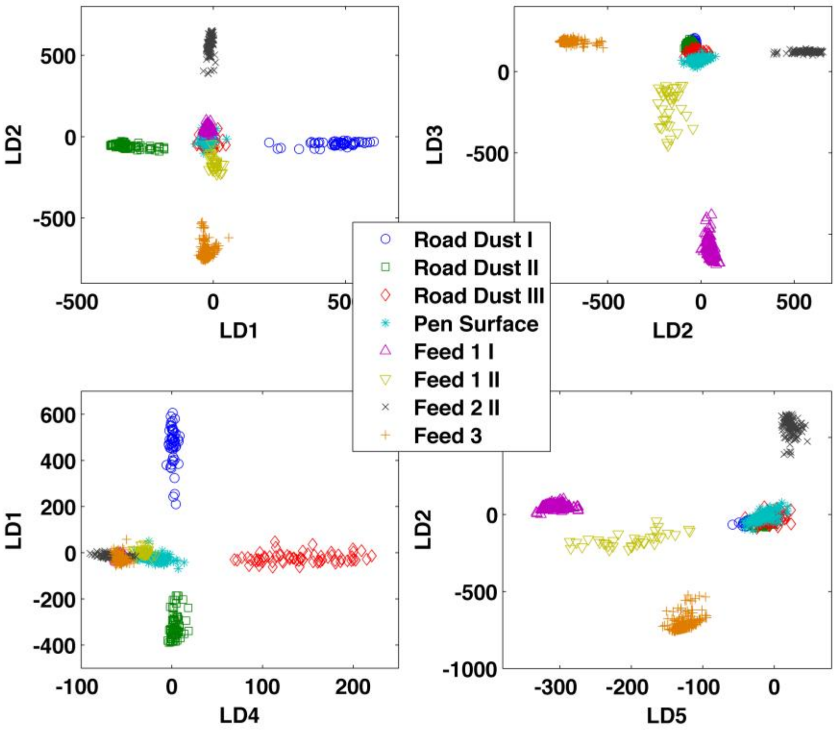

Figure 3-4: Projections of 899 spectra of training group in selected LD spaces.

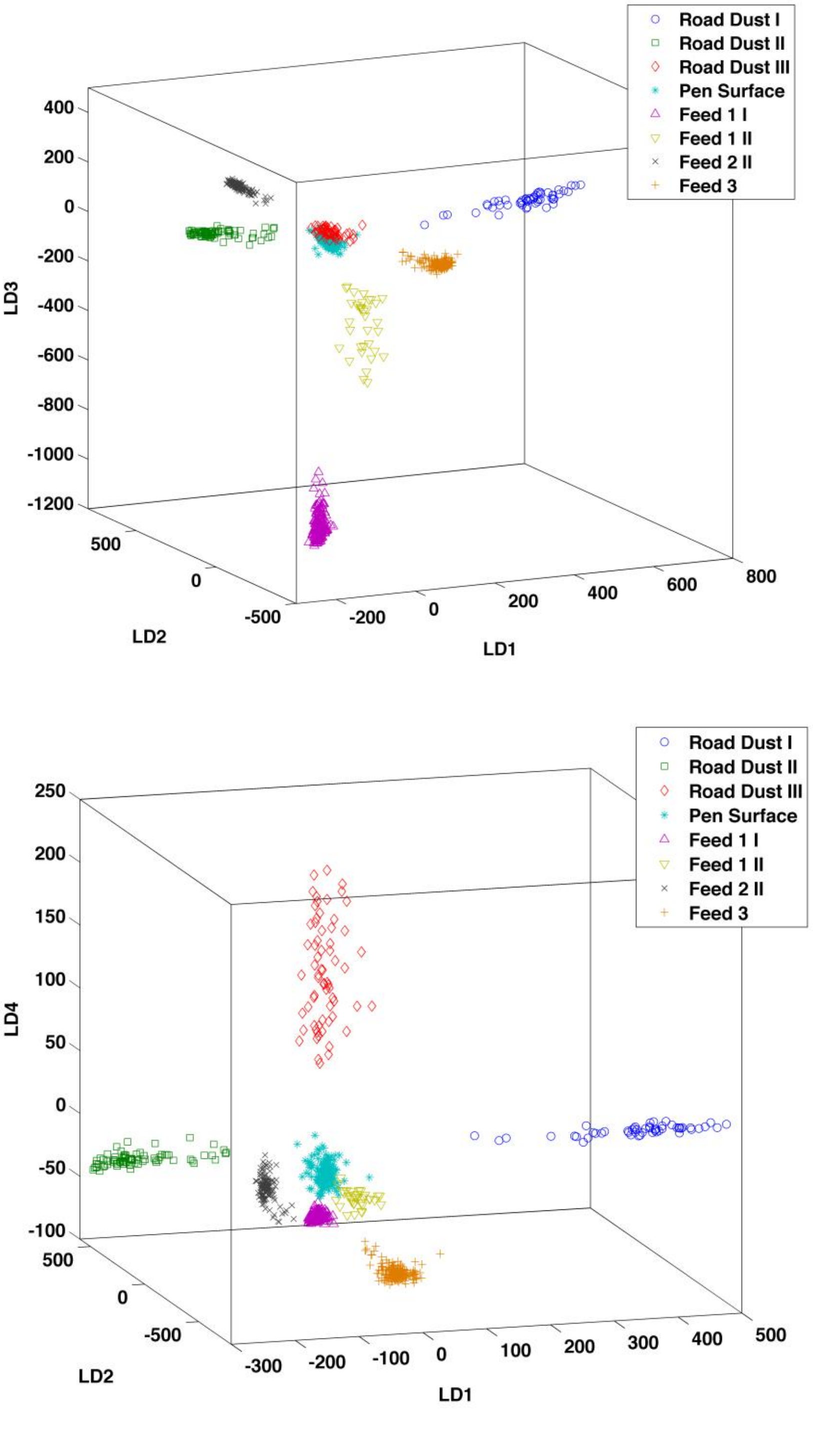

Figure 3-5: 3-D views for 899 spectra of training group in selected LD spaces.

3.3.3 PM SOURCE PROFILES

Two consecutive days, July 13th and 14th 2011, were selected to represent regular days in the summer time with temperature range of 20 to 38 ℃ and wind speed of about 5 mps. Two sampling runs from March 2011 were chosen to represent time period under rainy weather. They were selected because there were sufficient data available. PM_{10} mass concentrations and the environment conditions for these time periods are shown in Figure 3-6. The mass concentration data for some time periods are not reported due to one or some of four reasons: (1) wind direction was not due north or south 80% of the sampling time; (2) negative values (not enough measurable amount of dust collected); (3) upwind samplers were place in wrong location; and (4) visual inspection showed large particles on filters for PM_{10}. For the 2-day period, PM_{10} concentrations at the feedlot were significantly higher than the upwind level, indicating a large emission from the feedlot. Raining weather had obvious inhibition on the PM_{10} emission. For both selected time periods, temperature and relative humidity fluctuated in a consistent manner while wind speed showed no large variability. Relative humidity nicely followed an opposite trend of temperature.

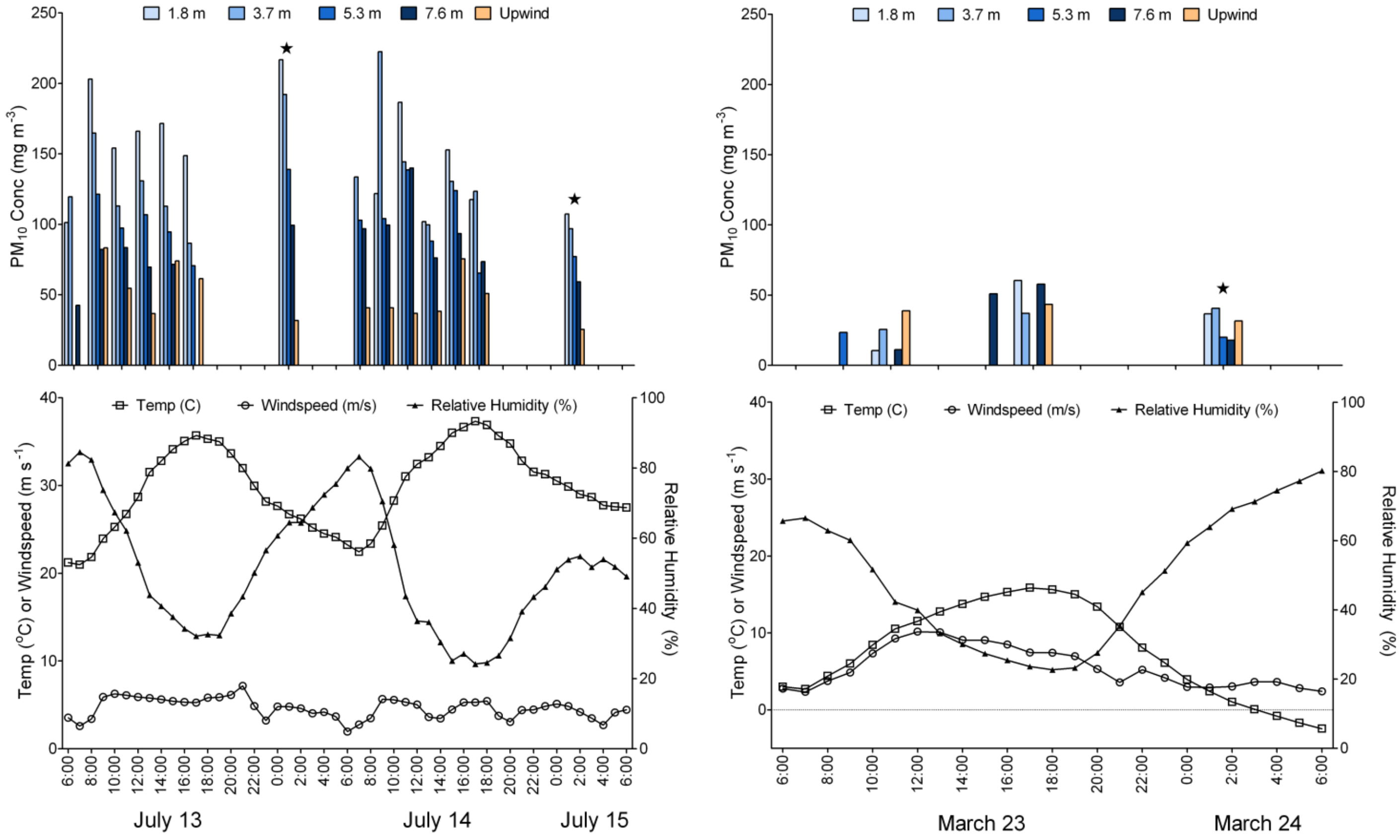

Figure 3-6: PM$_{10}$ mass concentration, ambient temperature, wind speed, and relative humidity data for July 13 and 14, and March 22 and 24.

For these two time periods, filter samples from the level 2 and level 4 of the sampling tower and the upwind station were analyzed. From every filter, 30 particles were randomly selected and classified by the PCA-LDA model. Since Linear Discriminant Analysis is unable to detect observations that do not belong to any class in the training group, these observations are classified as unidentified by visual inspection. All the analyzed particles were eventually classified as one of the four classes, which were Road Dust, Pen Surface, Feeds, and Other. Fractions of these four classes from the filter samples were shown in Figure 3-7.

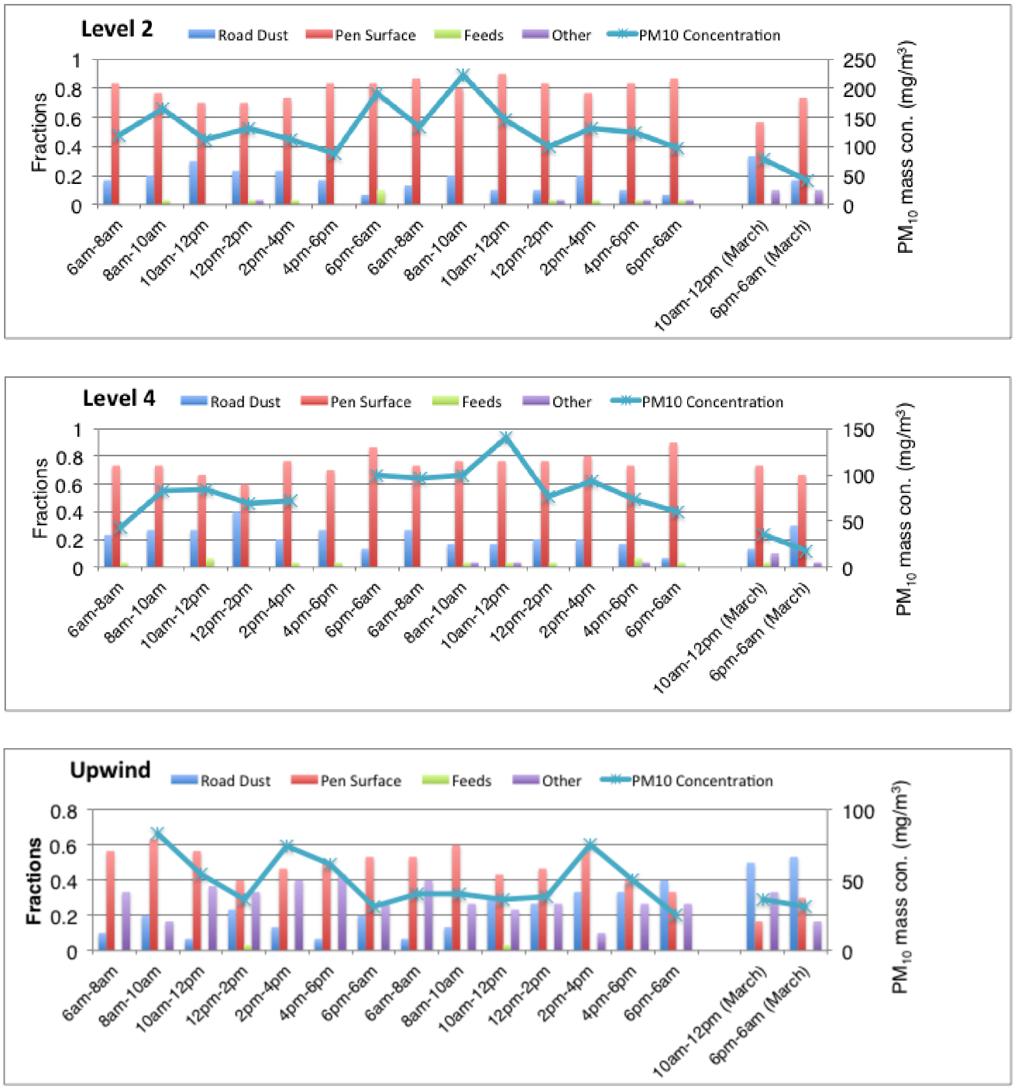

Figure 3-7: Fractions of sources for PM_{10} emission on July 13 and 14, and on March 22 and 23 (Labeled). PM_{10} mass concentrations are also plotted in the same time periods.

For the 14 runs in July, PM_{10} from Pen Surface accounted for the majority of the total amount from the cattle feedlot. The fractions of Pen Surface were 0.80 ±0.06 for Level 2 and 0.75 ±0.07 for Level 4 in July 13 and 14. During these two days, the fractions of Road Dust were 0.16 ± 0.07 for Level 2 and 0.21 ± 0.08 for Level 4. The significant standard deviation suggested that fractions of different sources varied in different time periods. The Pen Surface contributed the most from 6 pm to 6 am the next day due to more active behavior of cattle in the early evening and the lower moisture content resulted from daytime evaporation. During the daytime, Road Dust fractions were higher because of the operating vehicles travelling around for feed delivery or feedlot maintenances. Feed and Unidentified sources fractions were insignificant compared to the other sources with average of 0.02 and 0.01 for Level 2, and 0.03 and 0.01 for Level 4, respectively. It appeared that fraction of Road Dust was higher and Pen Surface was lower at Level 4 than Level 2 (t-test, α=5%), suggesting potential difference in PM_{10} distribution at different heights. The reason might be that wind brought in road dust at a relatively higher level in the plume from unpaved roads at upwind location. Samples from upwind station showed a significant fraction of 0.29 ± 0.09 for Other. They also exhibited a lower fraction of 0.50 ± 0.09 for Pen Surface and a similar fraction of 0.20 ± 0.11 for Road Dust compared with Level 4 (t-test, α=5%). This was consistent with the fact that upwind station was also exposed to unpaved road but away from the feedlot.

A box plot is shown in Figure 3-8 for this time period. Apparently, fractions of Pen Surface are much higher at the feedlot than the upwind location, where presented a distinctly large fraction of Other. Although t-test showed that fractions of Pen Surface and Road Dust were different between level 2 and level 4, they appear comparable in the box plot. More filters need to be analyzed to further investigate this issue. For the upwind station, fractions of Road Dust, Pen Surface, and Other exhibit large variability, indicating unpredictability of PM_{10} distribution at the upwind.

Samples from the 2 runs for rain event showed a small increase of the Other in the feedlot. At the upwind location, the Other showed similar values compared with the sampling tower, while the Pen Surface dropped dramatically and compensated with a larger fractions of Road Dust, indicating the effectiveness of moisture conditions on the PM emission from the pen.

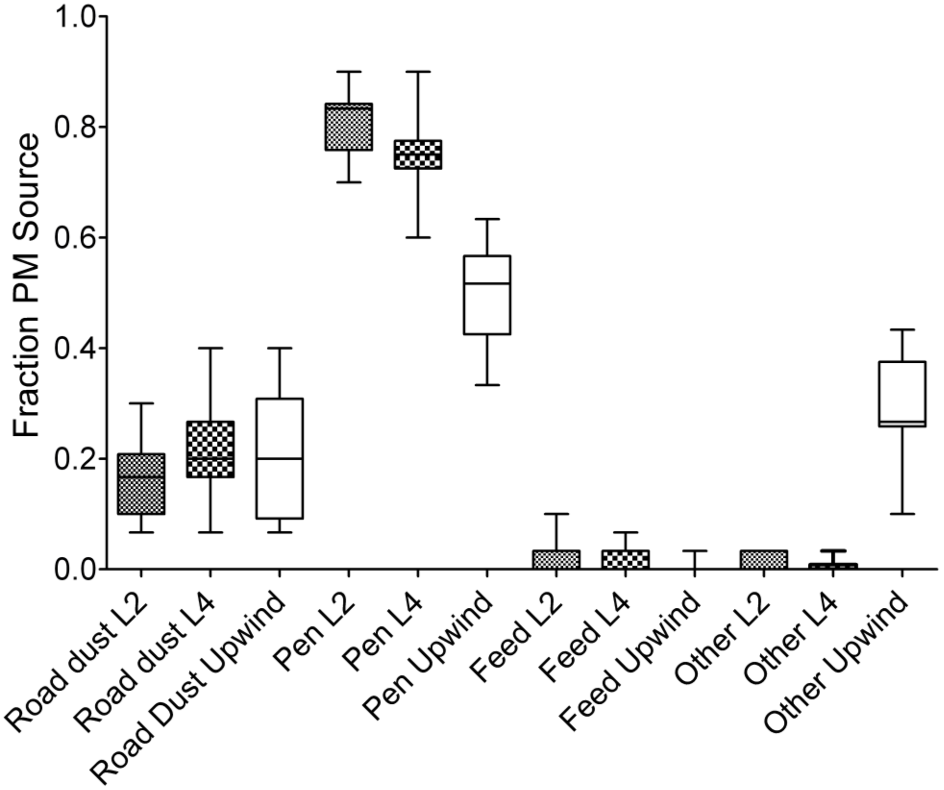

Figure 3-8: Box plot for July 13 and 14 on source fractions at level 2, level 4, and upwind station. Upwind exhibits distinction for fractions of Pen Surface and Other compared to those at the feedlot

3.3.4 RESAMPLING ANALYSIS

Simulation was performed to evaluate the results from 30 particles in representing the distribution of PM on the filter. Data collected from each of several filters across the 2-day period was analyzed in the simulation process. The resampling procedure was conducted using sample sizes as 15, 20, 25, and 30. For each filter, 500 samples were taken from the 30 particles with the particular sample size chosen. The proportion difference was compared for 4 particle types designated as Road Dust, Pen Surface, Feeds, and Unidentified. Samples were labeled as indistinguishable from the observed distribution of the 30 particles if any of the particle type exhibited a larger absolute proportion difference of 10% (δ=10%). The statistical power as the percentage of the indistinguishable samples is shown in Table 3-2. For sample size of 15, 64.30% of the samples exhibited the same distribution as that of the corresponding observed 30 particles. The number increased with bigger sample sizes. Simulation with sample size of 30 indicated a statistical power of 83.81% for estimation of ‘true’ values.

Four filters from overnight sampling at four levels on July 13 were analyzed with 100 particles randomly selected from each filter. The simulation was performed with ‘true’ distribution from 100 particles instead of 30 in order to test the performance of different sample sizes on a larger population. The results are shown in Table 3-3. Overall, the resampling indicates a better estimation of ‘true’ distribution with 95.00±0.78% of the samples having the same distribution for sample size of 30. This suggests that 30 be a number sufficient for an even larger population, as it is the case for the filters.

Table 3-2: Statistical power from samples with indistinguishable distribution (30 particles).

Time	Level	Statistical Power (500 samples from 30 particles), %			
		15 particles	20 particles	25 particles	30 particles
07/13/2011 6 am-8 am	2	61.60	78.20	77.40	83.80
07/13/2011 8 am-10 am	2	63.60	68.60	74.20	86.60
07/13/2011 10 am-12 pm	2	38.40	51.40	59.60	67.40
07/13/2011 12 pm-2 pm	2	56.60	53.00	62.20	71.60
07/13/2011 2 pm-4 pm	2	57.20	58.40	68.60	82.40
07/13/2011 4 pm-6 pm	2	71.60	77.00	82.40	87.80
07/13/2011 6 pm-6 am	2	60.40	75.00	83.40	82.00
07/14/2011 6 am-8 am	2	72.60	81.40	85.00	95.60
07/14/2011 8 am-10 am	2	68.00	70.00	78.40	83.20
07/14/2011 10 am-12 pm	2	93.20	96.20	97.00	97.40
07/14/2011 12 pm-2 pm	2	59.20	73.40	79.20	83.60
07/14/2011 2 pm-4 pm	2	66.00	66.20	71.20	84.60
07/14/2011 4 pm-6 pm	2	61.60	74.20	82.80	83.60
07/14/2011 6 pm-6 am	2	70.60	80.80	87.60	93.60
07/13/2011 6 am-8 am	4	61.00	59.20	66.20	81.40
07/13/2011 8 am-10 am	4	62.80	66.60	75.80	87.00
07/13/2011 10 am-12 pm	4	46.00	53.00	65.00	69.60
07/13/2011 12 pm-2 pm	4	58.80	62.20	70.60	71.40
07/13/2011 2 pm-4 pm	4	65.20	73.40	71.80	81.80
07/13/2011 4 pm-6 pm	4	59.80	56.80	63.80	73.20
07/13/2011 6 pm-6 am	4	74.40	82.60	87.40	95.40
07/14/2011 6 am-8 am	4	64.60	67.80	70.40	85.60
07/14/2011 8 am-10 am	4	68.40	64.40	67.40	86.00
07/14/2011 10 am-12 pm	4	67.00	63.00	68.40	86.20
07/14/2011 12 pm-2 pm	4	61.60	68.40	68.60	84.40
07/14/2011 2 pm-4 pm	4	66.60	73.60	79.60	83.20
07/14/2011 4 pm-6 pm	4	56.00	60.80	64.20	81.80
07/14/2011 6 pm-6 am	4	87.60	90.40	97.40	96.60
Average		64.30	69.50	75.20	83.81
Standard Deviation		10.54	11.07	10.02	7.87

Table 3-3: Statistical power from samples with indistinguishable distribution (100 particles).

Time	Level	Statistical Power (500 samples from 100 particles), %			
		15 particles	20 particles	25 particles	30 particles
07/13/2011 6 pm-6 am	1	67.00	83.20	86.80	94.20
07/13/2011 6 pm-6 am	2	91.80	93.80	94.40	95.20
07/13/2011 6 pm-6 am	3	82.40	85.40	90.40	94.60
07/13/2011 6 pm-6 am	4	93.40	91.80	95.80	96.00
Average		83.65	88.55	91.85	95.00
Standard Deviation		12.11	5.06	4.07	0.78

3.4 CONCLUSION

The combination of Raman microscopy with multivariate statistical analysis showed good potential for quantification of PM_{10} source contribution from the cattle feedlot. Spectral library of potential sources was built to serve as reference for identifying PM_{10} sampled from ambient air. Raman spectra from the source materials varied sufficiently between groups and could be well separated by multivariate statistical analyses. With a 99.76% correct classification rate, the developed model was employed to analyze filter samples. Results showed that pen surface and unpaved road dominated in PM_{10} emission at the feedlot, and the fractions of the sources varied with time, weather conditions, operations, and heights. Simulation also provided multiple sample sizes to meet different needs with specified accuracy. This method successfully estimated the fractions of PM_{10} sources with simple sample treatment and provided a feasible approach for study on other AFOs.

ACKNOWLEDGEMENTS

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CHAPTER 4: CONCLUSION

This study presents a method to identify and quantify source contribution to PM_{10} emission at a cattle feedlot. The method utilizes filters from PM_{10} mass concentration monitoring, which is common and usually mandatory for PM_{10} measurement. Since the method is non-destructive to the filter samples, it requires no additional sampling for source apportionment purpose. The filter samples are readily to use after mass concentration measurement without any sample treatment for Raman analysis. Raman microscopy involves simple operation, and is employed to analyze particles on a one-by-one basis, which is distinct from other studies. The entire sample analysis process is simple and direct but at the same time with capability of chemical composition characterization if needed.

The data analysis process is consisted of three multivariate statistical analyses. The multivariate statistical analyses works well with spectra data and serves to analyze the data in a more objective and efficient way than pure visual observation. The developed model has been proven to work for the complicated sources containing heterogeneous materials and result in high correct classification rate of 99.76%. Therefore the combination of Raman microscopy and the statistical model is powerful for identification of sources for particles on the filters.

Results from analysis on the filter samples show that fractions of different sources contributing to PM_{10} emission vary with time and locations. At the feedlot, pen surface dominates and accounts for more than 76% of the ambient PM_{10}, while unpaved roads account for more than 16%, making it the second biggest contributor.

The other sources appear insignificant in PM_{10} emission. It supports the hypothesis that pen surface and unpaved roads at the feedlot are two main sources of PM_{10}. However, another hypothesis that the fractions of PM_{10} emission from pen surface and unpaved roads are proportion to their terrestrial areas is rejected because other factors, such as time, weather condition, feedlot operations, and heights, have been found to play important role in determination of source fractions. Results show that pen surface contributes the most in the early evening due to more cattle activities and daytime evaporation of moisture content in the pen surface materials. Fraction of unpaved roads increases during the day when operating vehicles travel on the roads for feed delivery and feedlot maintenance. Fractions of Road Dust appeared to increase with height. At the upwind station, fraction of pen surface material is still significant, suggesting that the feedlot has a severe emission of PM_{10} to the ambient air. The variability of the wind direction and the particle dispersion and transportation in the air can lead to reception of PM_{10} at the upwind stations which are supposed to be outside the plume of pollution. The lost in pen surface contribution is compensated by the increase in unpaved roads emission and sources that are not identified. This is consistent with the locations of the upwind stations, which are exposed to unpaved roads and unknown sources. During the raining event, PM_{10} from pen surface drops dramatically at the upwind station, indicating the effectiveness of moisture condition in controlling the emission from pen surface. The fractions of pen surface and unpaved roads show no distinction from non-raining time, and the reason might be that the rain also inhibits emission from unpaved roads.

A simulation process is conducted to assess the number of particles taken to represent the distribution on the entire filter. The resampling results support the number of 30 to be sufficient in estimating fractions from different sources. The process also provides an approach to determine the sample size to meet different research needs for various situations. Smaller or larger size of sample might be taken depending on the accuracy specified by the researchers and the time available.

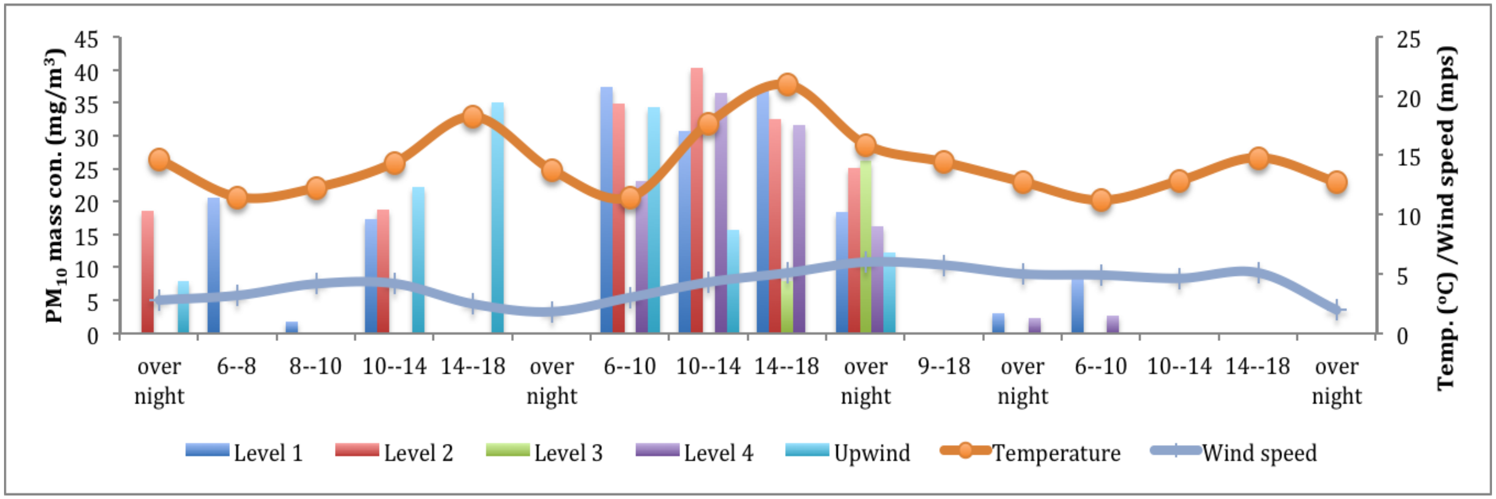
Future work for this study could be in two parts. One is to evaluate the statistical model and enhance the performance. More than 1000 spectra were collected for construction of source spectral library, which was used as training group for linear discriminant analysis. The model can be tested for fewer spectra so as to save time for building a yet reliable training group. In addition, the model can be revised to incorporate function to identified spectrum that belongs to none of the classes in the training group. One possible solution is a machine learning approach called relevance vector machine, which has powerful classification function with the benefit of providing probabilistic predictions (Tipping, 2001). One can detect sample belong to unidentified group by the low probabilistic values for classification.

On the other hand, analysis on more filter samples can contribute to a fuller profile of source distribution of PM_{10} emission. Various factors that have mutual impacts on the emission can be further investigated. The information would provide solid ground for regulation agencies in making standards and regulations specific for cattle feedlots, and offer solutions to feedlot managers/operators who are seeking cost-effective way to minimize dust emission. The study can be expanded to include other AFOs or agricultural operations for better control of PM_{10} emission.

APPENDIX A-1[a]: PM$_{10}$ mass concentration (mg/m^3) (2010 May)

	Level 1	Level 2	Level 3	Level 4	Upwind	Air temp. (℃)	Wind speed (mps)
05/16/2010 6 pm-6 am		18.633			7.879	14.67	2.78
05/17/2010 6 am-8 am	20.537					11.48	3.17
05/17/2010 8 pm-10 am	1.706					12.26	4.15
05/17/2010 10 pm-2 pm	17.286	18.734			22.222	14.390	4.170
05/17/2010 2 pm-6 pm					35.088	18.26	2.45
05/17/2010 6 pm-6 am						13.77	1.79
05/18/2010 6 am-10 am	37.380	34.824		23.178	34.343	11.450	3.000
05/18/2010 10 pm-2 pm	30.756	40.351		36.481	15.789	17.710	4.290
05/18/2010 2 pm-6 pm	36.895	32.514	7.967	31.676		20.970	5.070
05/18/2010 6 pm-6 am	18.328	25.064	26.159	16.278	12.325	15.910	5.980
05/19/2010 9 am-6 pm						14.420	5.730
05/19/2010 6 pm-6 am	3.109			2.224		12.750	4.980
05/20/2010 6 am-10 am	8.343			2.686		11.210	4.890
05/20/2010 10 am-2 pm						12.860	4.610
05/20/2010 2 pm-6 pm						14.790	5.080
05/20/2010 6 pm-6 am						12.730	1.940

APPENDIX A-1[a]: PM$_{10}$ mass concentration (mg/m^3) (2010 May)



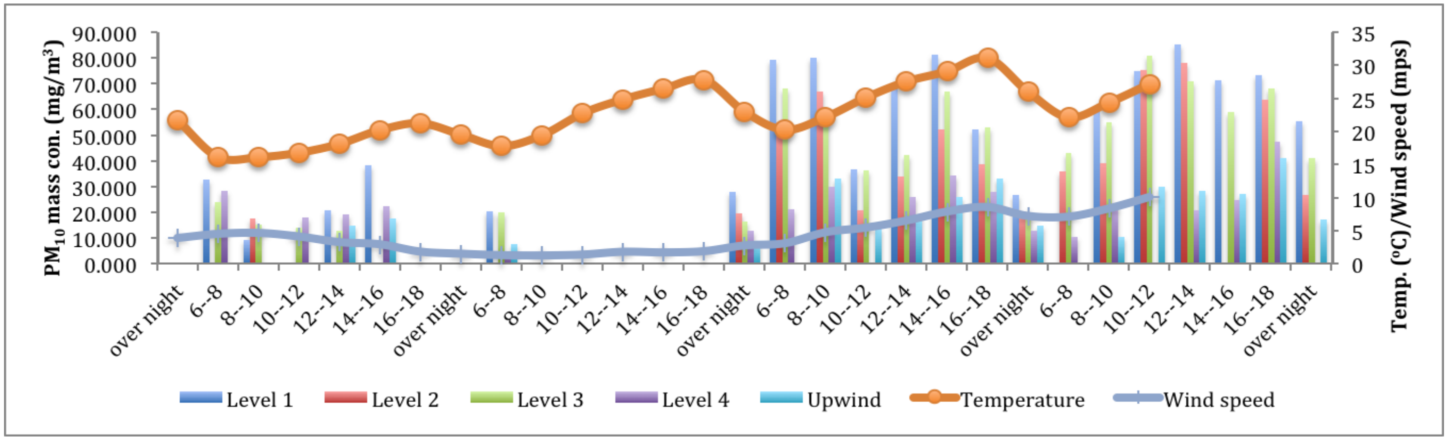
[a] The blank values mean one or some of the followings: (1) wind direction was not due north or south 80% of the sampling time. (2) Negative values (not enough measurable amount of dust collected). (3) Upwind samplers were placed in wrong location. (4) Visual inspection showed large particles on filters for PM$_{10}$.

APPENDIX A-2: PM$_{10}$ mass concentration (mg/m^3) (2010 June)

	Level 1	Level 2	Level 3	Level 4	Upwind	Air temp. (℃)	Wind speed (mps)
06/13/2010 6 pm-6 am						21.69	3.87
06/14/2010 6 am-8 am	32.584		24.188	28.412		16.160	4.500
06/14/2010 8 am-10 am	9.391	17.735	15.211			16.130	4.640
06/14/2010 10 am-12 pm			14.034	17.934		16.81	4.1
06/14/2010 12 pm-2 pm	20.715		12.781	19.055	15.000	18.140	3.250
06/14/2010 2 pm-4 pm	38.261			22.584	17.544	20.240	2.920
06/14/2010 4 pm-6 pm						21.260	1.810
06/14/2010 6 pm-6 am						19.540	1.500
06/15/2010 6 am-8 am	20.586		20.005	4.419	7.843	17.820	1.280
06/15/2010 8 am-10 am						19.450	1.240
06/15/2010 10 am-12 pm						22.750	1.370
06/15/2010 12 pm-2 pm						24.870	1.790
06/15/2010 2 pm-4 pm						26.480	1.700
06/15/2010 4 pm-6 pm						27.820	1.880
06/15/2010 6 pm-6 am	27.883	19.671	16.474	12.703	8.333	23.020	2.750
06/16/2010 6 am-8 am	79.365	55.181	68.166	21.293		20.280	3.080
06/16/2010 8 am-10 am	79.928	66.937	60.036	29.835	33.333	22.180	4.740
06/16/2010 10 am-12 pm	36.873	20.890	36.195		14.035	25.140	5.440
06/16/2010 12 pm-2 pm	69.144	34.062	42.198	25.810	19.048	27.560	6.510
06/16/2010 2 pm-4 pm	81.422	52.144	66.892	34.192	25.926	29.090	7.870
06/16/2010 4 pm-6 pm	52.247	38.849	52.888	28.035	33.333	31.120	8.560

APPENDIX A-2: PM_{10} mass concentration (mg/m^3) (2010 June)

	Level 1	Level 2	Level 3	Level 4	Upwind	Air temp. (℃)	Wind speed (mps)
06/16/2010 6 pm-6 am	26.686	19.375	20.142	13.068	14.754	26.050	7.210
06/17/2010 6 am-8 am		36.142	43.052	10.697		22.160	7.100
06/17/2010 8 am-10 am	59.289	39.186	55.126	22.976	10.526	24.370	8.340
06/17/2010 10 am-12 pm	74.761	75.296	80.723		30.000	27.180	10.070
06/17/2010 12 pm-2 pm	85.067	78.199	71.055	20.670	28.333		
06/17/2010 2 pm-4 pm	71.438		59.197	24.961	27.273		
06/17/2010 4 pm-6 pm	73.369	63.798	68.166	47.609	41.176		
06/17/2010 6 pm-6 am	55.251	26.788	41.066		17.073		

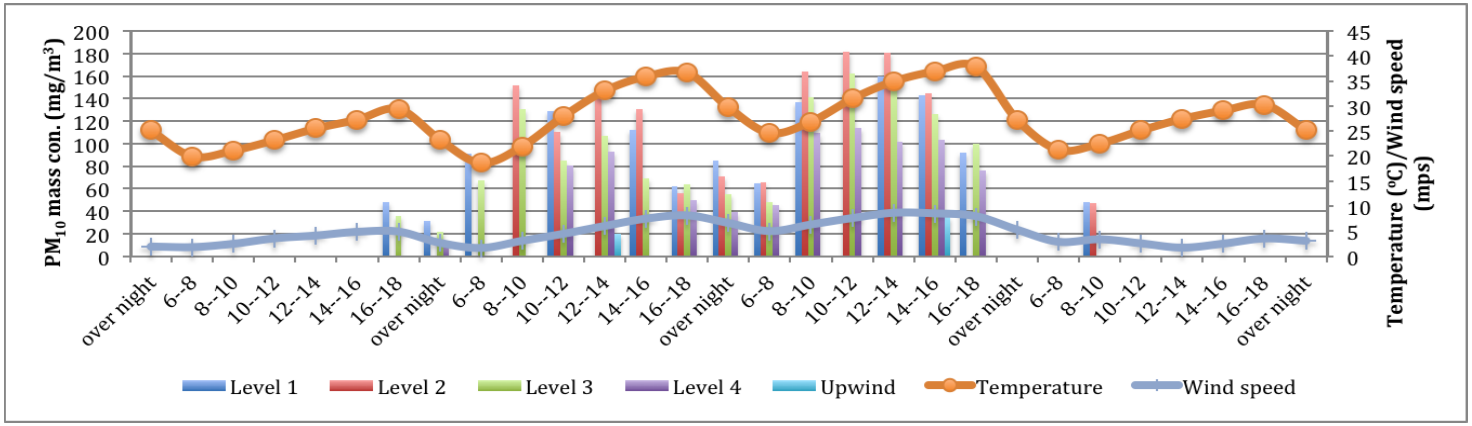


APPENDIX A-3: PM$_{10}$ mass concentration (mg/m^3) (2010 July)

	Level 1	Level 2	Level 3	Level 4	Upwind	Air temp. (℃)	Wind speed (mps)
07/11/2010 6 pm-6 am						25.15	1.92
07/12/2010 6 am-8 am						19.97	1.76
07/12/2010 8 am-10 am						21.14	2.43
07/12/2010 10 am-12 pm						23.22	3.52
07/12/2010 12 pm-2 pm						25.55	4.08
07/12/2010 2 pm-4 pm						27.31	4.82
07/12/2010 4 pm-6 pm	48.179		35.877			29.44	4.86
07/12/2010 6 pm-6 am	31.048		22.070	13.328		23.320	2.630
07/13/2010 6 am-8 am	90.909		67.485			18.63	1.6
07/13/2010 8 am-10 am		151.924	130.300			21.98	3.030
07/13/2010 10 am-12 pm	129.056	110.145	85.057	80.941		27.980	4.430
07/13/2010 12 pm-2 pm		146.638	107.362	93.157	20.000	33.060	5.990
07/13/2010 2 pm-4 pm	112.352	130.938	69.322			35.930	7.460
07/13/2010 4 pm-6 pm	62.070	55.902	63.584	49.532		36.690	8.100
07/13/2010 6 pm-6 am	85.346	70.735	54.893	39.011		29.750	6.580
07/14/2010 6 am-8 am	64.988	65.219	48.117	45.831		24.640	4.960
07/14/2010 8 am-10 am	136.873	164.100	140.915	109.312		26.910	6.280
07/14/2010 10 am-12 pm		181.727	162.125	113.528		31.490	7.570
07/14/2010 12 pm-2 pm	159.801	181.062	154.972	101.626		34.940	8.620
07/14/2010 2 pm-4 pm	142.906	144.362	126.418	103.474	35.185	36.960	8.510
07/14/2010 4 pm-6 pm	92.269		99.628	76.437		37.890	7.940

APPENDIX A-3: PM$_{10}$ mass concentration (mg/m^3) (2010 July)

	Level 1	Level 2	Level 3	Level 4	Upwind	Air temp. (℃)	Wind speed (mps)
07/14/2010 6 pm-6 am						27.280	5.230
07/15/2010 6 am-8 am						21.300	2.830
07/15/2010 8 am-10 am	48.125	47.492				22.520	3.330
07/15/2010 10 am-12 pm						25.150	2.510
07/15/2010 12 pm-2 pm						27.460	1.660
07/15/2010 2 pm-4 pm						29.130	2.460
07/15/2010 4 pm-6 pm						30.280	3.490
07/15/2010 6 pm-6 am						25.210	3.030

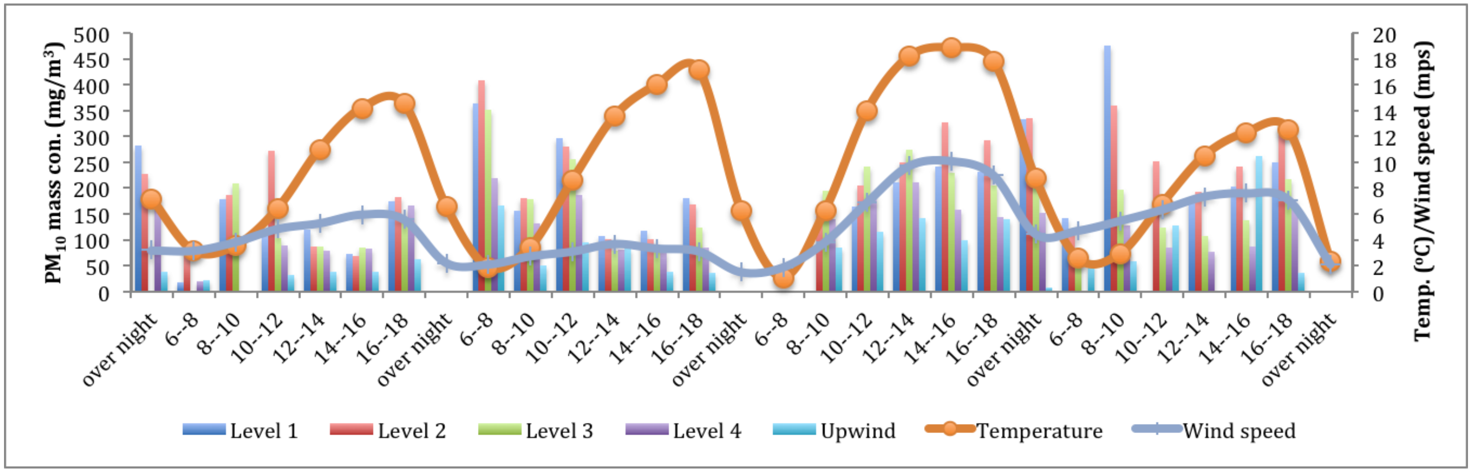


APPENDIX A-4: PM$_{10}$ mass concentration (mg/m^3) (2010 November)

	Level 1	Level 2	Level 3	Level 4	Upwind	Air temp. (℃)	Wind speed (mps)
10/31/2010 6 pm-6 am	282.065	227.215		175.264	38.793	7.180	3.200
11/01/2010 6 am-8 am	18.706	68.881		20.074	22.222	3.120	3.150
11/01/2010 8 am-10 am	178.774	186.515	208.321			3.530	3.820
11/01/2010 10 am-12 pm	107.204	271.277	104.179	88.204	31.579	6.410	4.840
11/01/2010 12 pm-2 pm	120.153	87.683	87.957	78.678	38.095	11.010	5.280
11/01/2010 2 pm-4 pm	73.211	68.525	84.205	81.984	38.596	14.180	5.950
11/01/2010 4 pm-6 pm	173.756	183.092	144.463	165.958	61.667	14.520	5.570
11/01/2010 6 pm-6 am						6.590	2.220
11/02/2010 6 am-8 am	363.168	409.274	352.076	220.015	166.667	1.860	2.090
11/02/2010 8 am-10 am	156.296	181.258	178.688	132.212	50.000	3.440	2.720
11/02/2010 10 am-12 pm	297.619	279.736	255.624	186.919	94.737	8.590	3.090
11/02/2010 12 pm-2 pm	108.225	100.484	77.904	80.656	83.333	13.540	3.680
11/02/2010 2 pm-4 pm	118.137	101.984	85.039	76.471	38.596	15.980	3.330
11/02/2010 4 pm-6 pm	181.087	169.415	123.776	85.580	36.667	17.160	3.100
11/02/2010 6 pm-6 am						6.290	1.500
11/03/2010 6 am-8 am						1.080	1.860
11/03/2010 8 am-10 am		149.874	194.761	140.341	85.000	6.250	3.820
11/03/2010 10 am-12 pm	164.141	205.055	240.854	189.702	115.556	14.010	6.890
11/03/2010 12 pm-2 pm	210.438	249.441	274.413	210.201	142.105	18.180	9.710
11/03/2010 2 pm-4 pm	241.521	326.810	228.889	158.499	100.000	18.840	10.090
11/03/2010 4 pm-6 pm	231.295	292.453	204.499	143.895	140.351	17.830	8.990

APPENDIX A-4: PM_{10} mass concentration (mg/m^3) (2010 November)

	Level 1	Level 2	Level 3	Level 4	Upwind	Air temp. (℃)	Wind speed (mps)
11/03/2010 6 pm-6 am	332.866	336.293	231.112	152.021	8.611	8.750	4.440
11/04/2010 6 am-8 am	142.045	114.002	61.776		53.704	2.560	4.700
11/04/2010 8 am-10 am	475.758	360.515	197.955	126.829	58.333	2.910	5.460
11/04/2010 10 am-12 pm		251.380	124.647	85.172	128.070	6.760	6.320
11/04/2010 12 pm-2 pm	173.898	193.133	107.827	77.605		10.470	7.340
11/04/2010 2 pm-4 pm	203.839	241.871	138.643	87.846	261.111	12.290	7.600
11/04/2010 4 pm-6 pm	250.329	317.223	216.947	160.834	36.667	12.540	7.100
11/04/2010 6 pm-6 am						2.320	2.100

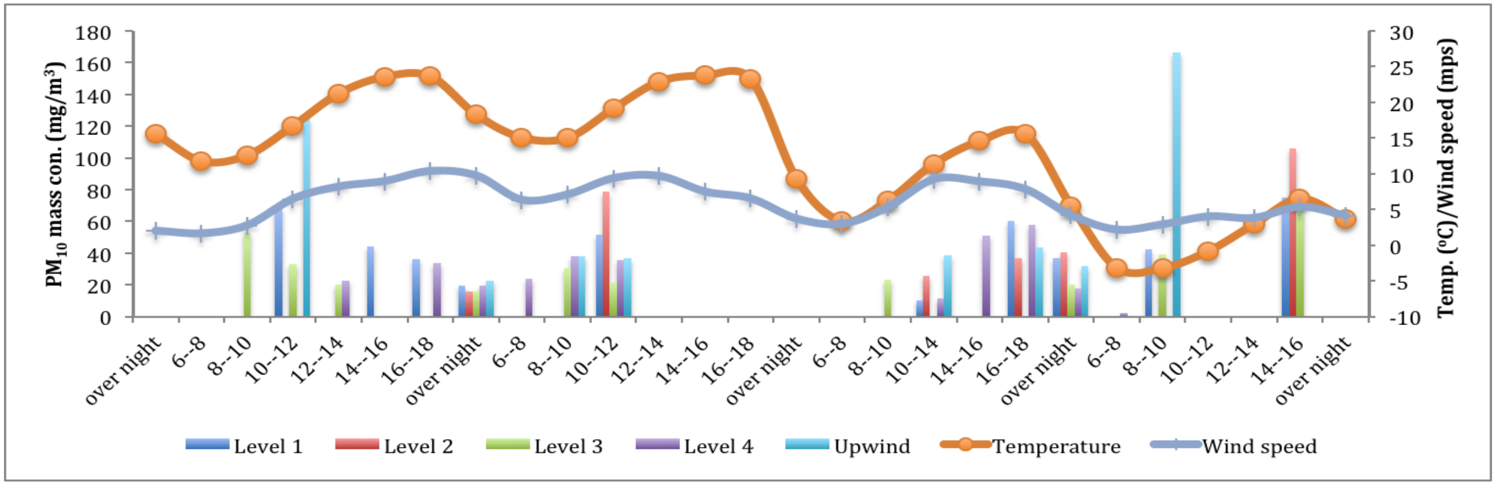


APPENDIX A-5: PM_{10} mass concentration (mg/m^3) (2011 March)

	Level 1	Level 2	Level 3	Level 4	Upwind	Air temp. (℃)	Wind speed (mps)
03/20/2011 6 pm-6 am						15.64	2.03
03/21/2011 6 am-8 am						11.79	1.61
03/21/2011 8 am-10 am			52.706			12.62	2.75
03/21/2011 10 am-12 pm	68.250		33.162		124.561	16.750	6.450
03/21/2011 12 pm-2 pm			19.839	22.752		21.27	8.170
03/21/2011 2 pm-4 pm	44.045					23.61	8.93
03/21/2011 4 pm-6 pm	36.489			33.565		23.64	10.34
03/21/2011 6 pm-6 am	19.530	16.014	15.816	19.581	22.701	18.290	9.700
03/22/2011 6 am-8 am				23.785		15.08	6.310
03/22/2011 8 am-10 am			30.579	37.991	37.778	15.060	7.070
03/22/2011 10 am-12 pm	51.502	79.060	21.526	35.658	36.842	19.150	9.340
03/22/2011 12 pm-2 pm						22.930	9.650
03/22/2011 2 pm-4 pm						23.790	7.460
03/22/2011 4 pm-6 pm						23.250	6.490
03/22/2011 6 pm-6 am						9.290	3.670
03/23/2011 6 am-8 am						3.380	2.940
03/23/2011 8 am-10 am			23.432			6.290	5.310
03/23/2011 10 am-2 pm	10.477	25.568		11.244	38.889	11.410	9.190
03/23/2011 2 pm-4 pm				50.813		14.600	8.890
03/23/2011 4 pm-6 pm	60.410	36.999		57.822	43.333	15.620	7.790
03/23/2011 6 pm-6 am	36.632	40.622	19.917	17.844	31.653	5.510	4.160

APPENDIX A-5: PM$_{10}$ mass concentration (mg/m^3) (2011 March)

	Level 1	Level 2	Level 3	Level 4	Upwind	Air temp. (℃)	Wind speed (mps)
03/24/2011 6 am-8 am				2.162		-3.170	2.130
03/24/2011 8 am-10 am	42.249		39.327		166.667	-3.190	2.870
03/24/2011 10 am-12 pm						-0.810	3.980
03/24/2011 12 pm-2 pm						2.960	3.780
03/24/2011 2 pm-4 pm	74.925	106.117	78.653			6.510	5.320
03/24/2011 4 pm-6 am						3.700	4.100

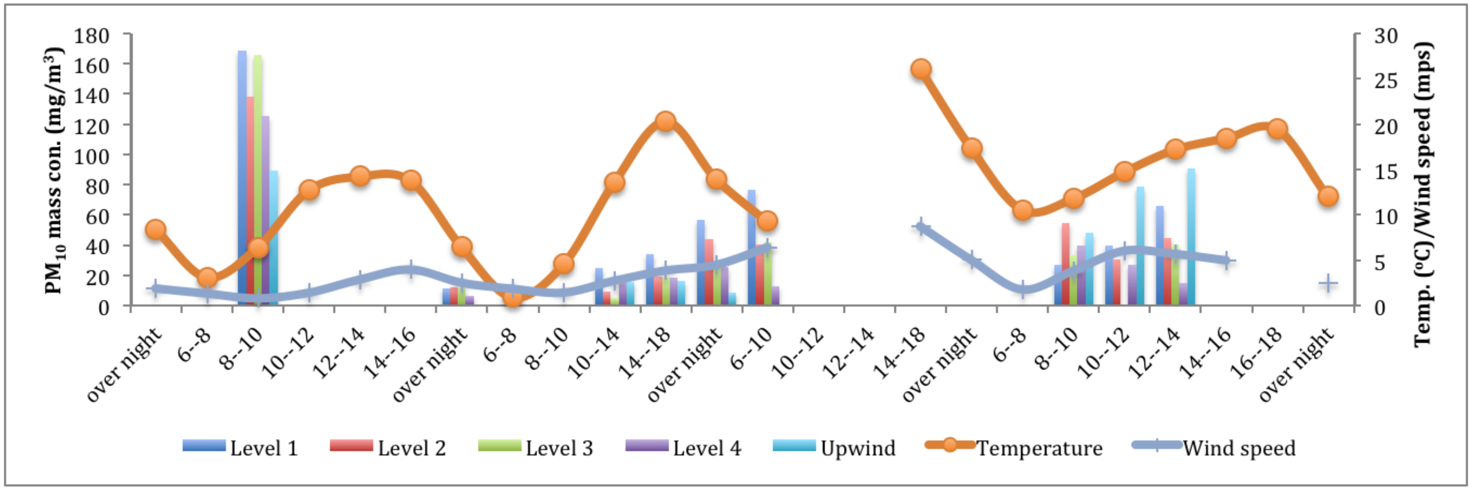


APPENDIX A-6: PM_{10} mass concentration (mg/m^3) (2011 May)

	Level 1	Level 2	Level 3	Level 4	Upwind	Air temp. (℃)	Wind speed (mps)
05/01/2011 6 pm-6 am						8.43	1.88
05/02/2011 6 am-8 am						3.14	1.34
05/02/2011 8 am-10 am	168.825	137.985	165.737	125.313	89.394	6.430	0.810
05/02/2011 10 am-12 pm						12.72	1.42
05/02/2011 12 pm-2 pm						14.25	2.88
05/02/2011 2 pm-4 pm						13.78	3.98
05/02/2011 4 pm-6 am	11.331	11.786	11.279	6.710		6.500	2.530
05/03/2011 6 am-8 am						0.95	1.87
05/03/2011 8 am-10 am						4.56	1.44
05/03/2011 10 am-2 pm	24.905	9.402	4.820	16.058	15.833	13.610	2.750
05/03/2011 2 pm-6 pm	34.014	19.262	18.653	18.276	16.216	20.320	3.870
05/03/2011 6 pm-6 am	56.651	44.092	29.309	25.679	8.743	13.950	4.510
05/04/2011 6 am-10 am	76.597	40.763	41.796	12.892		9.290	6.440
05/04/2011 10 am-12 pm							
05/04/2011 12 pm-2 pm							
05/04/2011 2 pm-6 pm						26.150	8.760
05/04/2011 6 pm-6 am						17.370	5.050
05/05/2011 6 am-8 am						10.580	1.790
05/05/2011 8 am-10 am	27.202	54.368	33.447	39.549	48.333	11.810	3.840
05/05/2011 10 am-12 pm	40.064	30.251		26.652	78.947	14.740	6.050
05/05/2011 12 pm-2 pm	65.629	44.944	40.766	14.761	90.476	17.220	5.700

APPENDIX A-6: PM_{10} mass concentration (mg/m^3) (2011 May)

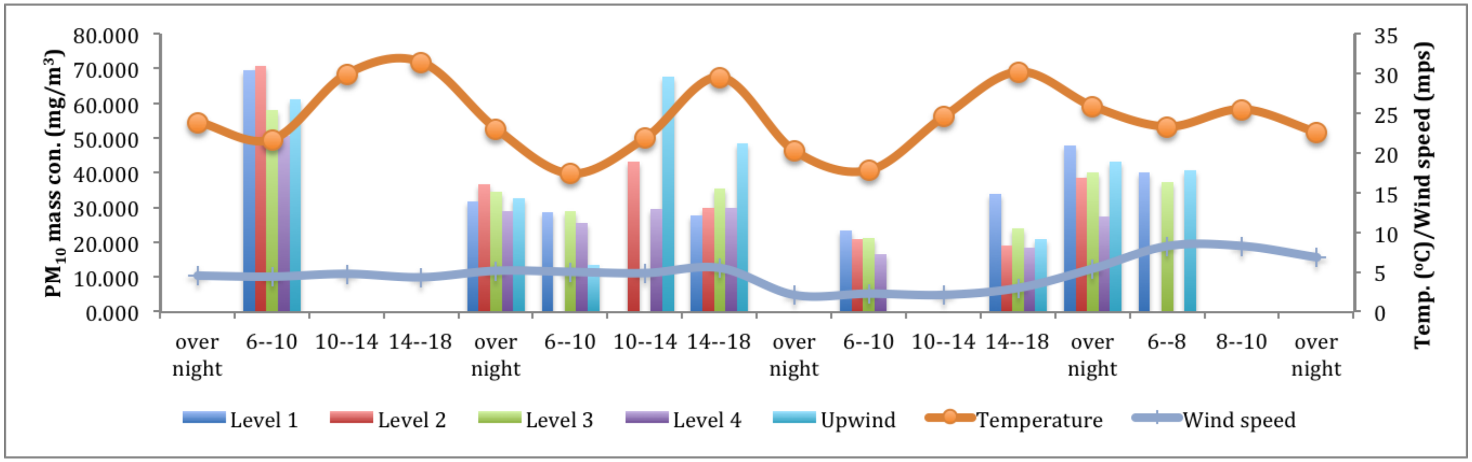
	Level 1	Level 2	Level 3	Level 4	Upwind	Air temp. (℃)	Wind speed (mps)
05/05/2011 2 pm-4 pm						18.470	5.000
05/05/2011 4 pm-6 pm						19.480	
05/05/2011 6 pm-6 am						12.000	2.55



APPENDIX A-7: PM$_{10}$ mass concentration (mg/m^3) (2011 June)

	Level 1	Level 2	Level 3	Level 4	Upwind	Air temp. (℃)	Wind speed (mps)
06/12/2011 6 pm-6 am						23.82	4.5
06/13/2011 6 am-10 am	69.589	70.813	58.050	50.690	61.111	21.660	4.390
06/13/2011 10 am-2 pm						29.91	4.74
06/13/2011 2 pm-6 pm						31.38	4.31
06/13/2011 6 pm-6 am	31.744	36.759	34.666	29.015	32.773	23.000	5.130
06/14/2011 6 am-10 am	28.706		28.912	25.458	13.333	17.350	4.990
06/14/2011 10 am-2 pm		43.188		29.720	67.521	21.860	4.840
06/14/2011 2 pm-6 pm	27.772	29.812	35.574	29.896	48.333	29.490	5.480
06/14/2011 6 pm-6 am						20.200	2.080
06/15/2011 6 am-10 am	23.396	20.784	21.112	16.680		17.780	2.250
06/15/2011 10 am-2 pm						24.530	2.090
06/15/2011 2 pm-6 pm	34.008	18.972	24.010	18.431	20.833	30.170	2.970
06/15/2011 6 pm-6 am	47.843	38.435	39.966	27.438	43.137	25.810	5.410
06/16/2011 6 am-8 am	40.221		37.446		40.741	23.270	8.240
06/16/2011 8 am-10 am						25.440	8.250
06/16/2011 6 pm-6 am						22.550	6.820

APPENDIX A-7: PM$_{10}$ mass concentration (mg/m^3) (2011 June)

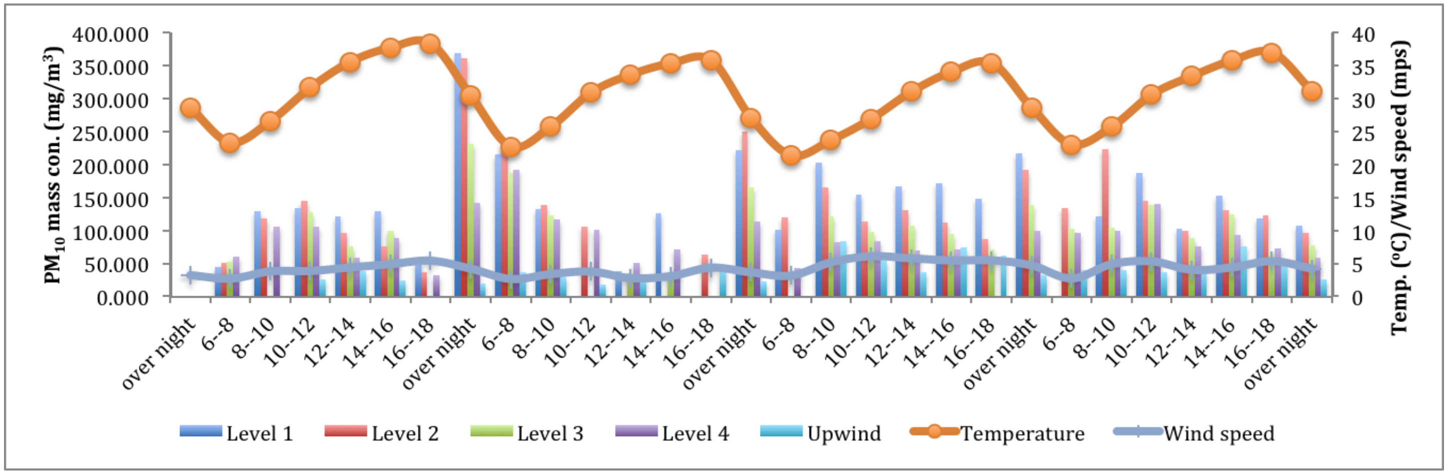


APPENDIX A-8: PM$_{10}$ mass concentration (mg/m^3) (2011 July)

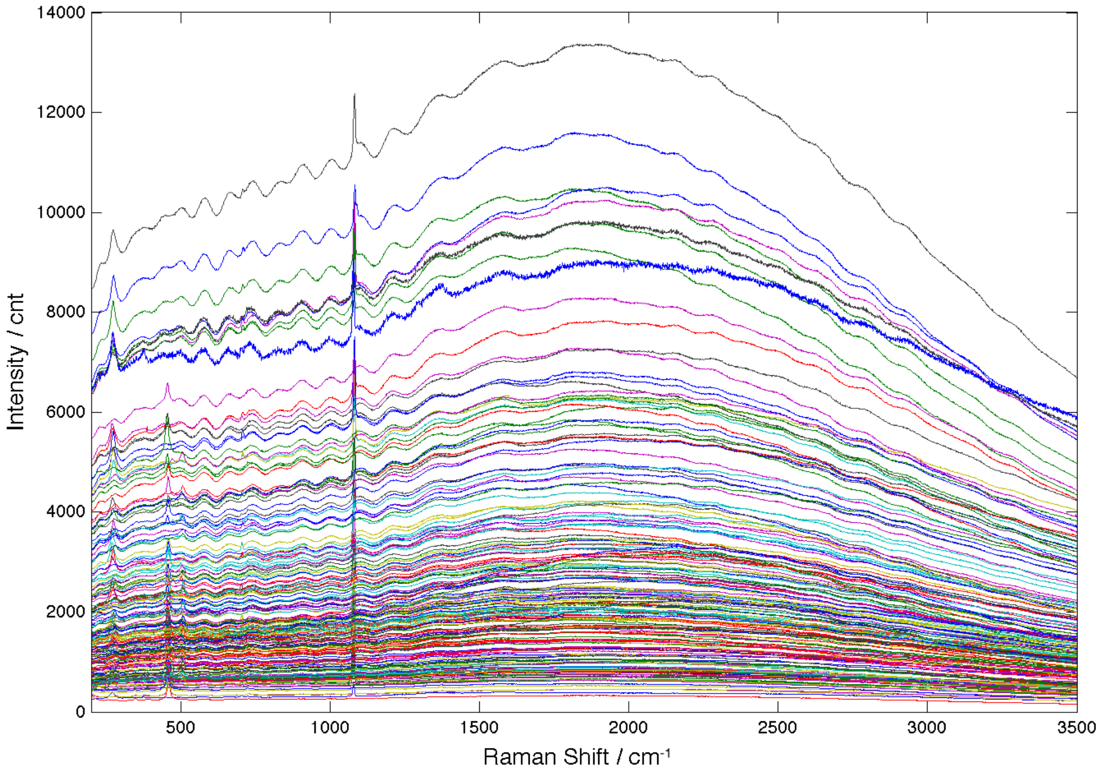
	Level 1	Level 2	Level 3	Level 4	Upwind	Air temp. (℃)	Wind speed (mps)
07/10/2011 6 pm-6 am						28.55	3.25
07/11/2011 6 am-8 am	45.365	50.420	53.045	59.603		23.310	2.710
07/11/2011 8 am-10 am	128.634	118.743		105.576		26.580	3.810
07/11/2011 10 am-12 pm	133.223	145.585	127.529	106.502	26.316	31.640	3.870
07/11/2011 12 pm-2 pm	121.111	95.828	75.828	58.092	38.596	35.550	4.410
07/11/2011 2 pm-4 pm	128.964	76.761	100.121	89.149	25.000	37.700	4.900
07/11/2011 4 pm-6 pm	51.905	36.857		32.919		38.310	5.420
07/11/2011 6 pm-6 am	369.281	361.587	230.467	141.305	19.672	30.410	4.210
07/12/2011 6 am-8 am	214.814	230.884	186.738	192.337	36.842	22.710	2.660
07/12/2011 8 am-10 am	132.079	138.806	122.790	116.288	29.412	25.730	3.390
07/12/2011 10 am-12 pm		105.042		100.693	17.544	30.870	3.770
07/12/2011 12 pm-2 pm	39.108		35.567	51.382	26.984	33.610	2.780
07/12/2011 2 pm-4 pm	126.302		34.467	71.647		35.320	3.100
07/12/2011 4 pm-6 pm		63.387			41.667	35.760	4.370
07/12/2011 6 pm-6 am	221.893	249.908	165.699	113.711	22.500	27.010	3.650
07/13/2011 6 am-8 am	101.334	119.497		42.530		21.360	3.180
07/13/2011 8 am-10 am	203.040	164.772	121.345	82.240	83.333	23.690	5.190
07/13/2011 10 am-12 pm	154.144	112.986	97.406	83.477	54.545	26.910	6.100
07/13/2011 12 pm-2 pm	166.096	130.842	106.849	69.711	36.667	31.020	5.780
07/13/2011 2 pm-4 pm	171.671	112.823	94.594	71.540	74.074	34.010	5.470
07/13/2011 4 pm-6 pm	148.794	86.614	70.658		61.404	35.360	5.480

APPENDIX A-8: PM$_{10}$ mass concentration (mg/m^3) (2011 July)

	Level 1	Level 2	Level 3	Level 4	Upwind	Air temp. (℃)	Wind speed (mps)
07/13/2011 6 pm-6 am	216.802	192.101	139.073	99.278	31.720	28.600	4.710
07/14/2011 6 am-8 am		133.511	102.822	96.965	40.741	23.020	2.740
07/14/2011 8 am-10 am	121.824	222.442	104.010	99.554	40.741	25.700	4.910
07/14/2011 10 am-12 pm	186.672	144.433	138.577	139.940	36.842	30.580	5.320
07/14/2011 12 pm-2 pm	102.020	99.609	88.070	76.121	38.333	33.380	4.040
07/14/2011 2 pm-4 pm	152.816	130.593	123.896	93.471	75.439	35.730	4.410
07/14/2011 4 pm-6 pm	117.651	123.470	65.488	73.584	50.877	36.960	5.350
07/14/2011 6 pm-6 am	107.385	96.872	77.221	59.173	25.410	31.070	4.230



APPENDIX B-1[a]: DESPIKED SPECTRA OF SOURCE MATERIALS (ROAD DUST)



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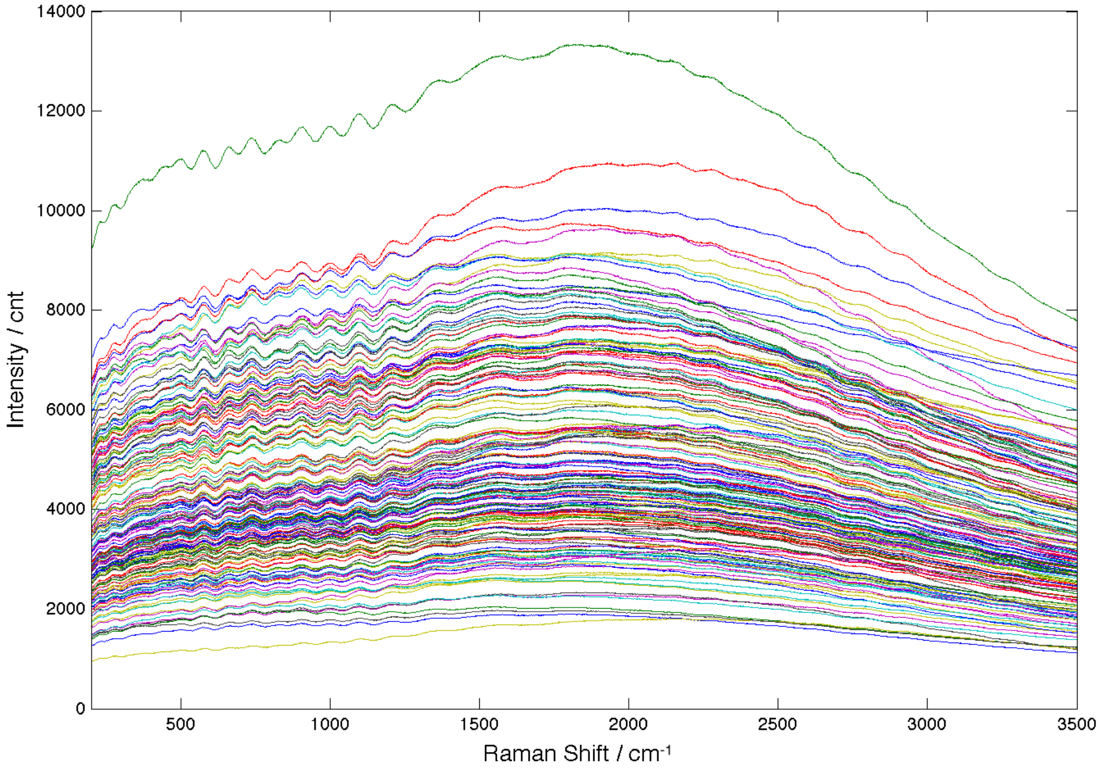
[a] 198 spectra collected from road dust.

APPENDIX B-2[b]: DESPIKED SPECTRA OF SOURCE MATERIALS (PEN SURFACE)



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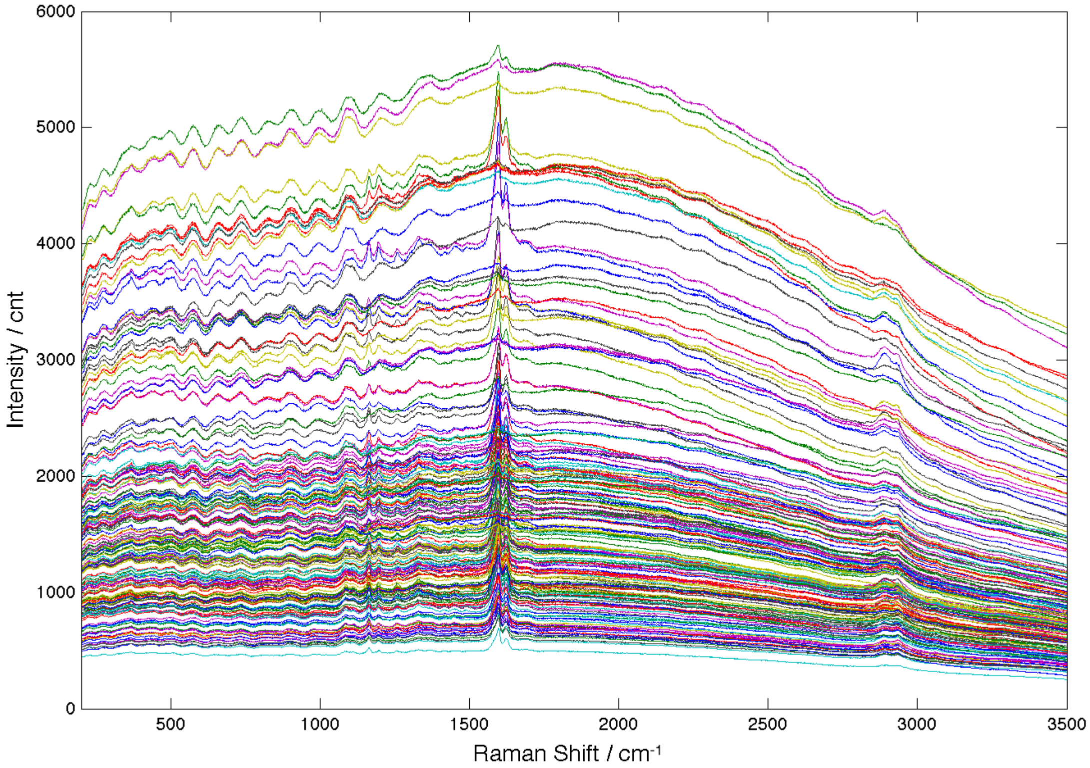
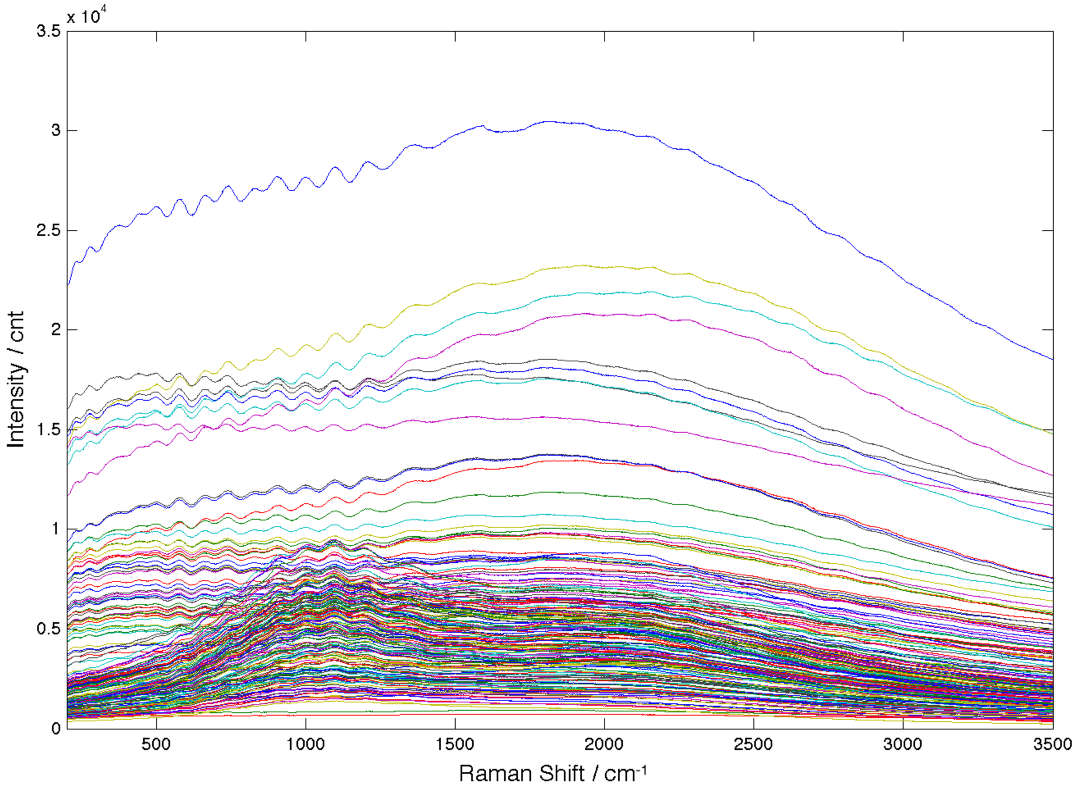
[b] 175 spectra collected from pen surface material.

APPENDIX B-3[c]: DESPIKED SPECTRA OF SOURCE MATERIALS (Feed 1)



[c] 199 spectra collected from feed 1.

APPENDIX B-4[d]: DESPIKED SPECTRA OF SOURCE MATERIALS (Feed 2)



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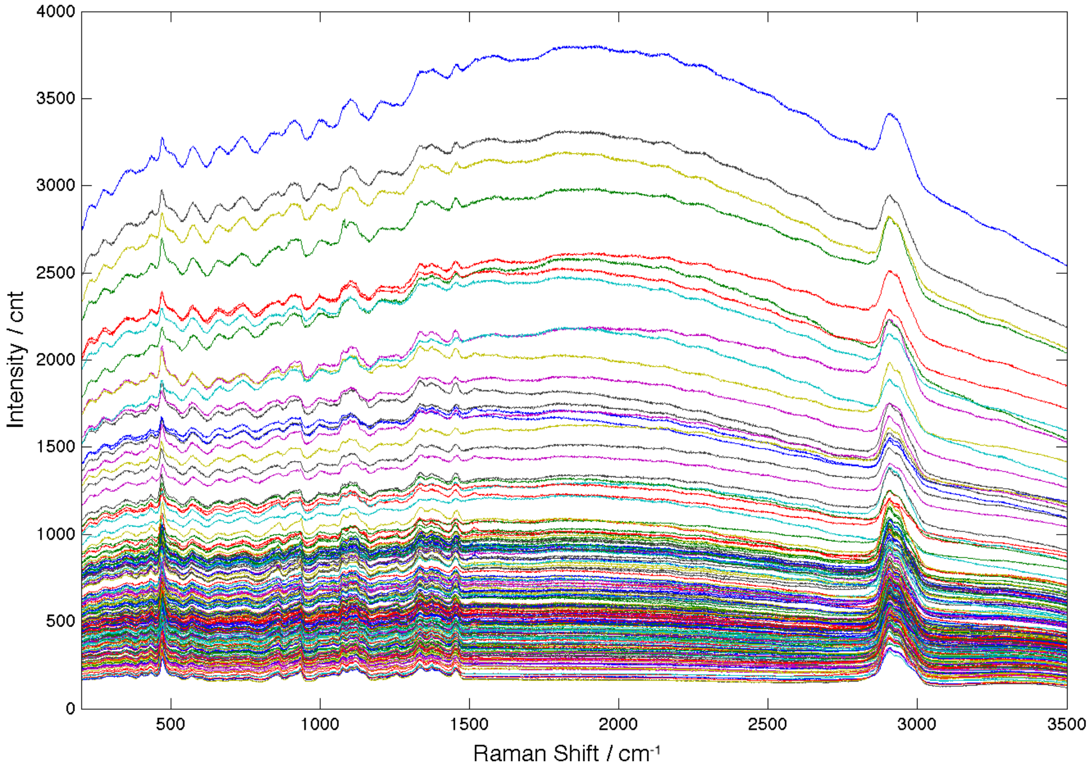
[d] 199 spectra collected from feed 2.

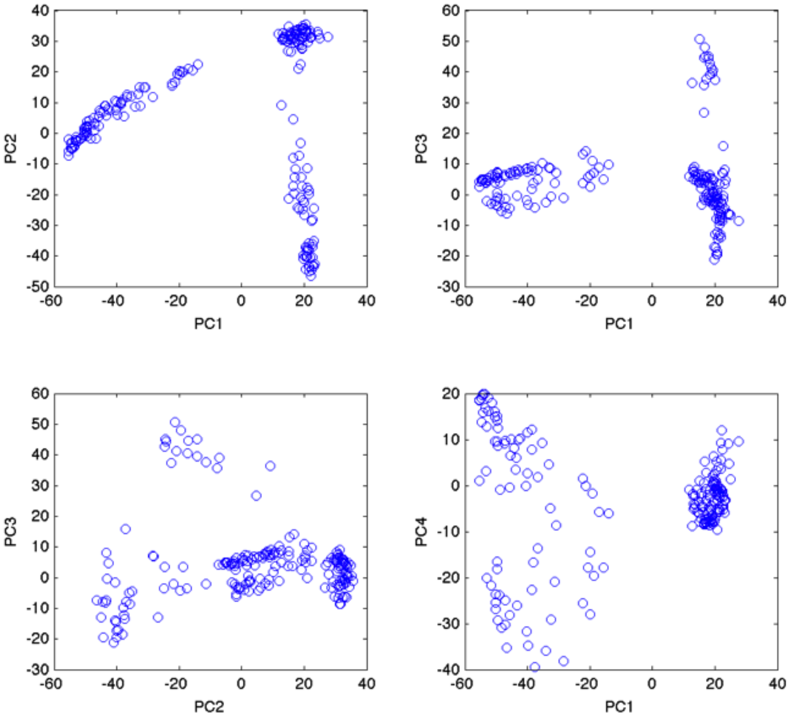
APPENDIX B-5[e]: DESPIKED SPECTRA OF SOURCE MATERIALS (Feed 3)



[e] 199 spectra collected from feed 3.

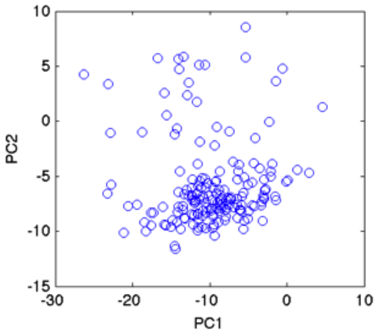
APPENDIX C-1: PCA ON SOURCE MATERIALS (ROAD DUST)

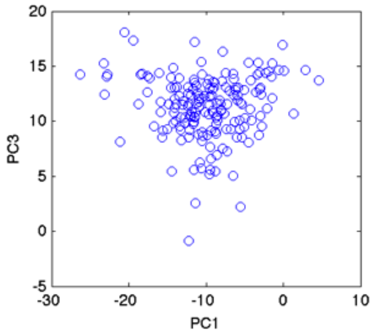
Road dust	Accumulated variance
PC1	0.4291
PC2	0.6966
PC3	0.7699
PC4	0.8357
PC5	0.8919
PC6	0.9360
PC7	0.9436
PC8	0.9490
PC9	0.9535
PC10	0.9570
PC11	0.9598
PC12	0.9625
PC13	0.9643
PC14	0.9659
PC15	0.9673

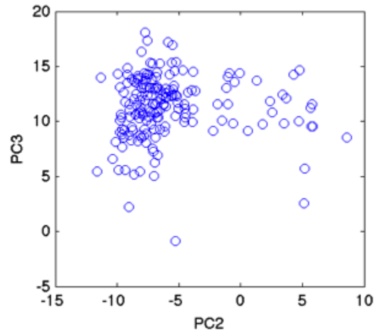


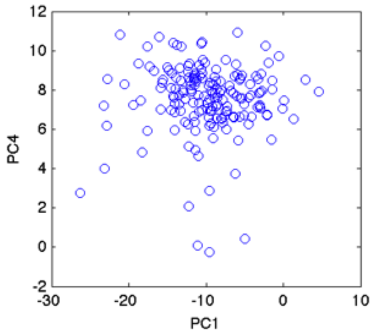
APPENDIX C-2: PCA ON SOURCE MATERIALS (PEN SURFACE)

Pen	Accumulated variance
PC1	0.1534
PC2	0.2456
PC3	0.2926
PC4	0.3101
PC5	0.3257
PC6	0.3398
PC7	0.3521
PC8	0.3644
PC9	0.3762
PC10	0.3878
PC11	0.3986
PC12	0.4092
PC13	0.4197
PC14	0.4298
PC15	0.4394



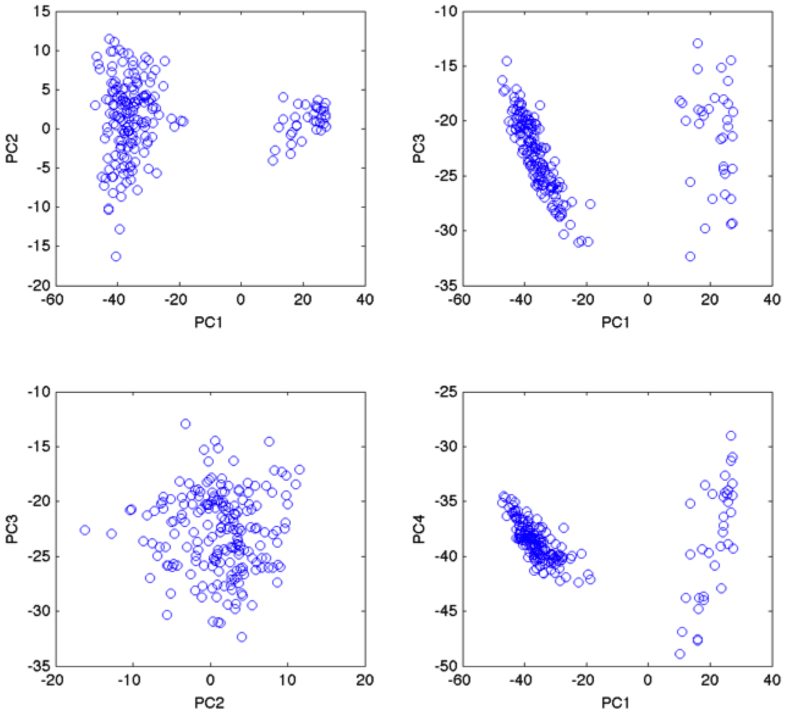






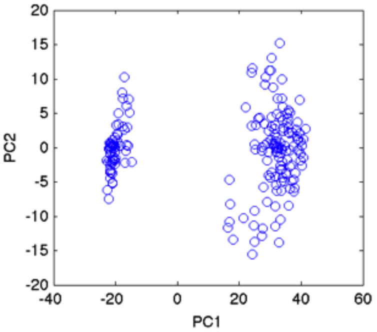
APPENDIX C-3: PCA ON SOURCE MATERIALS (FEED 1)

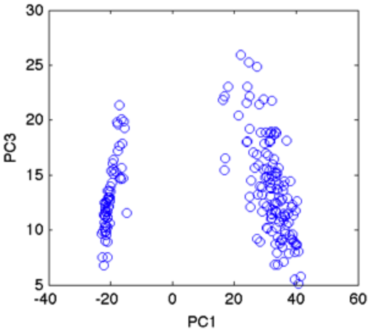
Feed 1	Accumulated variance
PC1	0.8097
PC2	0.8442
PC3	0.8651
PC4	0.8764
PC5	0.8835
PC6	0.8890
PC7	0.8938
PC8	0.8977
PC9	0.9008
PC10	0.9036
PC11	0.9061
PC12	0.9086
PC13	0.9109
PC14	0.9132
PC15	0.9153

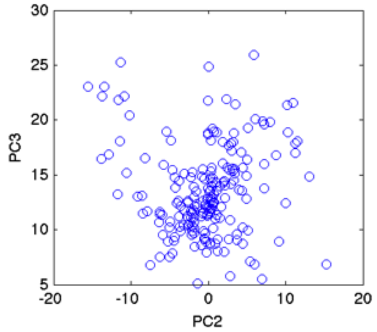


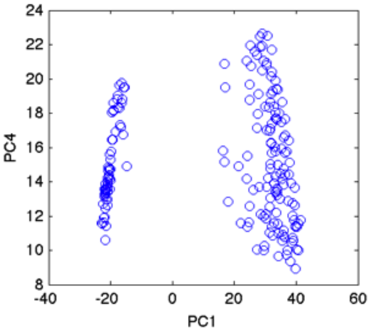
APPENDIX C-4: PCA ON SOURCE MATERIALS (FEED 2)

Feed 2	Accumulated variance
PC1	0.8285
PC2	0.8633
PC3	0.8849
PC4	0.8990
PC5	0.9044
PC6	0.9085
PC7	0.9122
PC8	0.9146
PC9	0.9168
PC10	0.9188
PC11	0.9206
PC12	0.9222
PC13	0.9238
PC14	0.9254
PC15	0.9269



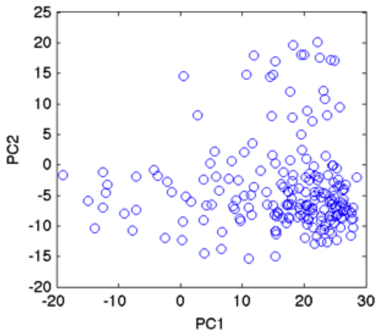


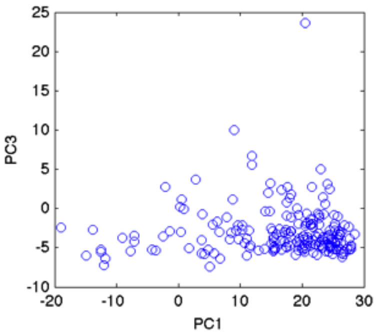


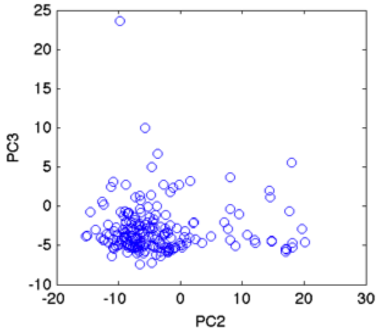


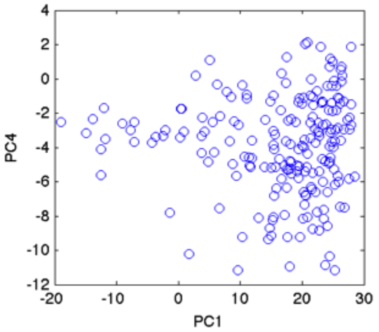
APPENDIX C-5: PCA ON SOURCE MATERIALS (FEED 3)

Feed 3	Accumulated variance
PC1	0.4134
PC2	0.6371
PC3	0.6799
PC4	0.7130
PC5	0.7295
PC6	0.7415
PC7	0.7496
PC8	0.7564
PC9	0.7623
PC10	0.7678
PC11	0.7730
PC12	0.7782
PC13	0.7831
PC14	0.7878
PC15	0.7923

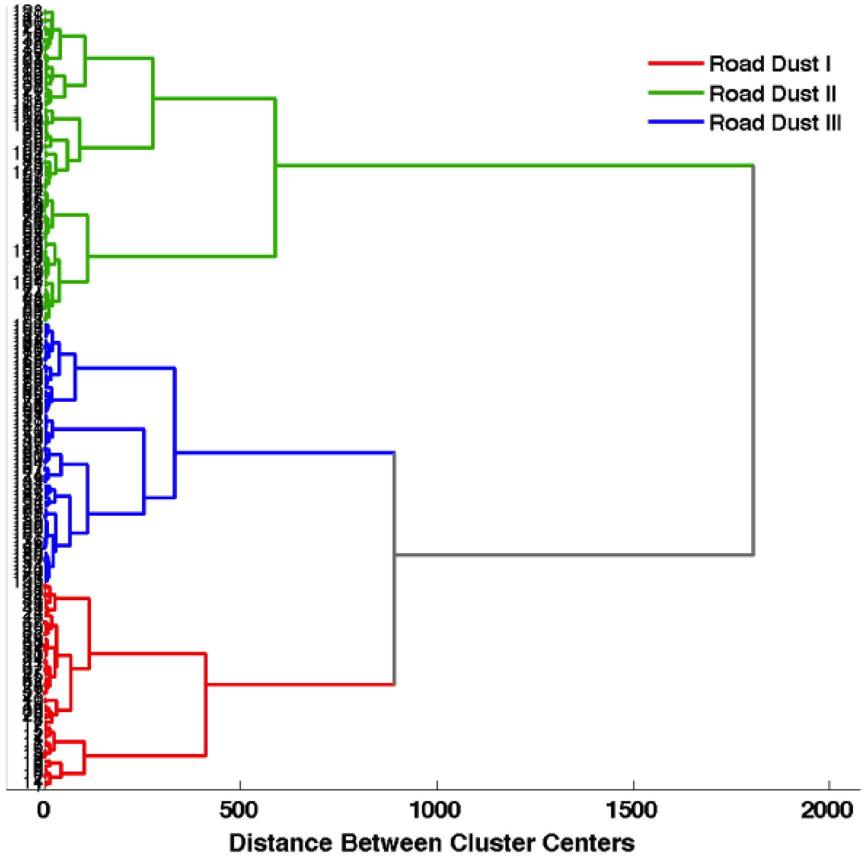




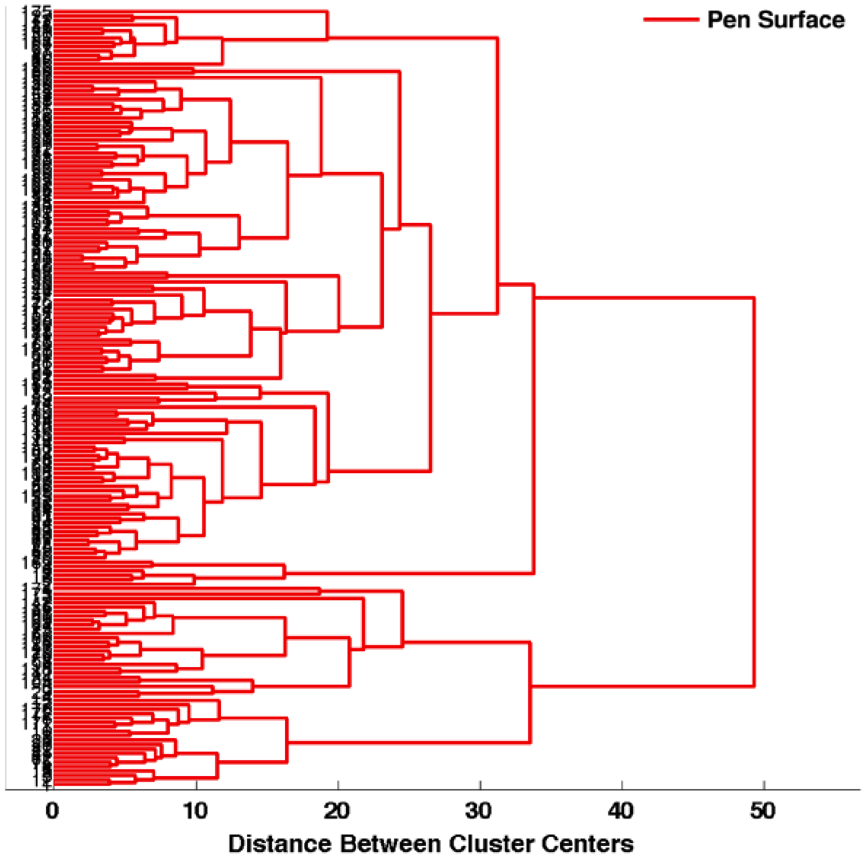




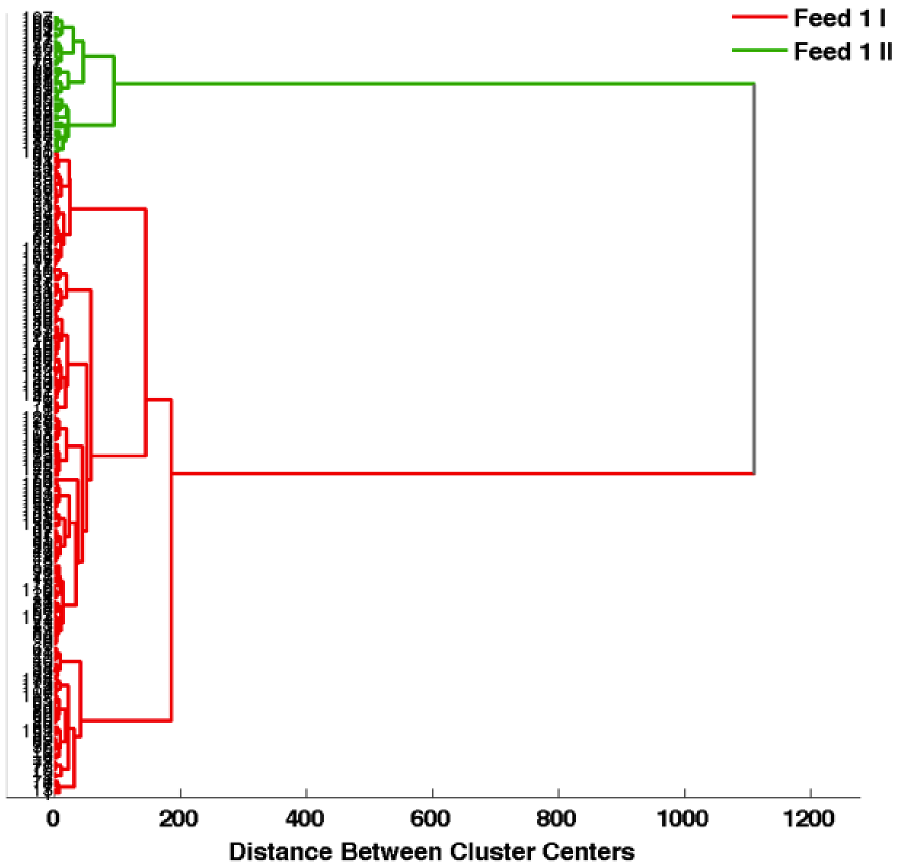
APPENDIX D-1: CLUSTER ANALYSIS ON SOURCE MATERIALS (ROAD DUST)



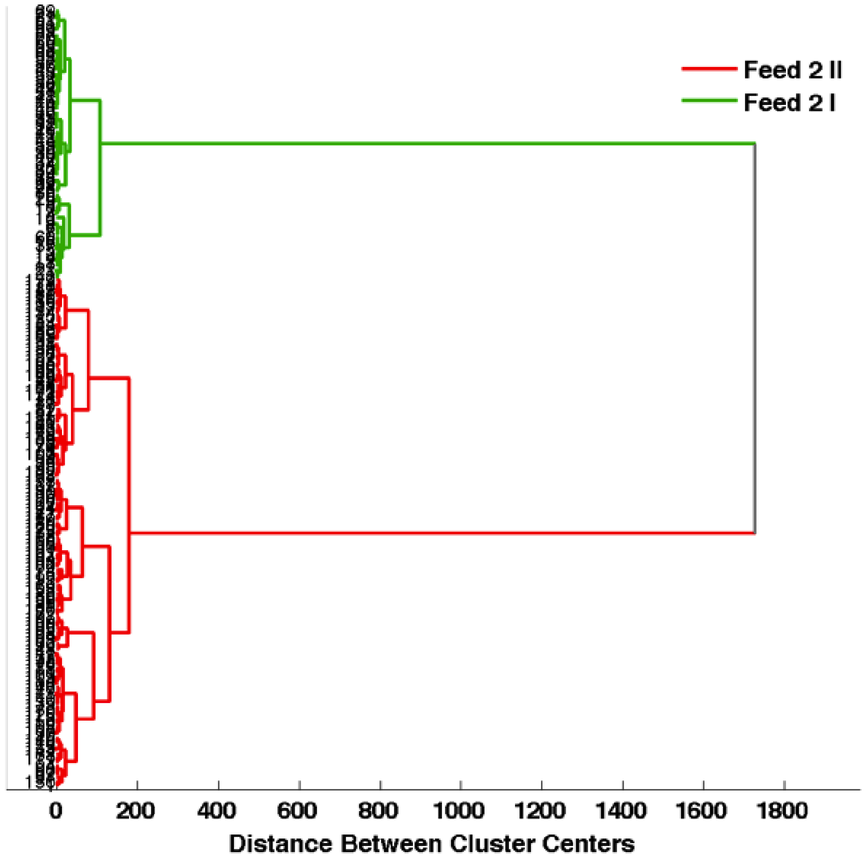
APPENDIX D-2: CLUSTER ANALYSIS ON SOURCE MATERIALS (PEN SURFACE)



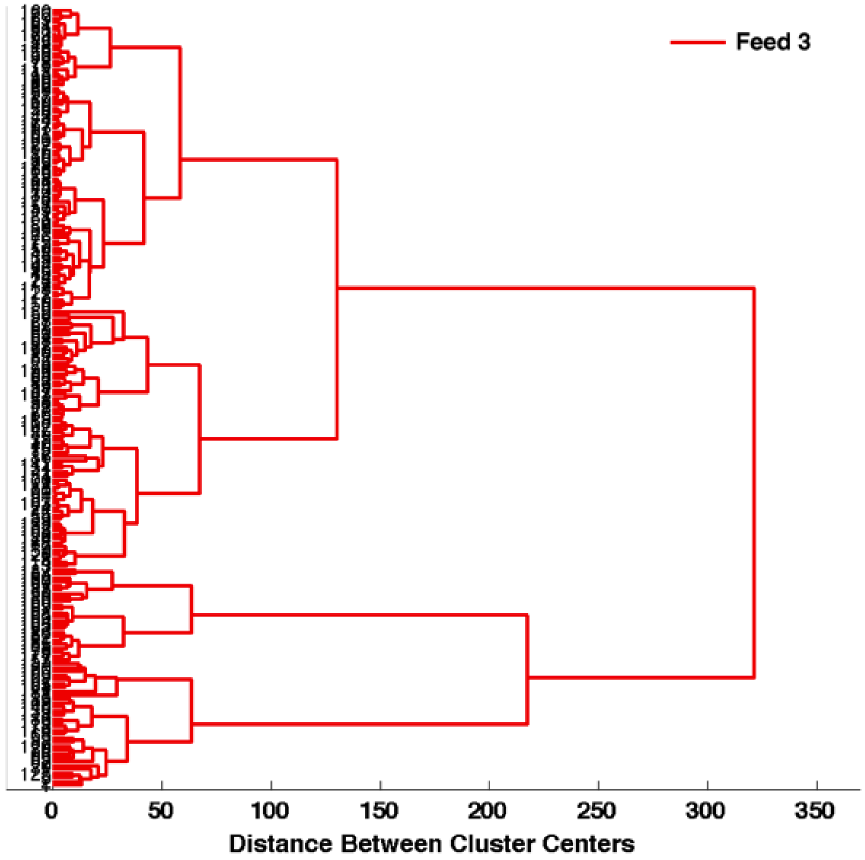
APPENDIX D-3: CLUSTER ANALYSIS ON SOURCE MATERIALS (FEED 1)



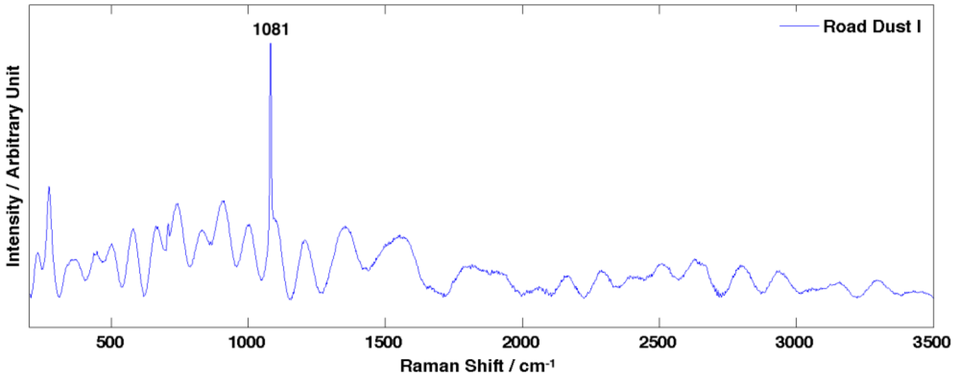
APPENDIX D-4: CLUSTER ANALYSIS ON SOURCE MATERIALS (FEED 2)

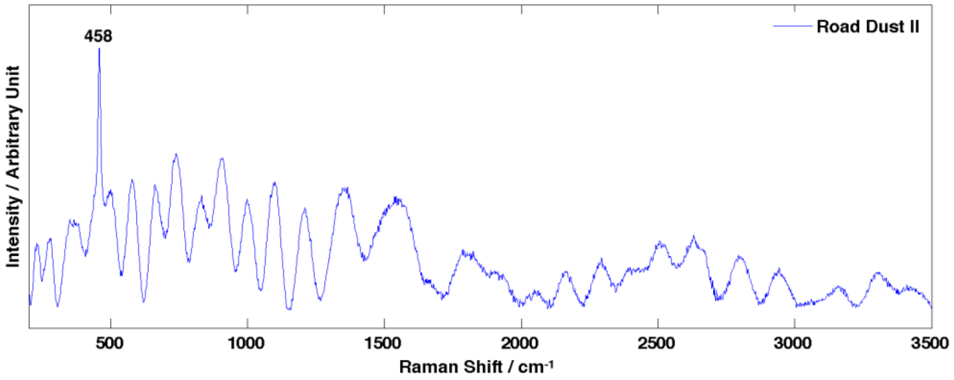


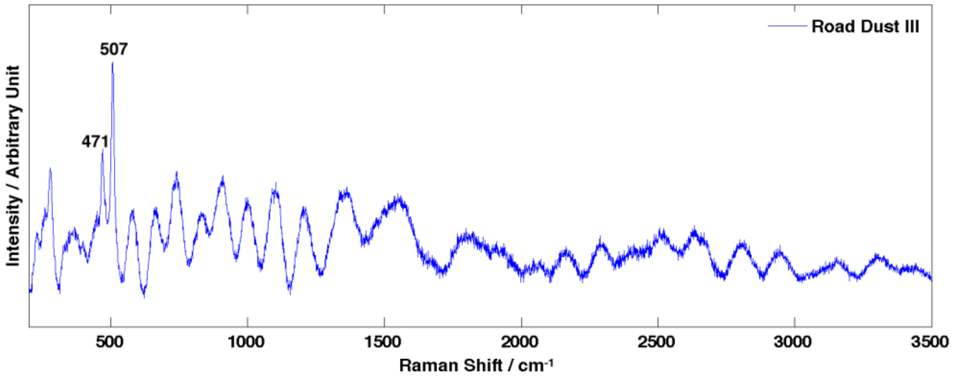
APPENDIX D-5: CLUSTER ANALYSIS ON SOURCE MATERIALS (FEED 3)



APPENDIX E[a]: TYPICIAL SPECTRA OF 9 CLASSES FROM SOURCE MATERIALS

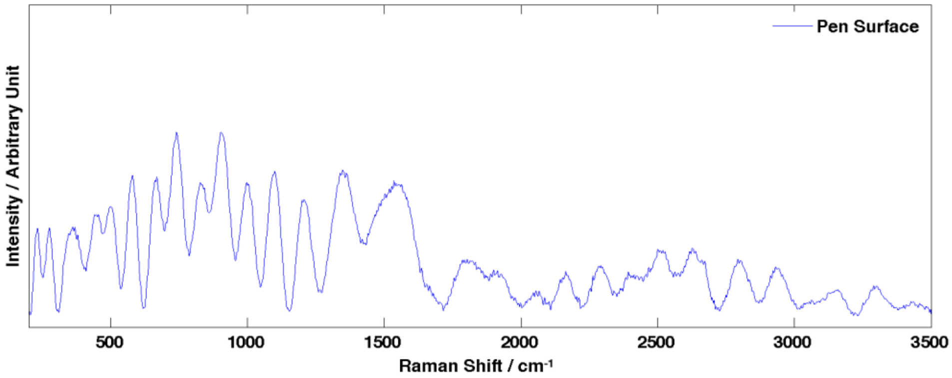


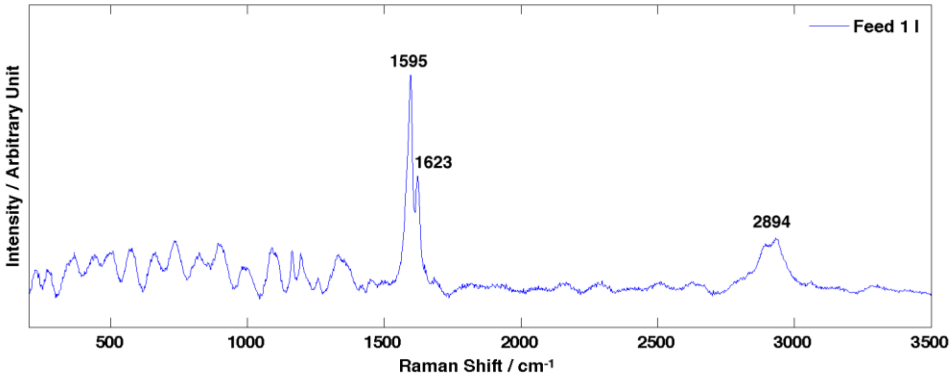


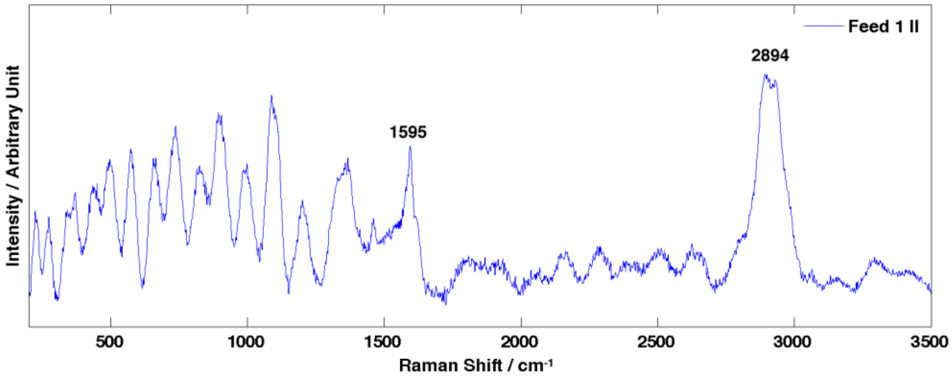


[a] Baseline correction was performed for all spectra to enhance Raman feature.

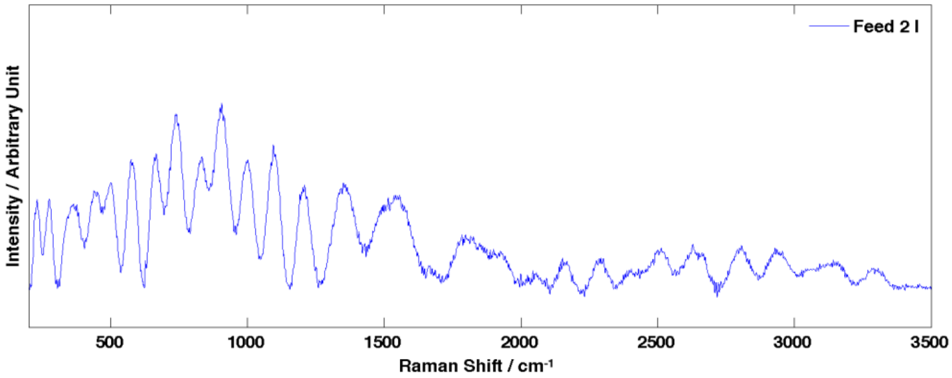
APPENDIX E: TYPICIAL SPECTRA OF 9 CLASSES FROM SOURCE MATERIALS

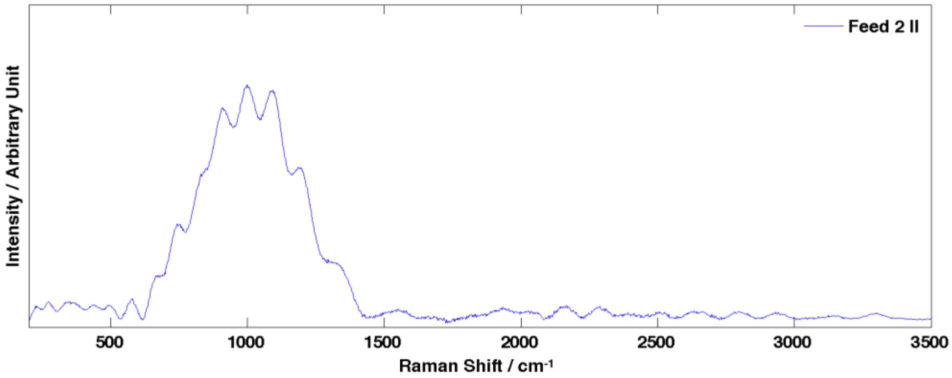


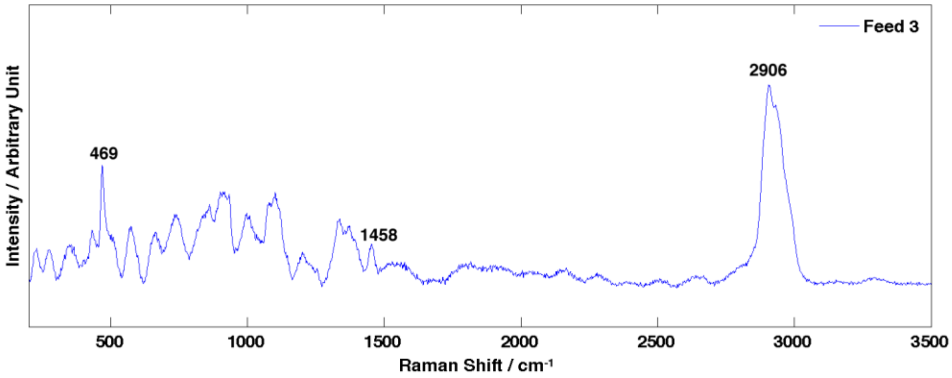




APPENDIX E: TYPICIAL SPECTRA OF 9 CLASSES FROM SOURCE MATERIALS







APPENDIX F: TRAINING GROUP FOR LDA

Classes	**Amount**	**Markers as Raman Shift / cm^{-1}**	**Compounds**
Road Dust I	52	1081	Calcium carbonate[a]
Road Dust II	80	458	Quartz[b]
Road Dust III	66	471 507	Si-O-Si or Si-O-Al bend/stretch[c]
Pen	175	-	-
Feed 1 I	164	1595 1623 2894	Lignin[d]
Feed 1 II	35	1595 2894	Lignin[d]
Feed 2 II	128	~700 to ~1300	-
Feed 3	199	469 1458 2906	Skeletal modes of pyranose ring[e,f] CH_2 bending[e] C-H stretching[e]
Total	899		

[a] on the basis of Hiranuma et al. (2011)
[b] on the basis of Hope et al. (2001)
[c] on the basis of Mernagh (1991)
[d] on the basis of Kihara et al. (2002)
[e] on the basis of Kizil et al. (2002)
[f] on the basis of Cael et al. (1973)

APPENDIX G: PCA-LDA PROCESS

PCA on Training Group (899 spectra)	
PC	Accumulated variance
PC1	0.3323
PC2	0.5943
PC3	0.7151
PC4	0.8135
PC5	0.8755
PC6	0.9007
PC7	0.9151
PC8	0.9289
PC9	0.9391
PC10	0.9448
PC11	0.9502
PC12	0.9548
PC13	0.9574
PC14	0.9593
PC15	0.9609

LDA	
Input	Scores of the first 11 PCs from training group
Error of classification	0.0024

APPENDIX H: FILTER SAMPLES ANALYSIS

	Particle Type[a]				
	Level 2				
Particle #	07/13/11 6am-8am	07/13/11 8am-10am	07/13/11 10am-12pm	07/13/11 12pm-2pm	07/13/11 2pm-4pm
1	4	2	4	1	4
2	4	4	3	4	2
3	4	3	4	4	4
4	3	4	4	4	4
5	4	1	1	9	4
6	4	4	4	4	4
7	1	4	4	4	4
8	4	4	1	4	4
9	4	4	4	4	1
10	4	4	1	4	4
11	4	4	4	4	4
12	4	1	4	1	1
13	4	4	1	3	4
14	1	8	4	2	2
15	4	4	1	4	4
16	4	4	4	4	4
17	4	4	4	4	1
18	4	4	4	4	4
19	1	4	4	6	4
20	4	2	4	4	4
21	4	4	2	1	4
22	4	4	4	1	4
23	4	4	4	4	4
24	4	4	4	4	6
25	4	4	3	4	1
26	4	4	4	4	1
27	4	4	4	3	4
28	4	4	4	4	4
29	4	4	2	4	4
30	2	1	4	4	4

[a] Particle types are: 1-Road Dust I; 2-Road Dust II; 3-Road Dust III; 4-Pen Surface; 5-Feed 1 I; 6-Feed 1 II; 7-Feed 2 II; 8-Feed 3; 9-Unidentified.

APPENDIX H: FILTER SAMPLES ANALYSIS

	Particle Type[a]				
	Level 2				
Particle #	07/13/11 4pm-6pm	07/13/11 6pm-6am	07/14/11 6am-8am	07/14/11 8am-10am	07/14/11 10am-12pm
1	4	4	4	4	4
2	4	8	4	1	4
3	4	4	4	4	4
4	4	4	4	4	3
5	4	4	1	4	4
6	1	3	2	4	4
7	1	4	4	4	4
8	4	4	4	4	4
9	4	4	4	1	4
10	4	8	4	4	4
11	4	4	3	4	4
12	4	4	4	4	4
13	1	4	4	4	4
14	4	4	4	4	4
15	4	8	4	4	4
16	4	4	4	4	4
17	4	4	4	4	4
18	2	4	4	1	4
19	4	4	4	4	4
20	4	4	4	4	4
21	4	4	4	4	4
22	4	4	4	1	4
23	4	4	4	1	4
24	4	4	4	4	4
25	4	4	4	4	4
26	4	4	4	4	2
27	4	2	1	1	4
28	4	4	4	4	4
29	4	4	4	4	1
30	1	4	4	4	4

[a] Particle types are: 1-Road Dust I; 2-Road Dust II; 3-Road Dust III; 4-Pen Surface; 5-Feed 1 I; 6-Feed 1 II; 7-Feed 2 II; 8-Feed 3; 9-Unidentified.

APPENDIX H: FILTER SAMPLES ANALYSIS

	Particle Type[a]			
	Level 2			
Particle #	07/14/11 12pm-2pm	07/14/11 2pm-4pm	07/14/11 4pm-6pm	07/14/11 6pm-6am
1	4	4	4	4
2	4	4	4	4
3	4	4	4	4
4	4	4	4	4
5	4	4	4	4
6	4	4	2	4
7	4	4	4	4
8	4	4	4	4
9	4	1	4	4
10	4	8	4	4
11	4	4	4	4
12	4	4	4	4
13	3	4	4	2
14	4	4	4	4
15	8	4	4	4
16	4	4	4	6
17	4	4	4	4
18	1	4	1	4
19	4	4	4	4
20	4	1	3	4
21	4	2	4	2
22	1	4	4	4
23	4	4	4	4
24	4	1	4	4
25	9	4	8	4
26	4	4	4	9
27	4	1	4	4
28	4	2	4	4
29	4	4	4	4
30	4	4	9	4

[a] Particle types are: 1-Road Dust I; 2-Road Dust II; 3-Road Dust III; 4-Pen Surface; 5-Feed 1 I; 6-Feed 1 II; 7-Feed 2 II; 8-Feed 3; 9-Unidentified.

APPENDIX H: FILTER SAMPLES ANALYSIS

	Particle Type[b]				
	Level 4				
Particle #	07/13/11 6am-8am	07/13/11 8am-10am	07/13/11 10am-12pm	07/13/11 12pm-2pm	07/13/11 2pm-4pm
1	4	4	4	4	4
2	4	4	4	1	4
3	1	4	4	3	4
4	4	4	4	4	4
5	4	4	4	4	1
6	4	4	3	1	4
7	4	4	4	3	6
8	3	4	4	2	2
9	1	4	1	4	4
10	4	2	4	4	2
11	1	4	4	4	4
12	4	4	8	1	4
13	4	4	2	4	4
14	4	2	4	2	3
15	4	2	4	2	4
16	4	4	3	4	4
17	4	4	4	1	4
18	4	2	4	4	4
19	4	4	4	4	1
20	4	4	4	3	1
21	1	4	6	2	4
22	4	4	4	4	4
23	4	4	4	4	4
24	4	4	2	4	4
25	4	2	3	4	4
26	4	4	4	4	4
27	8	2	4	4	4
28	4	3	1	3	4
29	2	3	4	4	4
30	1	4	1	4	4

[b] Particle types are: 1-Road Dust I; 2-Road Dust II; 3-Road Dust III; 4-Pen Surface; 5-Feed 1 I; 6-Feed 1 II; 7-Feed 2 II; 8-Feed 3; 9-Unidentified.

APPENDIX H: FILTER SAMPLES ANALYSIS

	Particle Type[b]				
	Level 4				
Particle #	07/13/11 4pm-6pm	07/13/11 6pm-6am	07/14/11 6am-8am	07/14/11 8am-10am	07/14/11 10am-12pm
1	2	4	4	3	4
2	3	4	4	4	4
3	4	4	4	4	4
4	4	4	4	1	1
5	4	3	4	4	4
6	4	4	4	4	9
7	2	4	1	4	4
8	4	4	2	4	1
9	1	4	4	4	3
10	4	4	4	4	4
11	3	4	4	4	4
12	4	4	4	2	4
13	6	2	4	4	4
14	4	4	1	4	4
15	4	4	4	4	1
16	4	3	4	4	6
17	4	4	4	4	4
18	4	4	4	9	4
19	4	4	3	1	4
20	4	4	4	4	4
21	4	4	3	4	4
22	4	4	4	4	4
23	4	4	4	4	4
24	2	4	4	4	4
25	4	4	1	6	4
26	2	4	3	4	3
27	4	4	4	2	4
28	4	3	4	4	4
29	2	4	2	4	4
30	4	4	4	4	4

[b] Particle types are: 1-Road Dust I; 2-Road Dust II; 3-Road Dust III; 4-Pen Surface; 5-Feed 1 I; 6-Feed 1 II; 7-Feed 2 II; 8-Feed 3; 9-Unidentified.

APPENDIX H: FILTER SAMPLES ANALYSIS

	Particle Type[b]			
	Level 4			
Particle #	07/14/11 12pm-2pm	07/14/11 2pm-4pm	07/14/11 4pm-6pm	07/14/11 6pm-6am
1	4	4	4	4
2	4	4	4	4
3	4	4	4	4
4	4	4	4	4
5	1	2	4	1
6	4	4	9	4
7	4	4	4	4
8	4	4	1	4
9	4	3	4	4
10	4	4	4	4
11	4	4	4	8
12	3	2	4	4
13	4	4	4	4
14	4	4	4	4
15	2	4	4	4
16	4	1	4	1
17	4	4	1	4
18	1	4	4	4
19	1	4	4	4
20	4	4	2	4
21	4	4	4	4
22	4	4	2	4
23	4	4	6	4
24	3	4	4	4
25	4	4	4	4
26	8	2	4	4
27	4	1	4	4
28	4	4	1	4
29	4	4	4	4
30	4	4	8	4

[b] Particle types are: 1-Road Dust I; 2-Road Dust II; 3-Road Dust III; 4-Pen Surface; 5-Feed 1 I; 6-Feed 1 II; 7-Feed 2 II; 8-Feed 3; 9-Unidentified.

APPENDIX H: FILTER SAMPLES ANALYSIS

	Particle Type[c]				
	Upwind				
Particle #	07/13/11 6am-8am	07/13/11 8am-10am	07/13/11 10am-12pm	07/13/11 12pm-2pm	07/13/11 2pm-4pm
1	4	9	4	4	4
2	4	9	9	9	9
3	4	4	4	1	4
4	9	4	4	4	2
5	2	4	4	4	9
6	4	2	4	1	9
7	4	4	9	9	9
8	4	4	4	4	3
9	4	4	4	4	9
10	4	4	4	9	4
11	4	9	4	9	9
12	9	4	4	1	4
13	4	9	4	4	9
14	4	4	3	9	9
15	4	4	9	3	9
16	9	3	9	9	2
17	1	9	4	9	9
18	9	4	1	4	4
19	9	1	9	2	9
20	4	4	9	1	4
21	9	4	9	2	4
22	4	2	9	4	4
23	9	4	4	4	9
24	9	4	9	4	4
25	2	4	9	6	4
26	9	4	4	9	4
27	4	3	9	4	4
28	4	4	4	9	4
29	4	4	4	9	4
30	9	2	4	4	2

[c] Particle types are: 1-Road Dust I; 2-Road Dust II; 3-Road Dust III; 4-Pen Surface; 5-Feed 1 I; 6-Feed 1 II; 7-Feed 2 II; 8-Feed 3; 9-Unidentified.

APPENDIX H: FILTER SAMPLES ANALYSIS

	Particle Type[e]				
	Upwind				
Particle #	07/13/11 4pm-6pm	07/13/11 6pm-6am	07/14/11 6am-8am	07/14/11 8am-10am	07/14/11 10am-12pm
1	4	4	4	4	3
2	4	4	4	9	2
3	4	4	4	4	9
4	1	9	9	9	4
5	4	2	9	9	4
6	9	9	9	4	4
7	4	4	9	4	4
8	4	4	4	4	9
9	9	4	4	4	4
10	9	4	4	9	4
11	9	9	4	4	4
12	4	2	4	4	4
13	4	9	4	2	9
14	4	9	9	4	9
15	4	3	4	1	9
16	9	9	9	4	3
17	9	1	4	4	3
18	4	4	4	4	3
19	9	3	9	9	3
20	9	4	4	4	4
21	9	4	4	9	2
22	9	4	9	4	4
23	4	4	3	9	4
24	4	9	3	2	2
25	4	4	4	4	4
26	4	4	4	4	6
27	9	9	9	4	1
28	9	4	9	9	9
29	3	4	9	4	9
30	9	1	9	2	4

[c] Particle types are: 1-Road Dust I; 2-Road Dust II; 3-Road Dust III; 4-Pen Surface; 5-Feed 1 I; 6-Feed 1 II; 7-Feed 2 II; 8-Feed 3; 9-Unidentified.

APPENDIX H: FILTER SAMPLES ANALYSIS

	Particle Type[c]			
	Upwind			
Particle #	07/14/11 12pm-2pm	07/14/11 2pm-4pm	07/14/11 4pm-6pm	07/14/11 6pm-6am
1	4	4	4	1
2	4	9	4	9
3	4	4	4	4
4	4	4	4	9
5	4	4	9	9
6	4	4	9	1
7	9	4	9	1
8	4	2	1	9
9	4	2	3	1
10	9	3	9	1
11	1	4	4	1
12	1	2	9	9
13	9	3	1	4
14	9	4	3	4
15	9	4	4	4
16	4	9	2	9
17	9	3	4	4
18	3	4	1	9
19	9	3	1	4
20	9	2	4	2
21	1	9	4	2
22	4	4	1	4
23	4	4	9	4
24	4	4	4	2
25	1	4	9	4
26	2	1	4	1
27	1	4	2	3
28	3	4	9	9
29	9	4	1	2
30	4	3	4	4

[c] Particle types are: 1-Road Dust I; 2-Road Dust II; 3-Road Dust III; 4-Pen Surface; 5-Feed 1 I; 6-Feed 1 II; 7-Feed 2 II; 8-Feed 3; 9-Unidentified.

APPENDIX H: FILTER SAMPLES ANALYSIS

	Particle Type[d]					
	Level 2		Level 4		Upwind	
Particle #	03/22/11 10am-12pm	03/23/11 6pm-6am	03/22/11 10am-12pm	03/23/11 6pm-6am	03/22/11 10am-12pm	03/23/11 6pm-6am
1	4	4	3	4	2	3
2	9	4	4	4	3	4
3	4	4	4	3	4	1
4	2	9	1	4	2	4
5	4	4	4	4	9	3
6	4	2	4	3	2	1
7	4	4	9	9	9	9
8	9	4	1	4	9	4
9	4	4	4	4	4	4
10	4	3	4	4	9	4
11	1	9	4	3	4	9
12	1	4	6	4	1	1
13	4	4	4	4	1	4
14	4	1	4	4	1	3
15	4	4	4	4	9	3
16	4	9	4	3	2	9
17	1	4	4	2	4	4
18	3	4	4	4	1	9
19	4	4	9	4	3	3
20	4	4	4	2	9	2
21	4	1	4	4	2	4
22	1	4	1	3	4	2
23	3	4	4	2	1	3
24	4	4	4	4	1	4
25	9	4	4	4	9	9
26	4	4	4	4	9	2
27	2	4	9	4	1	3
28	1	1	4	4	1	1
29	4	4	4	1	9	2
30	1	4	4	4	9	2

[d] Particle types are: 1-Road Dust I; 2-Road Dust II; 3-Road Dust III; 4-Pen Surface; 5-Feed 1 I; 6-Feed 1 II; 7-Feed 2 II; 8-Feed 3; 9-Unidentified.

APPENDIX H: FILTER SAMPLES ANALYSIS

	Fractions of 4 Particle Types			
	Level 2			
	Road Dust	Pen Surface	Feeds	Other
07/13/2011				
6am-8am	0.1667	0.8333	0.0000	0.0000
8am-10am	0.2000	0.7667	0.0333	0.0000
10am-12pm	0.3000	0.7000	0.0000	0.0000
12pm-2pm	0.2333	0.7000	0.0333	0.0333
2pm-4pm	0.2333	0.7333	0.0333	0.0000
4pm-6pm	0.1667	0.8333	0.0000	0.0000
6pm-6am	0.0667	0.8333	0.1000	0.0000
07/13/2011				
6am-8am	0.1333	0.8667	0.0000	0.0000
8am-10am	0.2000	0.8000	0.0000	0.0000
10am-12pm	0.1000	0.9000	0.0000	0.0000
12pm-2pm	0.1000	0.8333	0.0333	0.0333
2pm-4pm	0.2000	0.7667	0.0333	0.0000
4pm-6pm	0.1000	0.8333	0.0333	0.0333
6pm-6am	0.0667	0.8667	0.0333	0.0333
03/22/2011				
10am-12pm	0.3333	0.5667	0.0000	0.1000
03/23/2011				
6pm-6am	0.1667	0.7333	0.0000	0.1000

APPENDIX H: FILTER SAMPLES ANALYSIS

	Fractions of 4 Particle Types			
	Level 4			
	Road Dust	Pen Surface	Feeds	Other
07/13/2011				
6am-8am	0.2333	0.7333	0.0333	0.0000
8am-10am	0.2667	0.7333	0.0000	0.0000
10am-12pm	0.2667	0.6667	0.0667	0.0000
12pm-2pm	0.4000	0.6000	0.0000	0.0000
2pm-4pm	0.2000	0.7667	0.0333	0.0000
4pm-6pm	0.2667	0.7000	0.0333	0.0000
6pm-6am	0.1333	0.8667	0.0000	0.0000
07/13/2011				
6am-8am	0.2667	0.7333	0.0000	0.0000
8am-10am	0.1667	0.7667	0.0333	0.0333
10am-12pm	0.1667	0.7667	0.0333	0.0333
12pm-2pm	0.2000	0.7667	0.0333	0.0000
2pm-4pm	0.2000	0.8000	0.0000	0.0000
4pm-6pm	0.1667	0.7333	0.0667	0.0333
6pm-6am	0.0667	0.9000	0.0333	0.0000
03/22/2011				
10am-12pm	0.1333	0.7333	0.0333	0.1000
03/23/2011				
6pm-6am	0.3000	0.6667	0.0000	0.0333

APPENDIX H: FILTER SAMPLES ANALYSIS

	Fractions of 4 Particle Types			
	Upwind			
	Road Dust	Pen Surface	Feeds	Other
07/13/2011				
6am-8am	0.1000	0.5667	0.0000	0.3333
8am-10am	0.2000	0.6333	0.0000	0.1667
10am-12pm	0.0667	0.5667	0.0000	0.3667
12pm-2pm	0.2333	0.4000	0.0333	0.3333
2pm-4pm	0.1333	0.4667	0.0000	0.4000
4pm-6pm	0.0667	0.5000	0.0000	0.4333
6pm-6am	0.2000	0.5333	0.0000	0.2667
07/13/2011				
6am-8am	0.0667	0.5333	0.0000	0.4000
8am-10am	0.1333	0.6000	0.0000	0.2667
10am-12pm	0.3000	0.4333	0.0333	0.2333
12pm-2pm	0.2667	0.4667	0.0000	0.2667
2pm-4pm	0.3333	0.5667	0.0000	0.1000
4pm-6pm	0.3333	0.4000	0.0000	0.2667
6pm-6am	0.4000	0.3333	0.0000	0.2667
03/22/2011				
10am-12pm	0.5000	0.1667	0.0000	0.3333
03/23/2011				
6pm-6am	0.5333	0.3000	0.0000	0.1667

APPENDIX I: PROGRAM CODE IN MATLAB

PCA on each source materials (lines starting with % in green are comments):

```
% data input with two regions from the spectra
H1=[R.data(:,201:2125)];
T1=[R.data(:,3187:4249)];

% combine the two region
C=[H1 T1];

% PCA command
[pc, score, latent, tsquare] = princomp(C);

% calculate fractions of accumulated variance with increasing number of PC
A=cumsum(latent)./sum(latent);
A(1:15,1)

% plot the scores of selected PCs
subplot(2,2,1)
plot(C*pc(:,1), C*pc(:,2), 'o')
subplot(2,2,2)
plot(C*pc(:,1), C*pc(:,3), 'o')
subplot(2,2,3)
plot(C*pc(:,2), C*pc(:,3), 'o')
subplot(2,2,4)
plot(C*pc(:,1), C*pc(:,4), 'o')

% output scores for selected PCs
D=C*pc(:,1:6);
save('PCA1scoreRoad.mat', 'D')
```

PCA-LDA process (lines starting with % in green are comments):

```
% data input with two regions from the spectra in training group
H1=[R1.data(:,201:2125)];
T1=[R1.data(:,3187:4249)];
H2=[R2.data(:,201:2125)];
T2=[R2.data(:,3187:4249)];
H3=[R3.data(:,201:2125)];
T3=[R3.data(:,3187:4249)];
H4=[P.data(:,201:2125)];
T4=[P.data(:,3187:4249)];
H5=[F11.data(:,201:2125)];
T5=[F11.data(:,3187:4249)];
```

APPENDIX I: PROGRAM CODE IN MATLAB

```
H6=[F12.data(:,201:2125)];
T6=[F12.data(:,3187:4249)];

% Feed 2 I is excluded from training group
%{
H7=[PreProFeed31.data(:,201:2125)];
T7=[PreProFeed31.data(:,3187:4249)];
%}
H8=[F32.data(:,201:2125)];
T8=[F32.data(:,3187:4249)];
H9=[F5.data(:,201:2125)];
T9=[F5.data(:,3187:4249)];

% combine the two region
C1=[H1,T1];
C2=[H2,T2];
C3=[H3,T3];
C4=[H4,T4];
C5=[H5,T5];
C6=[H6,T6];
% Feed 2 I is excluded from training group
%{
C7=[H7,T7];
%}
C8=[H8,T8];
C9=[H9,T9];

% Combine all spectra to form training group as C
C=[C1;C2;C3;C4;C5;C6;C8;C9];

% PCA on training group
[pc, score, latent, tsquare] = princomp(C);

% calculate fractions of accumulated variance with increasing number of PC
A=cumsum(latent)./sum(latent);
A(1:15,1)

% data input from unknown spectra
FH1=[L.data(:,201:2125)];
FT1=[L.data(:,3187:4249)];

% combine two regions
FC1=[FH1,FT1];
```

APPENDIX I: PROGRAM CODE IN MATLAB

```
% transform the unknown to PC space with selected PCs
S1=FC1*pc(:,1:11);

% specify classes for each of spectra in training group
group = zeros(890,1);
group(1:52,1)=1;
group(53:132,1)=2;
group(133:198,1)=3;
group(199:373,1)=4;
group(374:537,1)=5;
group(538:572,1)=6;
group(573:700,1)=7;
group(701:899,1)=8;

% LDA with selected PCs as input for training group; S1 is to be classified
[class,err,POSTERIOR,logp,coeff] = classify(S1,C*pc(:,1:11),group);

% output of classification for the unknown
class

% error of classification
err

% plot training group in LD space
LD1=[C*pc(:,1:11)]*coeff(1,2).linear;
LD2=[C*pc(:,1:11)]*coeff(7,8).linear;
LD3=[C*pc(:,1:11)]*coeff(7,8).linear;
LD4=[C*pc(:,1:11)]*coeff(4,5).linear;
LD5=[C*pc(:,1:11)]*coeff(3,4).linear;
LD6=[C*pc(:,1:11)]*coeff(1,2).linear;
LD7=[C*pc(:,1:11)]*coeff(4,6).linear;
LD8=[C*pc(:,1:11)]*coeff(7,8).linear;
plot3(LD1(1:52,1), LD2(1:52,1), LD5(1:52,1), 'o',...
    LD1(53:132,1), LD2(53:132,1), LD5(53:132,1), 's',...
    LD1(133:198,1), LD2(133:198,1), LD5(133:198,1), 'd',...
    LD1(199:373,1), LD2(199:373,1), LD5(199:373,1), '*',...
    LD1(374:537,1), LD2(374:537,1), LD5(374:537,1), '^',...
    LD1(538:572,1), LD2(538:572,1), LD5(538:572,1), 'v',...
    LD1(573:700,1), LD2(573:700,1), LD5(573:700,1), 'x',...
    LD1(701:899,1), LD2(701:899,1), LD5(701:899,1), '+')
subplot(2,2,1)
plot(LD1(1:52,1), LD2(1:52,1), 'o',...
   LD1(53:132,1), LD2(53:132,1), 's',...
   LD1(133:198,1), LD2(133:198,1), 'd',...
```

APPENDIX I: PROGRAM CODE IN MATLAB

```
    LD1(199:373,1), LD2(199:373,1), '*',...
    LD1(374:537,1), LD2(374:537,1), '^',...
    LD1(538:572,1), LD2(538:572,1), 'v',...
    LD1(573:700,1), LD2(573:700,1), 'x',...
    LD1(701:899,1), LD2(701:899,1), '+')
subplot(2,2,2)
plot(LD3(1:52,1), LD4(1:52,1), 'o',...
    LD3(53:132,1), LD4(53:132,1), 's',...
    LD3(133:198,1), LD4(133:198,1), 'd',...
    LD3(199:373,1), LD4(199:373,1), '*',...
    LD3(374:537,1), LD4(374:537,1), '^',...
    LD3(538:572,1), LD4(538:572,1), 'v',...
    LD3(573:700,1), LD4(573:700,1), 'x',...
    LD3(701:899,1), LD4(701:899,1), '+')
subplot(2,2,3)
plot(LD5(1:52,1), LD6(1:52,1), 'o',...
    LD5(53:132,1), LD6(53:132,1), 's',...
    LD5(133:198,1), LD6(133:198,1), 'd',...
    LD5(199:373,1), LD6(199:373,1), '*',...
    LD5(374:537,1), LD6(374:537,1), '^',...
    LD5(538:572,1), LD6(538:572,1), 'v',...
    LD5(573:700,1), LD6(573:700,1), 'x',...
    LD5(701:899,1), LD6(701:899,1), '+')
subplot(2,2,4)
plot(LD7(1:52,1), LD8(1:52,1), 'o',...
    LD7(53:132,1), LD8(53:132,1), 's',...
    LD7(133:198,1), LD8(133:198,1), 'd',...
    LD7(199:373,1), LD8(199:373,1), '*',...
    LD7(374:537,1), LD8(374:537,1), '^',...
    LD7(538:572,1), LD8(538:572,1), 'v',...
    LD7(573:700,1), LD8(573:700,1), 'x',...
    LD7(701:899,1), LD8(701:899,1), '+')
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