

## Utilizing single particle Raman microscopy as a non-destructive method to identify sources of PM<sub>10</sub> from cattle feedlot operations

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### HIGHLIGHTS

- ▶ Sources of PM<sub>10</sub> were examined at a commercial cattle feedlot.
- ▶ Raman microscopy was used to analyze potential source materials.
- ▶ Developed multivariate statistical model to identify PM<sub>10</sub> sources.
- ▶ Manure and unpaved roads were two major sources of PM<sub>10</sub>.

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### ABSTRACT

Emissions of particulate matter (PM) from animal feeding operations (AFOs) pose a potential threat to the health of humans 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 as a non-destructive method to quantify the contributions of source materials to PM<sub>10</sub> emitted from a large cattle feedlot. Raman spectra from potential source materials (dust from unpaved roads, manure from pen surface, and cattle feed) were compiled to create a spectral library. Multivariate statistical analysis methods were used to identify specific groups composing the source library spectra and to construct a linear discriminant function to identify the source of particles collected on PM<sub>10</sub> sample filters. Cross validation of the model resulted in 99.76% correct classification of source spectra in the training group. Source characterization results from samples collected at the cattle feedlot over a two-day period indicate that manure from the cattle pen surface contributed an average of 78% of the total PM<sub>10</sub> particles, and dust from unpaved roads accounted for an average of 19% with minor contributions from feed. Results of this work are promising and provide support for further investigation into an innovative method to identify agricultural PM<sub>10</sub> sources accurately under different meteorological and management conditions.

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### 1. Introduction

Decades of research have shown that exposure to particulate pollution can lead to health problems, including asthma, lung cancer, and cardiovascular diseases (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). Particles with equivalent aerodynamic diameter of  $\leq 10$   $\mu\text{m}$  are often classified as PM<sub>10</sub>. Inhalable coarse particles are generally classified as between 10 and 2.5  $\mu\text{m}$  in diameter, PM<sub>10–2.5</sub>, and fine particles are smaller than 2.5  $\mu\text{m}$  in diameter, PM<sub>2.5</sub>. 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 (VOC)

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including odorous gases, and fugitive dust containing particulate matter (PM) of different classes (Blunden and Aneja, 2008; Cambra-López et al., 2010; Howard et al., 2010; Trabue et al., 2011). Particles emitted from AFOs carry bacteria, fungi, and endotoxins and can cause various respiratory problems in livestock as well as humans (Dungan, 2010; Heederik et al., 2007; Von Essen and Auvermann, 2005). Dust and odor emissions generally have the greatest impact on local air quality, while other pollutants like ammonia and reactive VOCs can influence regional air quality (National Research Council, 2003).

Emissions measurements of air pollutants from 25 sites over 2 years have recently been released by the United States Environmental Protection Agency (US EPA) National Air Emissions Monitoring Study (US EPA, 2011). Other studies have also found significant PM<sub>10</sub> emission from AFOs (Bunton et al., 2007; Cambra-López et al., 2010; Fabbri et al., 2007; Guo et al., 2011; Purdy et al., 2010; Redwine et al., 2002). Concerns over emissions from these AFOs may lead to stricter state or federal regulations for producers. While the Natural Resources Conservation Service (NRCS) has already developed a number of conservation practices that producers can use to reduce negative impacts on air quality (NRCS, 2011), improved practices will likely be required. These new environmental and agronomic practices will require information on PM size distribution, emission source identification, and source apportionment.

Studies have been conducted to develop and compare methodologies and instruments for quantification of PM concentrations and particle size distributions at AFOs (Buser et al., 2007, 2008; Guo et al., 2009; Wanjura et al., 2005); however, no standard methods exist to quantify the distribution of sources in downwind PM<sub>10</sub> samples. Lange et al. (2009) proposed a method using neutron activation analysis results combined with multivariate statistical analyses and US EPA's Chemical Mass Balance model to estimate the fraction of PM from a cattle feedlot. However, the method required complicated sample pre-treatment and destruction of PM samples.

In the recent San Joaquin Valley Fugitive Dust Characterization Study, surface soil samples were collected and analyzed by gas chromatography–mass spectrometry to identify distinctive molecular marker compounds (Rogge et al., 2006). Others have examined six types of geological dust in the San Joaquin Valley, including those from feedlot surfaces, using 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 and did not address the analysis of PM from ambient air.

Raman microscopy is a powerful technique for chemical analysis, and when combined with an optical microscope, spectral information can be obtained from a very small sample. This technique has the potential to analyze and characterize individual atmospheric particles. Scientists have used Raman microscopy to collect spectra from ambient air particles, including carbonaceous PM, diesel soot, humic-like substances, and inorganic compound 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 potential use in the present study.

In 2010–2011, a series of intensive field air sampling campaigns were conducted at a large commercial cattle feedlot in Kansas. The project was designed to develop accurate and simultaneous feedlot emission data of PM, selected volatile organic compounds, and greenhouse gases. Results from earlier studies conducted at the same site have provided qualitative observations and have indicated animal activity as the primary mechanism for PM emission

from the feedlot (Guo et al., 2011; Razote et al., 2007). The unpaved roads within and around the facility and outdoor feed processing are other potential sources of dust. In addition, previous studies showed that periodic water sprinkling decreased PM emissions significantly (Auvermann et al., 2006; Bonifacio et al., 2011; Pechan, 2006).

As part of the 2010–2011 air sampling campaigns, the present study was designed to develop a statistically robust, non-destructive method to determine the source profile of PM<sub>10</sub> particles emitted from the cattle feedlot. A Raman spectral library was compiled from samples of potential source materials, namely unpaved road dust, manure from the pen surface and components of the cattle feed. Multivariate statistical analysis methods were then used to construct a linear discriminant function to identify the source of particles collected on PM<sub>10</sub> ambient air sample filters based on their Raman spectra. Source profile results were developed from the analysis of PM<sub>10</sub> sample filters that were at the feedlot collected during a 48-h period in July 2011. Results suggest that this approach could be a useful tool for identifying and for determining the intensity or fraction of different PM sources from AFOs or other agricultural operations under different environmental conditions or under different management practices.

## 2. Materials and methods

### 2.1. Study site and PM<sub>10</sub> air sampling

The study cattle feedlot, which was surrounded by agricultural production fields, was located in Kansas (USA) and had a total area of approximately 850,000 m<sup>2</sup> and a capacity of 30,000 head of cattle (Fig. 1). Unpaved roads encircled and crossed the feedlot in a grid pattern and made up approximately 16% of the total area. Feed trucks delivered feed to the pens three times a day from a feed mill located at the southwest corner of the feedlot. The feed was

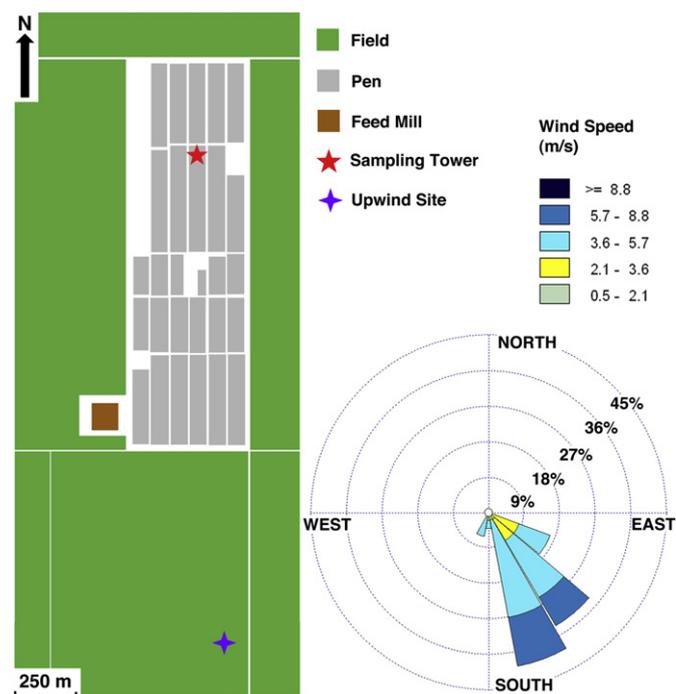


Fig. 1. Layout of the cattle feedlot used in the present study showing the locations of samplers and a wind rose diagram reflecting wind direction conditions during sample collection.

processed and mixed continuously and was loaded onto the feed trucks using an overhead truck loader outside the mill. The feed ration used at the feedlot was consistent over time and space. The soils at the feedlot were generally loamy fine sands and fine sandy loams. Pens were scraped and manure was removed from the feedlot facility annually. Measured precipitation at the site in 2010 was 488 mm. The typical prevailing wind direction was south–southeast in the summer and north–northwest in the winter; annual average wind speed for 2010 was  $16 \text{ km h}^{-1}$ . The producer utilized tanker trucks with sprinkler guns to apply water on the pens, alleys, and roads for dust control during each day of the sampling period.

Samples utilized for the present study were collected over a 48-h period beginning July 13, 2011 at 6:00. Six 2-h  $\text{PM}_{10}$  samples were collected each day from 6:00 to 18:00, and one 12-h  $\text{PM}_{10}$  sample was collected from 18:00 to 6:00 the next day.  $\text{PM}_{10}$  samples were collected simultaneously from two locations: the main sampling tower and the upwind site (Fig. 1). The sampling tower was mounted on a cement platform in the middle of a cattle pen in the middle of the feedlot. The tower was protected by a metal fence of approximately 1.5-m height. The upwind site was located at 880 m south of the feedlot. Wind conditions during sample collection were almost exclusively out of the south–southeast, and the site had no large obstructions to alter the air flow from the upwind site to the sampling tower.

Air samples were collected from the main sampling tower within the feedlot at 4 heights: 1.83 m, 3.75 m, 5.27 m, and 7.62 m. At each level of the main tower, a low-volume sampler (2100 Mini-Partisol, Thermo fisher Scientific, Franklin, Massachusetts) was used to collect particles through a  $\text{PM}_{10}$  size-selective inlet. A sampler of the same type was used at upwind sites, where samples were collected at 2 m only. Polytetrafluoroethylene (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 after mass concentration measurement.

## 2.2. Source materials sampling and preparation

Materials to be used in compiling a library of potential  $\text{PM}_{10}$  sources were collected directly from the feedlot at the time of air sampling. Fresh manure was collected from the pen surface and dried at  $105^\circ\text{C}$  for 12–16 h before being ground and sieved to fine particles (U.S. Standard Sieve Series A.S.T.M. E-11, Sieve No. 850, Microns 10). Individual sampling was conducted at 8 different locations from the unpaved road surrounding the feedlot and road dust was collected from road surface. The sampled road dust was combined, mixed and sieved with the same sieve used for manure samples. Three different feed ration components, corn stover, silage/hay, and corn grain, were collected from stockpiles at the feed mill located at the feedlot. Each feed sample was mixed well and ground into a fine powder without sieving. Source materials were subsequently placed on clean PTFE filters for single particle Raman measurement in order to obtain spectra characteristic of each source.

## 2.3. Raman microspectroscopy and spectral data 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  $\text{PM}_{10}$  particles on the filters and from source materials.  $\text{PM}_{10}$  particles were observed under the  $50\times$  objective and particles with diameter of 5–10  $\mu\text{m}$  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 exposure time of 1 s, and an accumulation number of 10 were used. All spectra were recorded over the range of  $200\text{--}3500 \text{ cm}^{-1}$  with a resolution of  $0.75 \text{ cm}^{-1}$  using LabSpec (HORIBA Ltd., Tokyo, Japan). Microscopic focus was adjusted to the surface of source material particles and PM on ambient samples to avoid interference from the PTFE filter material in Raman analysis.

## 2.4. Spectral data analysis

Chemometric methods were reported to be effective for discrimination and classification of Raman spectral 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 analysis methods were employed and combined to classify the spectra in this study. Principal component analysis (PCA) was performed as a data extraction method to reduce the number of variables of spectral data. Cluster analysis (CA) was used to investigate possible presence of multiple classes within one source material. Linear discriminant analysis (LDA) was applied to classify each unknown spectrum into one of the well-defined classes, or as an unidentified source.

All the spectra were despiked using the Horiba LabSpec software. Before any statistical analyses were carried out, 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, 1998) as the algorithm. PCA and LDA were coded in MATLAB.

The first derivative of each spectrum was taken (Savitzky–Golay algorithm, filter width: 15, polynomial order: 2, derivative order: 1), and then normalized by Standard normal variate scaling (scaling offset: 0) to remove the multiplicative effect. Subsequently, two regions of the spectrum,  $250\text{--}1800 \text{ cm}^{-1}$  and  $2600\text{--}3400 \text{ cm}^{-1}$ , were combined to represent the spectrum. This pre-processing procedure was applied prior to performing any multivariate statistical analyses.

Statistical analysis using *t*-tests were used to compare means of  $\text{PM}_{10}$  mass concentrations and source fractions results. Analyses were conducted using MATLAB, all *t*-tests were two-tailed with specified significance levels, *p*.

## 3. Results and discussion

### 3.1. Raman spectra of source materials

To identify and designate specific classes for the spectra, the first few PCs (principal components) that accounted for more than 90% variance in PCA were selected for cluster analysis. One hundred ninety-eight spectra were collected from the road dust particles. 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 from the 6 PCs of the 198 spectra as input. The dendrogram from cluster analysis (Fig. 2) indicated that three clusters could be distinguished with large distance values between each other. Visual observation of complete spectral data also indicated that there were three types of spectra within Road Dust group with unique sharp Raman peaks at specific wavenumbers (Fig. 3). This indicated that the road dust sample contained three different types of particles. Three classes were designated as Road Dust 1 with Raman peak at  $1081 \text{ cm}^{-1}$ ; Road Dust 2 with peak at  $458 \text{ cm}^{-1}$ ; and Road Dust 3 with peaks at

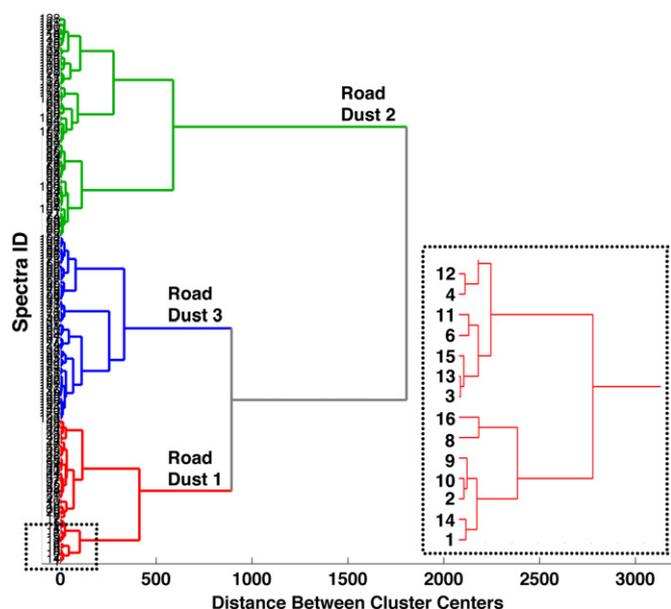


Fig. 2. Dendrogram resulting from the hierarchical cluster analysis of 198 Raman spectra of road dust material into three distinct groups. A section of the dendrogram is expanded for closer examination. Numbers listed on the y-axis of the dendrogram are identification codes for specific spectra and do not have any other significance.

471  $\text{cm}^{-1}$  and 507  $\text{cm}^{-1}$  (Table 1). Every spectrum from the road dust group was categorized as one of these three types.

For the manure material, the first 15 PCs only accounted for 44% of the total variance and cluster analysis with scores of the 15 PCs yielded poorly separated clusters. Furthermore, visual observation found no distinct difference among the 175 spectra. These all suggested that there were no different classes within the manure. For corn stover and silage/hay materials, two classes were found within each of the groups, while spectra of corn grain formed a single cluster. Therefore, 9 classes were identified and every spectrum from the source materials was assigned to a specific class (Fig. 3).

**Table 1**  
Spectral markers for different source classes and chemical compound or functional group assignment.

Source classes	Markers as Raman shift/ $\text{cm}^{-1}$	Compounds/functional group
Road Dust 1	1081	Calcium carbonate <sup>a</sup>
Road Dust 2	458	Quartz <sup>b</sup>
Road Dust 3	471 507	Si–O–Si or Si–O–Al bend/stretch <sup>c</sup>
Manure	–	–
Corn Stover 1	1595 1623 2894	Lignin <sup>d</sup>
Corn Stover 2	1595 2894	Lignin <sup>d</sup>
Silage/Hay 1	–	–
Silage/Hay 2	~700 to ~1300	–
Corn Grain	469	Skeletal modes of pyranose ring <sup>e,f</sup> CH <sub>2</sub> bending <sup>e</sup> C–H stretching <sup>e</sup>
	1458 2906	

<sup>a</sup> Hiranuma et al. (2011).

<sup>b</sup> Hope et al. (2001).

<sup>c</sup> Mernagh (1991).

<sup>d</sup> Kihara et al. (2002).

<sup>e</sup> Kizil et al. (2002).

<sup>f</sup> Cael et al. (1973).

PCA and visual inspection indicated that two classes, Manure and Silage/Hay 1, were indistinguishable in their Raman spectra. This result is reasonable since manure typically contains some undigested feed. It appears that undigested Silage/Hay is a significant component in the manure. While more investigation of this finding is needed, for the purpose of the present study, Manure and Silage/Hay 1 were combined to a single class called 'Manure'. Except for these two classes, unique peaks or regions were observed for all the other classes and were designated as markers (Table 1).

### 3.2. Classification of unknown spectra

LDA served to classify unknown spectra with respect to the identified sources as a supervised classification method. LDA

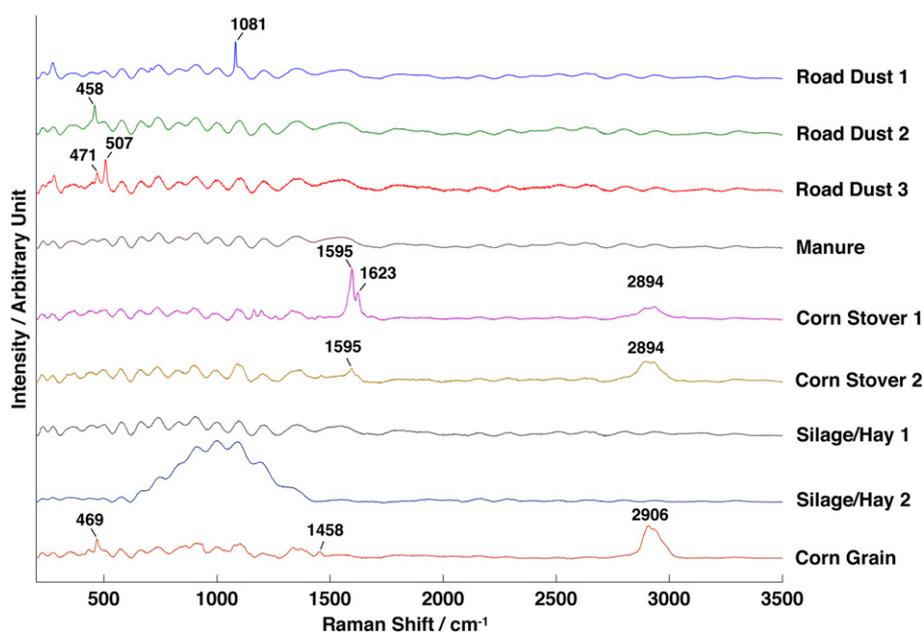


Fig. 3. Representative Raman spectra of 9 classes identified from source materials with unique spectral peaks indicated. Each spectrum displayed represents the complete spectral data collected from one particle with baseline correction. Labeled peaks were observed in all spectra included in each specific class.

method was accomplished using a training group comprised of all the source material spectra classified in the PCA–CA process. The resulting training group consisted of 899 spectra from 8 classes.

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 8 classes of spectra were well separated within the LDA space (Fig. 4). Evaluation of the LDA performance returned an estimated error rate of 0.0024 from internal validation, or a correct classification of the training group spectra at 99.76%.

### 3.3. Determination of number of particles for analysis from statistical simulation

During the method development, a statistical simulation approach was utilized in order to determine the minimum number of particle analyses needed to accurately characterize the source distribution of particles on a sample filter. Setting an upper limit of 100 particle analyses, four filters were used as test samples. One hundred randomly-selected particles from 5 to 10  $\mu\text{m}$  were analyzed, and the source of each particle was determined using the multivariate statistical method described above. The source distribution developed from the analysis of the 100 particles was assumed to be the ‘true’ distribution for that filter. The statistical simulation approach was used to determine the minimum number of particle analyses needed to achieve a statistically equivalent source distribution.

During each statistical simulation, the list of 100 particles with their identified source was randomly sampled up to a specific number of particles. Particles were sampled, one at a time; each time replacing the sampled particle before sampling the next one. The source distribution of the sampled particles was determined and compared with the ‘true’ source distribution for that filter. For each filter, 500 simulations were carried out at four sampling levels: 15, 20, 25, and 30 particles. The simulations were performed using SAS v9.3 (SAS Institute, Inc., Cary, North Carolina, USA).

For each simulation, the absolute difference between the proportion of each source in the sampled data and in the ‘true’ distribution was calculated. The maximum absolute difference was

used to represent how accurately the distribution of the simulated sampling of particles compared with the ‘true’ source distribution. Distributions were assumed statistically equivalent if the maximum absolute difference ( $\delta$ ) was  $\leq 10\%$ . For each filter and each sampling level, the percentage of the 500 simulations for which  $\delta \leq 10\%$  was calculated. This percentage was the statistical power (i.e., probability) that the simulated sample, with the specified number of particles, would be statistically equivalent to the ‘true’ particle source distribution. Results indicated that 25–30 particles are sufficient 90% of the time to provide equivalent distributions (Table 2). Therefore, the source distribution of all sample filters was based on the analysis of 30 randomly selected particles.

### 3.4. PM<sub>10</sub> source profiles from feedlot

Method performance was examined under conditions when the feedlot was likely an emission source of PM<sub>10</sub> to the atmosphere. Source profiles were developed for PM<sub>10</sub> samples collected from 6:00 July 13 to 6:00 July 15, 2011. Conditions in the region were dry with only one rain event of 0.25 mm in the two weeks prior to sample collection. Weather conditions during the sampling period were typical of Kansas in the summer. Temperatures ranged from 23 °C in the early morning hours to a maximum of 37 °C in the afternoon (Fig. 5). Relative humidity conditions were lowest in the afternoon (21–31%) increasing in the evening with lower temperatures (82–85%). Wind conditions were moderate, averaging 4.8 m s<sup>-1</sup> from the south–southeast (Fig. 1). Over the 48 h, measured PM<sub>10</sub> concentrations (Fig. 6A) ranged from 25 to 83  $\mu\text{g m}^{-3}$  at the upwind station. Concentrations measured from the sampling tower averaged  $150 \pm 38$ ,  $134 \pm 37$ ,  $102 \pm 24$ ,  $84 \pm 24 \mu\text{g m}^{-3}$  at the four sampling heights from 1.8 to 7.6 m, respectively. Average PM<sub>10</sub> concentrations measured at the sampling tower were significantly different ( $p < 0.05$ ) from the upwind station for each height indicating that the feedlot is a source of PM<sub>10</sub> during this period.

Filter samples were analyzed from two of the four sampling heights (3.7 and 7.6 m) and the upwind station for each sampling period during the 48 h. Using the validated method, 30 particles were randomly selected from each of the filters, analyzed by Raman microscopy, and classified by the PCA–LDA model. Since the PCA–LDA model was not able to detect classes other than those in the training group, a separate source class of ‘Other’ was created for such observations (identified by visual inspection of the operator). All the PM<sub>10</sub> particles were classified as one of the four classes, which were Road Dust, Manure, Feed, and Other, and source distribution was calculated for each filter.

Results from individual samples collected over the two days indicate that particles from Manure were by far the most prevalent

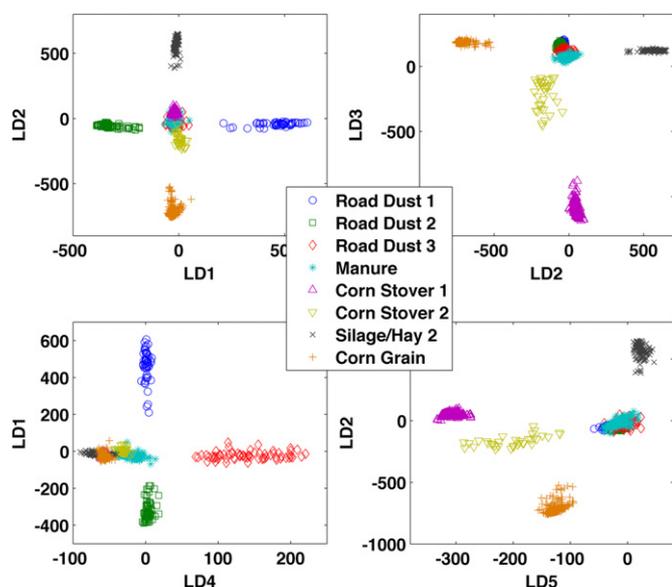


Fig. 4. Representative projections of spectra ( $n = 899$ ) from training group in linear discriminant space illustrating separation of different source groups.

Table 2

Results of statistical simulation analysis of 100 classified particles from four different ambient PM<sub>10</sub> filter samples collected in July 2011 from the feedlot sampling tower. The statistical power represents the percentage of simulations at four different sampling rates whereby the source distribution from the sampled group was indistinguishable from the true distribution based on an allowed  $\delta$  value of 10%.

Filter #	Statistical power (%) <sup>a</sup>			
	15 particles	20 particles	25 particles	30 particles
1	67.00	83.20	86.80	94.20
2	91.80	93.80	94.40	95.20
3	82.40	85.40	90.40	94.60
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

<sup>a</sup> Based on 500 simulations.

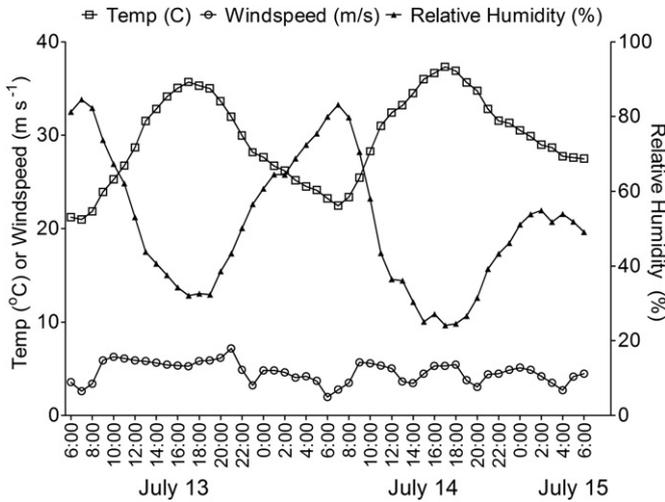


Fig. 5. Results of hourly temperature, relative humidity, and wind speed measurements from the feedlot from 6:00 July 13 to 6:00 July 15, 2011.

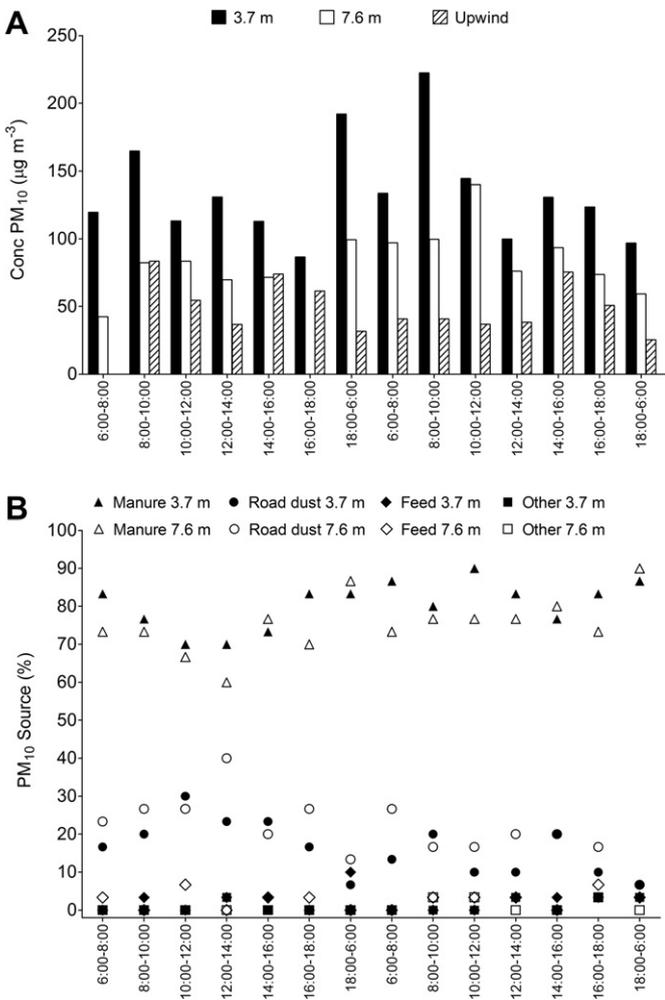


Fig. 6. PM<sub>10</sub> mass concentrations and source fraction results collected from 6:00 July 13 to 6:00 July 15, 2011. The overnight sampling time is 12 h; whereas, all the other samples were collected over two hours.

in all samples ( $\geq 60\%$ ) from both levels of the main sampling tower (Fig. 6B) followed by Road Dust (between 6% and 40%) and then Feed and Other (all  $< 5\%$ ). The overall average fraction of PM<sub>10</sub> particles that were classified as Manure was  $80 \pm 6\%$  and  $75 \pm 7\%$  for the 3.7 and 7.6 m height samples, respectively (Fig. 7). Road Dust particles were found to contribute  $16 \pm 7\%$  and  $21 \pm 8\%$  to the two heights, respectively. Feed particles and those in the other category were only occasionally detected, usually only 1–2 particles in 30 were found, resulting in average source fractions of  $\leq 3\%$  for the two sampling heights.

Source distribution results for the upwind station also indicate a large contribution from Manure particles,  $50 \pm 9\%$ , which was significantly lower ( $p < 0.0001$ ) than observed at the two sampling heights of the main tower. Road dust contributed a similar fraction to the upwind station  $20 \pm 11\%$  compared to the main tower samples ( $p > 0.05$ ). Only two feed particles were found in any of the upwind sample filters, but there were many more unidentified particles observed at this station resulting in an Other source fraction averaging  $29 \pm 9\%$ . The relative similarity in source distribution at the upwind station and the feedlot was not surprising because the wind direction is not constant 100% of the time, and particles from the feedlot may be transported to the upwind site. The same type of gravel roads were also present near the upwind site, probably contributing to the observed road dust particles.

Examining the source fraction results from the 3.7 m height on a temporal scale indicates that under these conditions, the contribution from Manure particles is relatively stable, but the Road Dust particles appear to be increasing during the day (Fig. 6B). This is likely a response to use of trucks to deliver feed or conduct feedlot maintenance, but wind speeds were also generally higher during the day potentially leading to greater road dust emission. At this feedlot, the producer utilizes water trucks to sprinkle water on the feedlot pens, road, and alleys as a dust control management practice. It appears from this work that some moderate reduction in PM<sub>10</sub> emissions could be achieved by applying water more frequently to the roads during dry, windy periods.

Finally, samples from all four sampling heights that were collected overnight on July 13 were analyzed in detail at 100 particles per filter. For this set of samples the fraction of Manure particles was generally higher than the day results, ranging from 89 to 91%, with corresponding lower contributions from Road Dust particles at 4 to 6%. As expected, road dust contributions were lower since these were overnight samples with less traffic on the roads. Further analysis of samples collected under different

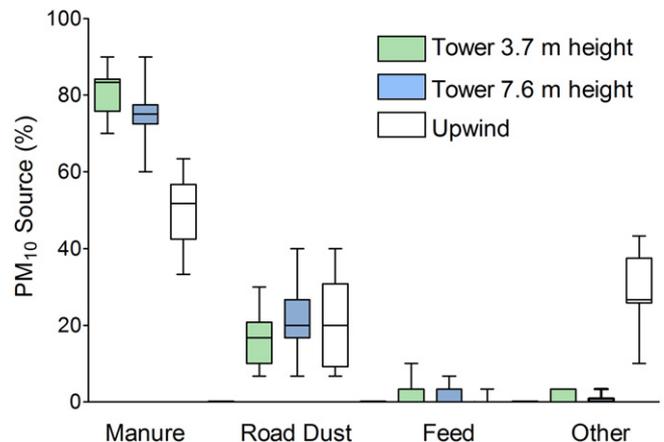


Fig. 7. Combined source fraction data collected during the sampling period from two levels of the sampling tower and from the upwind station.

weather and wind speed conditions are needed to see if further management practice improvement recommendations can be provided.

#### 4. Conclusions

Results of the present study indicate that Raman microscopy combined with multivariate statistical analyses can be used to develop source distribution profiles for PM<sub>10</sub> emissions from cattle feedlots. Raman spectra from heterogeneous source materials varied sufficiently to allow unambiguous classification for use in ambient PM<sub>10</sub> particle identification. Analysis of a limited number of test samples indicates that particles from the manure and unpaved road were the most important sources of PM<sub>10</sub> emitted from this feedlot. Analysis of additional samples from the multiple sampling campaigns carried out as part of this project will likely reveal critical factors controlling PM<sub>10</sub> source distribution emitted from feedlots in arid regions like Western Kansas.

The approach utilized in this work is practical because it can be used to analyze filter samples that are typically collected in dust measurement studies. It does not require any sample preparation, and it does not alter the particle in any way prior to analysis. It will be useful in analyzing total suspended particulate samples and may be useful for the analysis of PM<sub>2.5</sub> samples. Application of this approach to different types of agricultural operations would be very useful in identifying the source of PM and its strength for different air quality management practices.

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