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# Characterization and Speciation of Fine Particulate Matter inside the Public Transport Buses Running on Bio-Diesel

**Final Report** 



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# Characterization and Speciation of Fine Particulate Matter inside the Public Transport Buses Running on Bio-Diesel

## **ABSTRACT**

Air pollution with respect to particulate matter was investigated in Toledo, Ohio, USA, a city of approximately 300,000, in 2009. Two study buses were selected to reflect typical exposure conditions of passengers while traveling in the bus. Monitoring inside the bus was done in the spring and summer seasons. Particulate matter levels found inside the bus were well below the USEPA standards. Scanning electron microscope analysis was used to identify the possible sources. Particle shape and size distribution analysis was conducted and aspect ratios were determined; the results will be used to find out the potential particle dynamics inside the bus. Polycyclic aromatic hydrocarbons were analyzed to determine potential carcinogenic matter exposure to passengers. The absence of carcinogens in all the samples suggests healthful air quality levels inside the bus. SEM methodology is a valuable tool for studying the distribution of particulate pollutants. These patterns represented the morphological characteristics of single inhalable particles in the air inside the bus in Toledo. The size distribution was generally multi-modal for the ULSD but uni-modal for the B20-fueled bus. The aspect ratio found for different filters collected inside the bus fueled by both the B20 blend and ULSD ranged 2.4-3.6 and 2.3-2.9 in average value with standard deviation range 0.9-7.4 and 1-7.3 respectively. The square and oblong particles represented the single inhalable particles' morphology characteristics in the air of a Toledo transit bus.

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## **<u>1. Introduction</u>**

## Background

This document constitutes a condensed report on the project, "Characterization and Speciation of Fine Particulate Matter inside the Public Transport Buses Running on Bio-Diesel" completed under the aegis of Michigan-Ohio University Transportation Consortium (MIOH-UTC); implemented by the Air Pollution Research Group in the Civil Engineering Department of The University of Toledo, Toledo, Ohio, USA. The project commenced on January 1, 2009, and was closed formally on August 31, 2009. With the specific objectives to disseminate the project findings and to share the subject knowledge among a wider scientific and technical community, project members are writing articles in scientific journals; this report is presented for wider circulation and information dissemination.

Previously, the Air Pollution Research Group (APRG) developed a five-year, large scale comprehensive research project to understand and assess the impacts of using a mixture of renewable bio-fuel and diesel fuel (B-20: 20% bio-fuel and 80% ultra-low sulfur diesel compared to ultra-low sulfur diesel (ULSD) under a research grant from the TARTA to the ITI at The University of Toledo. The purpose of the APRG portion of the study is to investigate the impact of using ULSD and B-20 made with ULSD on engine emissions and air quality inside the bus.

## **Project Objectives**

Bio-diesel (BD) confers some environmental benefits such as the virtual absence of sulfur (S) and aromatic compounds. The superiority of BD over petroleum diesel promotes serious consideration of BD for improving air quality in urban areas. Latest air pollution studies world over have focused on fine particulates and their inorganic and organic contents. To develop the scientific understanding of physical and chemical characteristics of fine particulates and exposure of particulate matter to a passenger, one needs to perform a characterization study by monitoring actual pollutant and changes in the buses. The following are the objectives of this study:

- To describe the physical and chemical characteristics of particulate matter (PM) and factor those that affect ambient source impacts.
- To find relations between mass and number concentrations of particles in different size ranges of PM collected by GRIMM Instrument and Sioutas Cascade Impactor.

The specific objective of the project was to design and implement a characterization study in Toledo which may be helpful in understanding the impact on a passenger's health that has been exposed to particulates. In other words, the purpose of the study funded by MIOH - UTC is twofold: first, to improve both the quality and quantity of available scientific and technical information; secondly, to improve our capabilities to interpret the public health significance of the information on hand. The focus of the study was on sampling, monitoring, and analyzing the particulate matter physically and chemically. The major tasks involved in the project and their sequencing are presented in Figure 1.

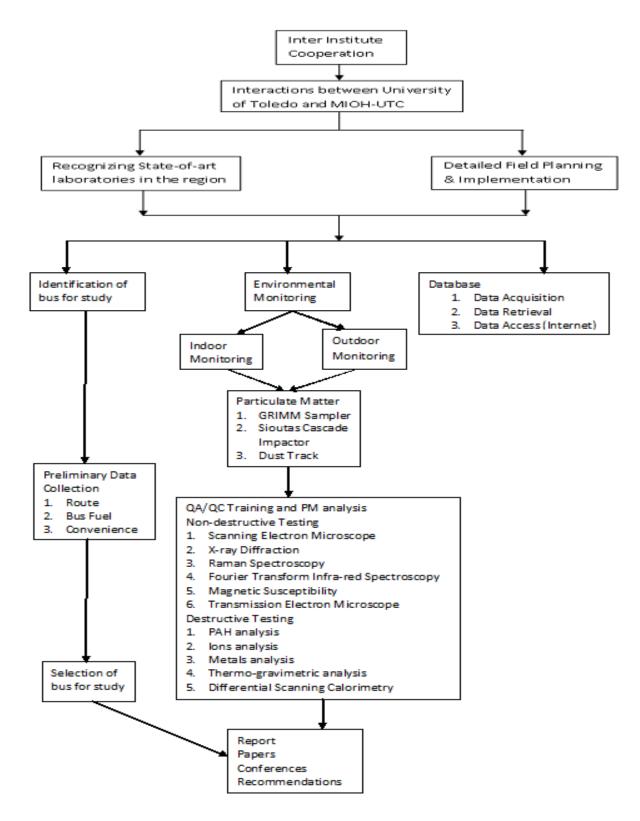


Figure 1. Overview of the Project

## 2. Sampling and Analysis: Methods and Quality Assurance

## Sampling Bus

Toledo is a city in the state of Ohio, and is the county seat of Lucas. In the 2000 census, the city proper had a population of 313,619, the fourth-largest in the state. TARTA has been the "Ride of Toledo" since 1971. With 180 buses running continuously, TARTA contributes a significant percentage of the total passenger travel in the region (http://www.tartabiodiesel.org/).

TARTA buses apply three types of fuels: ultra low sulfur diesel (ULSD) containing <15 ppm S content; ULSD supreme having some extra additives; and B20 grade BD (20% methyl ester bio-fuel + 80% ULSD). The chemical properties of the BD fuels have been obtained from TARTA for this project. The bio-diesel used by TARTA meets the requirements of ASTM 6751.

The selection of the bus and the route was an important task for carrying out this study. The bus route was selected by a previous APRG member (Vijayan,  $2007^1$ ) for initial TARTA study. This bus route covers the majority of Toledo. The bus selected for the study is from the fleet of 500 series Thomas built buses (acquired by Detroit Diesel) of the TARTA line up, with a Mercedes Benz MBE 900 engine; the route selected is Route # 20 (refer Figure 1), which runs between TARTA garage and Meijer on the *Central Avenue Strip*. The characteristics of the bus and the route map used for the run are presented in Table 1 and Figure 2, respectively.

Fleet Number	Engine	Chassis	Number of BD Buses
200	6V92 Detroit Diesel	RTS	2
300	ISB 275 Cummins	Bluebird	5
400	Series 50 Detroit Diesel	TMC	N/A
500	MBE 900 Mercedes Benz	Thomas	19
600	Series 40 International Navistar	Gillig	N/A
700	Series 40 International Navistar	Gillig	N/A
900	6V92 Detroit Diesel	Flexible	N/A

 Table 1. TARTA Fleet Details

<sup>&</sup>lt;sup>1</sup> Vijayan, A., 2007, Characterization of Vehicular Exhaust Emissions and Indoor Air Quality of Public Transport Buses Operating on Alternative Diesel Fuels, Ph.D. Dissertation, University of Toledo, Toledo, 2007.

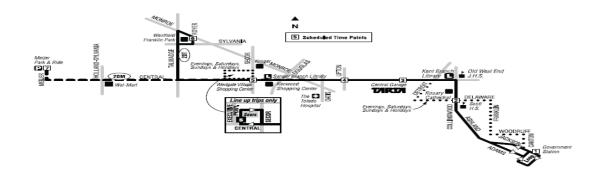


Figure 2. Map Showing Route #20 (Source: TARTA website, 2008)

A biodiesel and a ULSD bus were selected from the TARTA fleet and run daily on a preassigned route. The A locations of the buses, when on the run, were identified by the GPS unit located inside them.

### Sampling and Analysis: Materials and Methods

Field monitoring has been conducted in public buses over a four-year period. Measurements of air toxics, PM, and criteria gases are being collected continuously for about four years. Monitoring started in the winter of 2006. Target pollutants monitored in the study were PM–mass and numerous concentrations of particles in 15-different size fractions and PM collected using the Sioutas Cascade Impactor.

The instruments used to assess the IAQ are the Grimm Dust Monitor 1.108 and Sioutas Cascade Impactor. A set of these instruments is placed in the bus used for the run. A summary of the functionality of the instruments is given in Table 2. Continuous monitoring of particulate matter in the biodiesel and ULSD bus was done using a Sioutas Cascade Impactor and a Grimm Dust Monitor 1.108 unit. The Grimm monitor unit, when used in combination, also provided the flexibility to obtain particulate mass and number concentrations simultaneously at one location. The instruments draw power continuously from the adapters connected to the bus, and a wired mesh box is provided to safeguard the instruments. The instruments are held in place by Velcro attachments.

Under this study two kinds of experimental studies have been performed; these include outdoor and indoor monitoring of PM and speciation of PM for physical and chemical characteristics. The details of instruments and their applications used in the project are presented in Table 2.

#	Instrument	Make	Application	Place
$\frac{\pi}{1}$	Indoor Particulate	Grimm, Germany, Model	To measure indoor	Inside bus
	Sampler	1.108	PM levels	in Toledo
2	Outdoor Particulate Sampler	Grimm, Germany, Model 1.108	To measure outdoor PM levels	Outside bus in Toledo
3	MicroBalance	CAHN Microscale and Mettler Balance	For gravimetric analysis and weighing	Toledo
4	Scanning Electron Enlarge all spaces so words fit on one line microscope (SEM)	Environmental SEM with energy dispersive x-ray detector (EDS)	For physical and chemical characterization	Ann Arbor
5	Raman Spectroscopy	Jobin Yvon Horiba Confocal Raman Spectrometer	Molecular Characterization	Toledo
6	Differential Scanning Calorimetry (DSC)	PerkinElmer Diamond (DSC)	Thermal Characterization	Toledo
7	X-ray Diffraction (XRD)	Rigaku Ultima III XRD with Small Angle X-ray Scattering (SAXS)	Crystalline Characterization	Toledo
8	Thermogravimetric Analysis (TGA)	TA Instruments Q50 TGA	Thermal Characterization	Toledo
9	Inductively Coupled Plasma- Mass Spectrometer (ICP-MS)	Thermo Scientific XSeries2 ICP-MS	For metal analysis	Toledo
10	Fourier Transform Infrared (FTIR) Spectrometer	Varian Excalibur Series FTIR instruments, the FTS-4000 Spectrometer and the UMA-600 Microscope	Molecular Characterization	Toledo
11	Gas Chromatography- Mass Spectroscopy (GC-MS)	GC-MS	Polycyclic Aromatic Hydrocarbons	A&AC, California

 Table 2. Instrumentation Used During the Program

## Sampling Procedures

GRIMM Sampler was calibrated at the GRIMM Instruments Inc. before the start of each season's sampling. Sioutas Cascade Impactor was calibrated every time the sample filter papers were changed by the proposer, with the help of software provided by the company. Dust Trak was calibrated at the company's facility before the start of any sampling.

During the sampling, the operator used tweezers and gloves to handle all the filter paper and the filter paper was removed in a timely manner and carried to the laboratory in casings supplied by SKC, Inc. Zip Lock bags were used to save the exposed filter from any kind of contamination. The exposed filters were desiccated for 24 hours before and after the sampling. Thereafter, the filters were analyzed gravimetrically on the Cahn and Mettler microbalances.

### Physical and Chemical Analysis

Exposed filters are being physically and chemically analyzed for organic and inorganic pollutants. We partitioned our analysis in two categories: destructive analysis and non-destructive analysis. The destructive analysis proposed and being carried out is PAH analysis, ions analysis, metals analysis, thermo-gravimetric analysis, and differential Scanning Calorimetry. The non-destructive analysis proposed and being carried out is scanning Electron Microscope, X-ray diffraction, Raman spectroscopy, Fourier Transform Infra-red Spectroscopy, magnetic susceptibility, and transmission electron microscope. To date we have finished the electron microscopy analysis, PAH analysis, X-ray diffraction, Fourier Transform Infra-red Spectroscopy, and magnetic susceptibility. Out of these analyses, the results of PAH analysis, SEM, and XRD analysis are published and are presented here. We are still working on the remaining data under the TARTA grant.

### **Scanning Electron Microscope Analysis**

Air particles were analyzed by the Environmental Scanning Electron Microscopy (ESEM). Since the technique is nondestructive, particles of interest can be relocated as needed. Using these analytical techniques, individual particle analysis was undertaken for morphology. The particle analysis was carried out by the use of ESEM coupled to an automatic computer imaging system with a resolution of 10 nm. The size, morphology, and shape of the particles were analyzed with a SEM. Particles were measured in the ESEM micrographs. Approximately 20 samples from the buses running on biodiesel, with respect to particle size, distribution, and appearance were analyzed.

Note that it takes about three weeks to collect one good sample using the GRIMM instrument. The filters were prepared for an electron microscopic investigation. For the analyses of the samples from the TARTA buses, an ESEM (Quanta 3D) with an image analyzer in the Electron Micro-beam Analysis Laboratory, at The University of Michigan (in Ann Arbor, Michigan), was used. The full filter was mounted on the bulk sample holder with silver adhesive. About 20 visual fields were distributed evenly over the sample and analyzed at a 10000x magnification.

The images from the ESEM were transmitted directly to an image analyzer and the individual particles diameter (D) and area were measured. The analyses were done by interactive automatic measurement. Line charts showing the distribution were drawn and the total area and volume for each class were calculated. The samples were also investigated in the ESEM, at a magnification of 2000x. The fields for counting and size distribution analysis were randomly selected. All particles within a field of view were counted and their D and area measured. Tightly bound agglomerates were counted as single particles. Volumes of the particles were approximately calculated from the area measurements by assuming the D as thickness. The interaction of the electron beam with the sample produces various effects that can be monitored with suitable detectors. The resulting signals include secondary electrons that are used for imaging. The secondary, backscattered, and X-ray signals were collected in synchronization with the position of the electron beam to provide the highly detailed spatial and compositional information of microscopic features. However, PM10 characterization requires more detailed quantification. Signal strength is proportional to particle volume. Therefore, longer integration time was needed to analyze PM10.

## **PAH Analysis**

PAH analysis was performed out by an external laboratory (Atmospheric Analysis and Consulting, California) using the EPA method TO-13A, based on Gas Chromatography/Mass Spectroscopy. The filter papers were transferred for the analysis in sealed packs of filter paper surrounded by blue ice to keep the temperature constant as mentioned in the EPA procedures.

### **XRD** Analysis

An X-ray diffractometer with a scintillation counter, a graphite (002) monochromator, and a copper anode rotated target X-ray tube (that was operated at 50 kV with 200 mA) was used to analyze airborne particulates.

### **Quality Control Procedures in Project Implementation**

Quality assurance and quality control (QA/QC) in entire project planning and implementation at all levels was designed in advance and hands-on training was imparted to the project team before beginning of any sampling and analysis. The major features of QA/QC are briefly described:

- 1. Bus/Route Selection: Bus and Route were carefully selected to get representative samples of indoor and outdoor air. In addition to convenience for sampling, selection of buses for sampling was to cover different types of fuel and routes covering major parts of Toledo (details of bus/route selection are included in the first annual report to TARTA in 2006-07).
- 2. All the procedures were developed in consultation with the EPA procedure, an instrument manual, and were reviewed by the principle investigator. Whenever necessary, the procedures were adjusted to meet the field challenges.
- 3. While monitoring was conducted, these points were considered:
  - a. Calibration method
  - b. Frequency

- 4. While conducting physical and chemical analysis, these points were considered :
  - a. Description of method
  - b. Standards to be used
  - c. Laboratory and field blanks
  - d. Internal and recovery standards
  - e. Database development
  - f. Record keeping
  - g. Traceability of calculations

For example, the Quality control results for analyzing the PAH are stated in the Tables 3 and 4.

# Table 3. Quality Control Results for PAH Determination in Filter Paper Collected from GRIMM Sampler\*

Analytes	LCS	LCS	LCS	LCS	LCS	LCS	LCS	LCS/LCSD	LCS	
	Conc.	Recov	%	DUP	DUP	DUP	RPD	% Limit	RPD	
			REC	Conc	Recov	% REC	% REC		% Limit	
Acenaphthene	10	8.86	88.6	10	8.8	88	<1	60-130	<30	
Acenaphthylene	20	17.3	86.6	20	17.4	87	<1	60-130	<30	
Anthracene	1	0.99	99	1	0.974	97.4	1.6	60-130	<30	
Benzo(a)anthracene	1	1.11	111	1	1.13	113	1.8	60-130	<30	
Benzo(a)pyrene	1	1.14	114	1	1.12	112	1.8	60-130	<30	
Benzo(b)fluoranthene	2	2.32	116	2	2.32	116	<1	60-130	<30	
Benzo(g,h,i)perylene	2	2.02	101	2	2.04	102	<1	60-130	<30	
Benzo(k)fluoranthene	1	1.14	114	1	1.13	113	<1	60-130	<30	
Chrysene	1	1.1	110	1	1.11	111	<1	60-130	<30	
Dibenzo(a,h)anthracene	2	2.16	108	2	2.14	107	<1	60-130	<30	
Fluoranthene	2	2.1	105	2	2.1	105	<1	60-130	<30	
Fluorene	2	1.87	93.4	2	1.84	92	1.5	60-130	<30	
Indeno(1,2,3-cd)pyrene	1	1.01	101	1	1.08	108	6.7	60-130	<30	
Naphthalene	10	7.74	77.4	10	7.68	76.8	<1	60-130	<30	
Phenanthrene	1	1.01	101	1	0.998	99.8	1.2	60-130	<30	
Pyrene	1	1.05	105	1	1.05	105	<1	60-130	<30	
Surrogates										
p-Terphenyl-D14	5	5.4	108	5	5.4	108	<1	60-130	<30	

\*(LCS prepared: 08/27/2009; LCS Analyzed: 09/01/2009)

## Table 4: Quality Control Results for PAH Determination in Filter Paper Collected from Sioutas Cascade Impactor\*

nom sloutas cascade impactor									
Analytes	LCS	LCS	LCS	LCS	LCS	LCS	LCS	LCS/LCSD	LCS
	Concen	Recov	%	DUP	DUP	DUP	RPD	% Limit	RPD
			REC	Concen	Recov	% REC	% REC		% Limit
Acenaphthene	10	6.83	68.3	10	7.25	72.5	6.0	60-130	<30
Acenaphthylene	20	14.0	69.8	20	14.7	73.5	5.2	60-130	<30
Anthracene	1	0.820	82.0	1	0.830	83.0	1.2	60-130	<30
Benzo(a)anthracene	1	1.10	110	1	1.05	105	4.7	60-130	<30
Benzo(a)pyrene	1	1.06	106	1	0.960	96.0	9.9	60-130	<30
Benzo(b)fluoranthene	2	2.18	119	2	2.02	101	7.6	60-130	<30
Benzo(g,h,i)perylene	2	1.67	83.5	2	1.60	80.0	4.3	60-130	<30
Benzo(k)fluoranthene	1	1.09	109	1	1.03	103	5.7	60-130	<30
Chrysene	1	1.08	108	1	1.02	102	5.7	60-130	<30
Dibenzo(a,h)anthracene	2	1.77	88.5	2	1.66	83.0	6.4	60-130	<30
Fluoranthene	2	1.84	92.0	2	1.79	89.5	2.8	60-130	<30
Fluorene	2	1.45	72.5	2	1.51	75.5	4.1	60-130	<30
Indeno(1,2,3-cd)pyrene	1	1.06	106	1	0.980	98.0	7.8	60-130	<30
Naphthalene	10	5.96	59.6	10	6.42	64.2	7.4	60-130	<30
Phenanthrene	1	0.810	81.0	1	0.800	80.0	1.2	60-130	<30
Pyrene	1	0.910	91.0	1	0.880	88.0	3.4	60-130	<30
Surrogates									
p-Terphenyl-D14	5	5.45	109	5	5.15	103	5.7	60-130	<30

\*(LCS prepared: 07/14/2009; LCS Analyzed: 07/15/2009)

Units: µg/sample; where %Limit: Percent acceptable limits; %REC: Percent recovery; Concen: Added concentration to the sample; LCS: Laboratory control sample; Recov: Recovered concentration in the sample; RPD: Relative Percent Difference; DUP: Duplicate.

Another example, a brief QA/QC adopted for SEM analysis is presented:

- Particles were measured in the ESEM micrographs using image J and Genesis software.
- The reproducibility of the data collected was checked by performing repeat analyses on some of the filter papers.
- It was made sure that filter paper had collected enough PM so that interference of filter paper surface interference was neutralized and we could only get the characteristics of surface particles deposited on the PM cake on the filter paper. The surface interference was generally due to the use of different types of filter papers, namely Teflon, in our case. Polycarbonate filters were used in the year 2009 for sampling, which was considered ideal for SEM analysis.
- The visual fields were selected at random on the filter paper at a minimum of 20 different spots, to assure the uniformity of the filter surface for considering the particles for analysis.

## Sampling Plan

There were two components of sampling inside the bus: GRIMM indoor sampling and Sioutas Cascade Impactor sampling. The sampling was spread January through August 2009. The details of sampling plan executed in the project implementation are described while discussing the results. Two seasons, spring and summer, were covered during the study.

## **3. Results and Discussion**

This section is divided into two sections: particulate matter collection and physical and chemical characterizations. The physical and chemical characterizations are further divided in four sections: size distribution, shape factor determination, aspect ratio, and source apportionment.

### **Particulate Matter Collection**

The particulate matter was collected on the filter paper inside the public transit bus fueled by biodiesel blend (B20-a blend of 20%t of biodiesel and 80%ultra low sulfur diesel). Twenty samples that were not analyzed in the TARTA study were available for this study. Six samples were collected during the study period of 2009. Therefore, 26 samples were available at the end of the project for analysis. This section will be discussed in more detail.

### Seasonal Variation

The seasonal variation of particulate matter was studied using particle number concentration collected using the GRIMM sampler. The data evaluated the seasonal variation for winter and spring against the summer season.

### Winter+Spring ULSD PSD

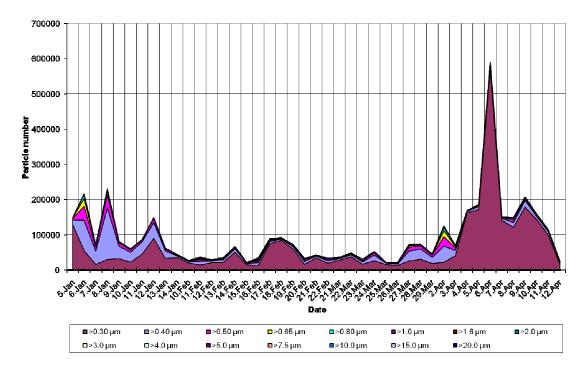


Figure 3. Particle Size Distribution in Winter and Spring in the Bus Fueled by ULSD

#### Winter+Spring Biodiesel PSD

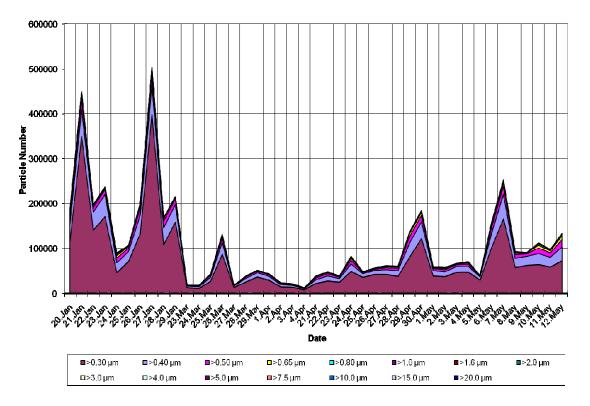


Figure 4. Particle Size Distribution in Winter and Spring in the Bus Fueled by Biodiesel

Particle number concentrations inside the biodiesel and ULSD buses were pretty constant in the range of 10000-20000, except a few peaks on some days. During winter, particle concentration of particle size <0.30 $\mu$ m were dominating the particle size distribution found in both the buses, although particle concentration of particle size <0.40 $\mu$ m were also considerable.

#### Summer Blodiesel PSD

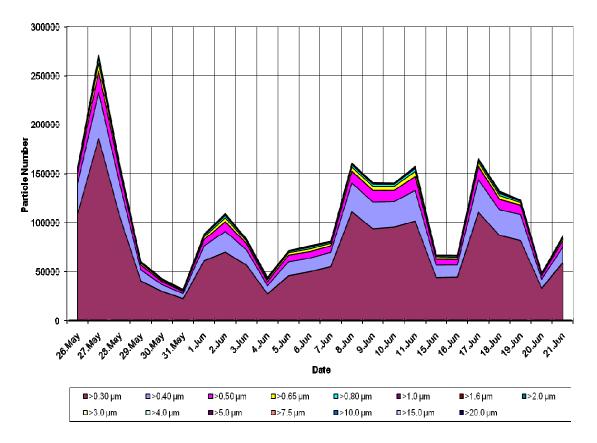


Figure 5. Particle Size Distribution in Summer in the Bus Fueled by Biodiesel

#### Summer ULSD PSD

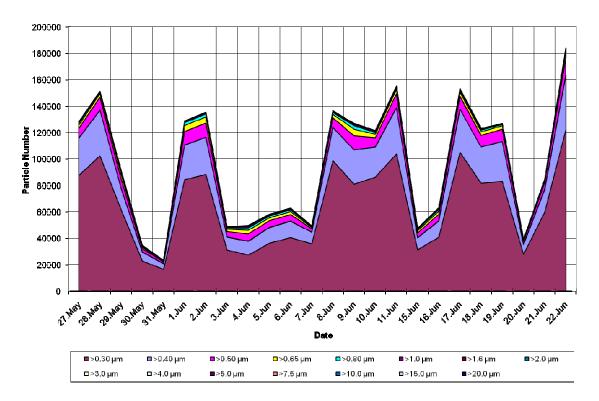


Figure 6. Particle Size Distribution in Summer in the Bus Fueled by ULSD

During summer, particle number concentration inside the ULSD bus was comparatively lower than the particle number concentration found in the biodiesel fueled bus. During summer, apart from particle size  $<0.30\mu m$  other particle size fractions were also considerable.

### **Physical and Chemical Characterization**

Extensive physical characterization of fine particulates was carried out by using Environmental Scanning Electron Microscope in the EMAL lab in the Space Research Center at The University of Michigan.

All the analyses proposed can be classified in two categories viz. destructive and nondestructive analysis. SEM, XRD, Magnetic Susceptibility and FTIR analysis are nondestructive analysis. All the samples have undergone under non-destructive analysis to date. The destructive analysis include: PAH analysis with Gas Chromatography and High Performance Liquid Chromatography, Thermo-gravimetric analysis, Differential Scanning Calorimetry, Metals Analysis with Atomic Absorption Spectroscopy, and Ions Analysis with Ion Chromatography. The particle size distribution was carried out on the filter paper collected from the GRIMM sampler and by using its laser counter. The authors are investigating the correlation between both the particle size distributions. The limited data obtained by Sioutas Cascade Impactor is not enough for comparing the PSD against the GRIMM sampler. The filters collected from Sioutas Cascade Impactor are used for analyzing the PAHs. The study has evaluated and described the physical and chemical characteristics of PM and the factors that determine the impact of various ambient sources on outdoor concentrations in public bus concentrations, and the spatial variability of these concentrations in relation to the source locations. This was done by carrying out morphological analysis using ESEM. The physical and chemical characteristics of PM and the factors that determine the impact of various ambient sources on outdoor concentrations, inside public bus concentrations and the spatial variability of these concentrations in relation to the source locations, are addressed in the paper submitted by authors to the Journal of Environmental Sciences.

### Size Distribution

We collected a total of 17 airborne PM samples distributed among five different urbanpublic transit buses (inside) fueled over 22 months by biodiesel blend and ULSD (Table 1). The data collection was occasionally discontinued due to technical problems or maintenance issues. A mode is defined as a peak in the PSD, which can also be described by a lognormal function for the number size distribution of PM. In context, a mode sometimes represents a category of particles that are formed by the same processes. The modality and peak found in the distribution are reported in Table 5.

The multi-modal size distribution was found near the higher size range because of the multiplicity of the sources and strong agglomeration properties of fine particulates. Multi-modal peaks observed in the coarse mode indicate the presence of particulates from several other sources (i.e. road dust, re-suspended tire dust from paved roads, windblown dust from arid regions), and their concentrations heavily dependent on meteorological conditions. The particles may have been modified by evaporation or growth processes that favor one particle size over another.

However, the uni-modal size distribution indicates the absence of particulates from many sources. This is attributed to the meteorological condition.

After studying the Table 5 and size distribution curves, the findings can be listed:

- 1. Size distribution for filter paper collected inside the biodiesel-fueled bus were mainly uni-modal for the months of March, May, September, October, and December 2007; bi-modal for November 2007, and February and October 2008; and multi-modal for January, February, and August 2008.
- 2. The variation in PSD was noted for individual winter and fall months, despite having individual similar climate conditions for a season.
- 3. Size distribution for filter paper collected inside the ULSD-fueled bus was mainly multi-modal for January, March, and December 2007, and for January, August, and October 2008; and uni-modal for September, October, and November 2007, and for February 2008.
- 4. The peaks in uni-modal or bi-modal distribution were found at 0.1, 0.2, 0.5, and  $0.6\mu$ m.
- 5. In the summer, the particle size distribution was multi-modal for both buses.
- 6. In the spring, the bus fueled by the biodiesel blend had uni-modal particle size distribution and the ULSD-fueled bus had multi-modal PSD.

- 7. In the winter, both bus results are not sufficiently decisive to formulate any meaningful conclusions.
- 8. In the fall, the bus fueled by the biodiesel blend had uni-modal and bi-modal particle size distribution, and the ULSD-fueled bus had uni-modal and multi-modal PSD.
- 9. The peaks in multi-modal distribution have shown varied patterns.

Almost all particles were found to be less than 20µm, which shows that the GRIMM sampler worked efficiently. The peak at a smaller size in a particular size distribution shows the dominance of smaller particles. The peak for filter paper collected inside the biodiesel-fueled bus was found in the small particle size range, so one can conclude that smaller particles dominate inside the biodiesel-fueled bus. The shape of the particles will be discussed in the next section to explain the difference of modality of particles deposited on the filter paper collected inside the biodiesel and ULSD fueled buses. The ultrafine mode is near 0.1µm and the coarse mode is beyond 0.3µm. The uni-modal and bi-modal peak lies in the ultrafine mode region. Multi-mode peaks were found mostly in the coarse mode region. The ultrafine modes are seen to possess such a small, narrow size distribution (between 0.2 or 0.3 µm) that they cannot be formed directly from natural mineral particles, which are usually discrete grains larger than 1-µm. The wellestablished vaporization-condensation mechanism can explain the ultrafine mode formation. Agglomerates of stretched particles are common morphologies. Such particles are expected to have higher surface-to-volume ratios than the coarse mode. This reveals that these large particles are produced directly from mineral grains when the carbon matrix is burned from them. Further investigation of this will be assessed in other publications. Multi-modal PSD implies lower health risks due to rising large particle sizes. On the other hand, uni-modal and bi-modal PSD (generally found around  $PM_{0.1}$ ) corresponds to particles with long atmospheric residence times, which are much less affected by short-term events and indoor-outdoor climate fluctuations. An explanation of our data is that the degree of air PM pollution in the biodiesel-fueled bus is because of the persistence of these small particles.

	-				Size Distribution			
Fuel	Month	Year	Counts	Aspect	Size Distribut			
				Ratio	Modality	Peaks		
B20	Mar	2007	14096	2.8±7.4	Uni-modal	0.1		
B20	May	2007	16142	2.4±2.6	Uni-modal	0.2		
B20	Sept-Oct	2007	13166	3.6±7.2	Uni-modal	0.1		
B20	Nov	2007	12137	2.9±4.1	Bi-modal	0.2 and 0.5		
B20	Dec-Jan	07-08	3714	2.4±0.9	Uni-modal	0.2		
B20	Jan-Feb	2008	8567	2.7±1.1	Multi-modal	9.5, 10.6, 11.6, 12.5,		
						13.4, 14.2, 14.9, 15.6,		
						16.3, 17, 17.6, 18.3,		
D20	E.L	2009	15(0	25121	D:	18.9, 19.4, 20		
B20	Feb	2008	1568	2.5±2.1	Bi-modal	0.2 and 0.6		
B20	Aug	2008	8766	2.7±1.6	Multi-modal	5.5, 8.9, 9.9, 10.9, 11.7, 12.5, 13.3, 14, 14.7,		
						12.3, 15.3, 14, 14.7, 15.3, 15.9, 16.5, 17.1,		
						17.7, 18.2, 18.8, 19.3, 17.1, 17.7, 18.2, 18.8, 19.3		
						19.8		
B20	Oct	2008	1884	2.6±1.9	Bi-modal	0.2 and 0.5		
ULSD	Jan	2007	15292	2.7±1.3	Multi-modal	4.8, 5.3, 5.8, 6.3, 6.7,		
						7.1, 7.5, 7.9, 8.2, 8.5,		
						8.9, 9.2, 9.5, 9.7, 10,		
						10.3, 10.6		
ULSD	Mar	2007	3316	2.9±6.7	Multi-modal	0.1, 0.6, 1, 1.2, 2, 3		
ULSD	Sept-Oct	2007	22702	2.9±2.1	Uni-modal	0.1		
ULSD	Nov	2007	4587	2.9±7.3	Uni-modal	0.1		
ULSD	Dec-Jan	2007-	15484	2.6±1	Multi-modal	0.1, 1.7, 2, 2.2, 4.8, 5.3,		
		08				5.8, 6.3, 6.7, 7.1, 7.5,		
						7.9, 8.2, 8.5, 8.9, 9.2, 9.5, 9.7, 10, 10.3, 10.6,		
						9.5, 9.7, 10, 10.5, 10.0, 10.8, 11.1, 11.3, 11.6,		
						11.8, 12.3, 12.5, 12.7,		
						12.9, 13.4, 13.6		
ULSD	Feb	2008	5737	2.7±2.7	Uni-modal	0.5		
ULSD	Aug	2008	7248	2.9±1.4	Multi-modal	0.1, 8.9, 9.9, 10.9, 11.7,		
						12.5, 13.3, 14, 14.7,		
						15.3, 15.9, 16.5, 17.1,		
						17.7, 18.2, 18.8, 19.3,		
		2000	14020	0.0.1		19.8		
ULSD	Oct	2008	14020	2.3±1	Multi-modal	8.9, 9.9, 10.9, 11.7,		
						12.5, 13.3, 14, 14.7, 15.3, 15.9, 16.5, 17.1,		
						15.5, 15.9, 10.5, 17.1, 17.7, 18.2, 18.8, 19.3,		
						and 19.8		
	1	L	1	1		with 17.0		

 Table 5. Sampling Periods, Particles Counted, Aspect Ratio, and Size Distribution

## **Particle Shape Analysis**

The SEM/EDX coupled Genesis Software in real time was used to measure the shape factor distribution of the particles collected on the filter paper, with each particle shape factor distribution plotted for each filter paper. Qualitative assessment of the images shows that most of the visible particles are composed of small chains and unidentifiable rough circular particles. Particle agglomerates are common morphologies. Such particles are expected to have higher surface-to-volume ratios than the coarse mode. The release of gas species from particles can account for the formation of these particles. The EDS spectra indicate that these particles are mainly Na–Si–S structures.

The purpose of this research is to improve scientific information on the particle morphology and microstructure of engine-emitted particulates, as they should be useful to further assess the indoor health impact of particulates. The different particle shapes are described:

## 1. Square:

Irregular-shaped square grains (Shandilya and Kumar,  $2009b^2$ : Figure 5A) are quantitatively high in the samples detected in the urban transit bus in Toledo. There are three impressed surface patterns of the square particles inside the bus: smooth (Shandilya and Kumar, 2009b: Figure 5A), semi-coarse (Shandilya and Kumar, 2009b: Figure 5B), and coarse (Shandilya and Kumar, 2009b: Figure 5C). Each pattern corresponds to different elemental components: the smooth square (size ~3µm) to Na, Cl-dominant; the semi-coarse (size ~5µm) to Al, Si-dominant; and the coarse to Mo-dominant, especially when the squares are captured separately. The squares show the presence of other elements that illustrate they conglutinated. The smooth square particles were found to contain Na, Mo, Cl, Ca, Al, Si, S, K, Pd, Mg, Ag, Ti, V and Fe. The semi-coarse square particles were found to have Al, Mo, Cl, Pd, Na, Mg, and Ca. Some irregular diamonds have rather smooth and flat surfaces, with obvious Ca peak in the elemental spectrum. The amount of particles with smooth surfaces is relatively more than the coarse particles.

## 2. Pentagon:

Irregular-shaped pentagon particles (Shandilya and Kumar, 2009b: Figure 5D) are also present in the samples detected in the urban transit bus in Toledo. Most of the pentagon particles had coarse surfaces and irregular shapes, which indicates the presence of Al, Si, Mo, Ca, and Mg. The surfaces of these particles were coarse and holed, with the average diameter of  $5 \,\mu$ m.

## 3. *Hexagon*:

Irregular-shaped hexagon particles (Shandilya and Kumar, 2009b: Figure 5E) were almost equal to pentagonal particles in the samples detected in the urban transit bus in Toledo. Most of the hexagonal particles had coarse surfaces that showed the presence of Na, As, Al, Si, Cl, and K. The surfaces of these particles were coarse and smooth, with an average diameter of  $6 \mu m$ .

<sup>&</sup>lt;sup>2</sup> Shandilya, Kaushik K., Kumar, A., 2010, 'Morphology of Single Inhalable Particle inside Public Transit Biodiesel Fueled Bus', Journal of Environmental Sciences, 22(2) 263–270.

## 4. *Agglomerate*:

Agglomerate-shaped particles (Shandilya and Kumar, 2009b: Figure 5F) are less quantitative than the irregular diamond, but are a little larger in size. Element components of agglomerate particles are quite similar to those of the irregular square particles but with a different X-ray counts rate. In some particle surfaces of agglomerates, elements Na, Si, and S are measured by the EDS. These agglomerate particles are actually the combination of more than two particles.

## 5. Sphere:

Sphere particles (Shandilya and Kumar, 2009b: Figure 5G) are generally smaller than square particle types, with an average diameter under 5  $\mu$ m. Spherical particles are considered as geometrically round. The round particles were found to have Al, Mo, Cl, and Pd. The particle surface was coarse and holed.

## 6. Column or Stick:

These particles are shaped long and conical. This sort of grain usually bears some external physiological texture, and can be found in samples inside the urban transit bus in Toledo. The X-ray detecting counts for these particles are quite low, which demonstrates that they are biomass.

## 7. Oblong:

Shaped long and triangular, this sort of grain (Shandilya and Kumar, 2009b: Figure 5H) usually bears some physiological texture externally, and can be found in samples inside the urban transit bus in Toledo. These were found to contain Na, Si, Mo, In, Ca, Mg, Fe, Zn, and Al.

8. *Triangle*:

Triangular particles (Shandilya and Kumar, 2009b: Figure 5I) were also found on the filter. The elements found were Na, Mg, Al, Si, Mo, Cl, K, Ca, Ti, V, Fe, and S. The average diameter was 5 µm.

9. Unknown:

Some deformed or nondescript particles (Shandilya and Kumar, 2009b: Figure 5J) just account for the minority in the samples with elemental spectrum peaks of Na and S, which may be explored.

Particle shapes result in a different particle exterior surface area-to-volume ratios and non-uniform heat fluxes in the particle, which can further affect the condensation and oxidation rates. Both cylinders and plates have higher surface-area-to-mass ratios than spheres, and the difference is clearer with a larger aspect ratio.

As for particle shape, a spherical shape is usually assumed in modeling work for convenience. The characteristic dimension is taken as the spherical-equivalent diameter (a sphere diameter with the same volume/mass as the non-spherical particle). The particles can be classified according to their shapes and structures using SEM in 12 microstructure types: strip, oblong, triangle, square, pentagonal, hexagonal, heptagonal, octagonal, nonagonal, decagonal, round, and agglomerate or unknown or irregular particles.

The shape factor distribution for particles collected inside the bus fueled by the biodiesel blend shows the majority are agglomerates. The authors mention that the agglomerate term used here refers collectively to agglomerate, unknown, irregular, and floccules.

The authors are still working to separate the components of agglomerates (even though agglomerates are the highest fraction) will not be further considered as the major fraction fragment in the following discussion. After discarding agglomerates, the major fraction of the particles collected inside the urban-transit public bus, fueled by biodiesel blend, was either oblong or square-shaped. By observing the shape factor distribution, one can conclude that most particles were oblong in 2007, while most particles were square in 2008. It is also interesting to note that particle size distribution in the year 2008 was a multi-modal distribution.

The major fraction of the particles collected inside the urban-transit public bus fueled by ULSD was either oblong or square. By observing the shape factor distribution, one can conclude that most of the particles were square-shaped except in February 2008 (particle size distribution was uni-modal). It is interesting to note that whenever the particle size distribution was bi-modal or there was the presence of coarse mode particles, the oblongshaped particles were almost equal in number to the number of square particles. All the filters collected many of the smooth globular particles (referred as round particle) approximately  $<2 \mu m$  in size; these may be derived from the vehicle combustion processed. SEM micrographs of the various particle shapes were shown previously (Shandilya et al., 2009b). The angular shape of any natural particle indicates that the shape has one or more sharp angles on its surface. Fused particles consist of various shapes, such as heptagonal, pentagonal, and hexagonal, which are referred to as irregular. High agglomeration is observed in the morphology of particles due to the autogenously breakage mechanism that allows particle breakage along the weak planes and minimizes surface energy. Unlike natural particles, the fused particles morphology shows agglomeration.

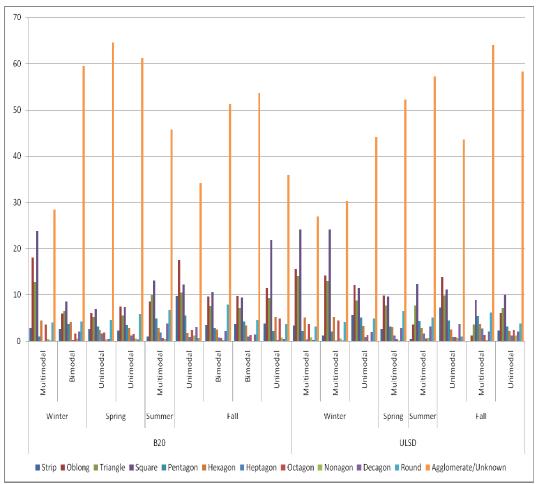


Figure 7. Shape Factor Distributions and Modality with Changing Fuel Type

When the PSD is uni-modal or bi-modal, the oblong particles are prevalent in the sample; when the PSD is multi-modal, the square particles are prevalent in the sample. The exception to this statement is the spring sample collected inside the ULSD-fueled bus. Particle shape affects the settling, separation during flow, viscosity, and particle dynamics. Anisometric particles, with difference in length versus width, are more likely to agglomerate than particles having similar dimensions in length and width (isometric particle). This is because the high surface area will provide more contact area and will have a higher potential to reinforce the matrix.

## **Aspect Ratio**

The aspect ratio found for different filters collected inside the bus fueled by the biodiesel blend were in the average range of 2.4-3.6, while standard deviation value ranged 0.9-7.4. The aspect ratio found for different filters collected inside the bus fueled by ULSD were in the average range of 2.3-2.9, while standard deviation value ranged 1-7.3. An elongated particle is characterized by a length longer than the width of the particle (i.e. high aspect ratio >1). Elongated particles dominate the indoor environment of both buses. The variation of aspect ratio is still unexplainable and needs further investigation. The aerosol mixtures inside both the buses are dynamic in nature.

The aspect ratio is defined by the particle length: thickness ratio. In this study, the aspect ratio of silica particles was calculated based on the number of particles counted using SEM micrographs with the help of Genesis Software. The Figure 3, below, shows the aspect ratio average for different samples. It is clear that most of the time the aspect ratio of all the particles was in the range of 2.5, though the standard deviation varied often. It is believed that particle aspect ratios and shapes do not change as dynamically as size during condensation. The non-spherical nature of the particles increases with larger size and aspect ratios.

While interpreting these results, certain facts need to be kept in mind that both triangle and plates have higher surface-area-to-mass ratios than rounds (in three dimensions), and the difference is more clear with an increasing aspect ratio. A high aspect ratio provides a high surface area; therefore, it results in more contact area between the particles for agglomeration and reaction. Presumably, due to good adhesion between the particles, a positive reinforcement effect occurs in elongated particles. This may strengthen those particles as the elongated particle shape has a higher particle surface, resulting in more contact area between the particles. This agglomeration property shows a permanent bonding of particles during their flow in the environment.

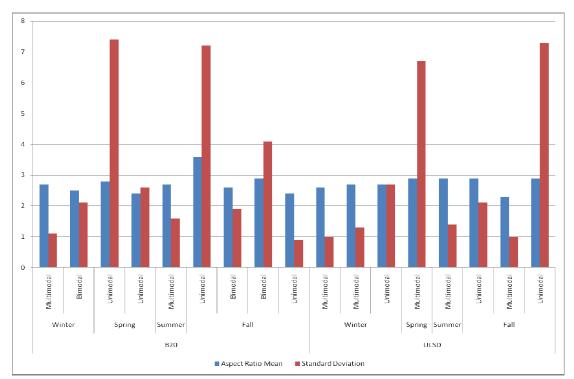


Figure 8. Aspect Ratio and Standard Deviation of Particles with Fuel Type

## **<u>4. Sources of the Particulate Matter (PM)</u>**

## **Morphological Features**

In Toledo, a distinct environmental problem is the fugitive dust derived from bare soil, construction activities, vehicle discharge, industry emission, and street deposit. Due to repeated depositing, accumulating, and re-suspending processes, the particles from the above sources mix and create dust, which is a serious nuisance. The detection of PM particles by ambient sampling represents intermingling of each original discharge source and re-suspension of street dust. The ratio of particle number percentage by calculation under SEM can only show source categories.

## **Chemical Composition**

Elements found under the microscope are Na, Mg, Al, Si, Mo, Ca, Cl, K, Ti, V, Fe, Pd, S, As, Ag, In, and Zn. The possible sources are listed in Table 3. The strong correlation of sodium and chlorine suggests that chloride is converting to sodium chloride in the atmosphere. The major source of smooth and shiny square particles is the salt that usually is put on the road and sidewalks to prevent skidding. Table 3 lists the possible sources contributing to the particles found inside the urban-transit bus in Toledo. Based upon the prevalence of square particles, it can be concluded that major sources contributing to the aerosol levels inside the public transit bus include road salt, lake bed, road dust, soil, vegetative burning, incinerator, oil-fired power plant, smelter fine, motor vehicle, construction, coal-fired boiler, and road traffic background.

The particle shape distribution of particles collected is identical for the first three dominant shapes in both the buses. It possibly suggests that similar sources are contributing to particulate levels inside the buses. Interestingly, however, particle size distribution has very distinct features for the particulates collected in both the buses. This possibly suggests differences in particulate chemical composition and source origin.

Element	Possible Sources
Na	Road salt, lake bed, paved and unpaved road dust, agriculture and natural soil,
	vegetative burning, incinerator, oil-fired power plant, smelter fine.
Mg	Natural soil, smelter fine.
Al	Motor vehicle, incinerator, paved and unpaved road dust, construction,
	agriculture and natural soil, lake bed, oil fired power plant, coal fire-boiler.
Si	Motor vehicle, incinerator, paved and unpaved road dust, agriculture and
	natural soil, lake bed, oil-fired power plant, coal-fired boiler, construction.
Mo	Secondary/industrial sources, re-suspension, salt, diesel vehicles, road traffic
	background (Harrison <i>et al.</i> , 2003 <sup>3</sup> ).
Ca	Motor vehicle, paved and unpaved road dust, construction, agriculture and
	natural soil, lake bed, incinerator, smelter fine, coal-fired boiler, oil-fired
<u></u>	power plant, vegetative burning.
Cl	Incinerator, motor vehicle, lake bed, agriculture and natural soil, paved and
17	unpaved road dust, vegetative burning, coal-fired boiler.
Κ	Paved and unpaved road dust, construction, agriculture and natural soil, lake
	bed, incinerator, coal-fired boiler, oil-fired power plant, smelter fine, vegetative burning.
Ti	Paved and unpaved road dust, construction, agriculture and natural soil, lake
11	bed, incinerator, smelter fine, coal-fired boiler.
V	Coal-fired boiler, smelter, oil fired power plant, and incinerator.
Fe	Vegetative burning, motor vehicle, paved and unpaved road dust,
10	construction, agriculture and natural soil, lake bed, incinerator, coal-fired
	boiler, smelter fine.
Pd	Auto catalyst, incinerator.
S	Paved and unpaved road dust, construction, agriculture and natural soil,
	vegetative burning, lake bed, motor vehicle, incinerator, coal-fired boiler, oil
	fired power plant, smelter fine.
As	Coal-fired boiler, oil-fired power plant, smelter fine.
Ag	Incinerator.
In	Smelter.
Zn	Paved and unpaved road dust, construction, agriculture and natural soil,
	vegetative burning, motor vehicle, incinerator, coal-fired boiler, oil-fired
	power plant, smelter fine.

## **Table 6. Elements and Their Possible Sources**

### Mass and Number Concentration Relation

The relation between particulate matter mass and number concentrations was drawn for the samples collected by GRIMM. The summary of particles collected by the GRIMM sampler is summarized in Table 7.

<sup>&</sup>lt;sup>3</sup> Harrison *et al.*, 2003, Harrison, R.M., Tilling, R., Romero, M.S.C., Harrad, S., Jarvis, K., 2003, A study of trace metals and polycyclic aromatic hydrocarbons in the roadside environment Atmospheric Environment, 37, 2391–2402.

There is a direct relation between mass and particle number if two of the points given in Table 4 are not considered. The exception for BD-fueled bus is 26  $\mu$ g/m3 and the concentration is related to a very few number of particles, and the same case of ULSD 20  $\mu$ g/m3. The weak relationship for both observations can be explained on the basis of particle number dominance in size ranges of 1-20 $\mu$ m for these periods.

Table 7. GRIVIIVI Samples														
Start	End	Filter	PM	Air	TSP	Particle #	Analysis	Sampling						
Date	Date	Paper	(µg)	(L)	$(\mu g/m^3)$			Comment						
04/21	05/12	PC	660	35538	19	2701753704	PAH	Indoor B20-506						
04/21	05/12	PC	840	30520	28	1785799623	PAH	Outdoor B20-506						

 Table 7. GRIMM Samples

03/21	04/12	PC	630	33336	19	34052855	PAH	ULSD-536
01/05	02/22	PTFE	780	38592	20	66109566	TGA	ULSD-536
05/27	06/22	PC	900	45575	20	3754457299	Ions	ULSD-536

03/23	04/04	PC	450	17280	26	9886670	PAH	B20-506
01/20	01/29	PTFE	280	16704	17	54996147	N/A	B20-506
05/26	06/21	PC	720	34660	21	3092247671	Ions	B20-506

PC: Polycarbonate PTFE: Teflon

The outdoor particulate matter concentrations were found higher than the indoor concentrations. All the PM mass concentration is rounded off to the nearest whole number. The particle number and particle mass concentration by GRIMM sampler during different periods are plotted in Figures 9 and 10.

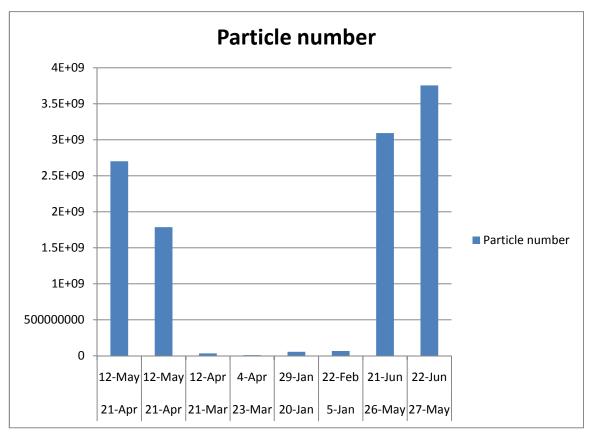


Figure 9. Number of Particles Collected by GRIMM Sampler in Different Months

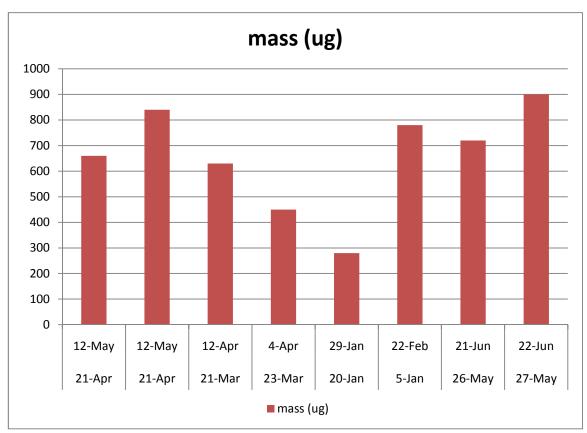


Figure 10. Particulate Mass Collected by GRIMM Sampler in Different Months

## Sioutas Cascade Impactor

This Impactor actually did not work as expected. The samples collected are summarized in the following Table 8:

Start	End	Size (µm)	Impactor	Air Flow	$\mu g/m^3$	PAH
			Stage			
10/25/08	11/12/08	2.5-10.0	А	230	7	ND*
10/25/08	11/12/08	1.0-2.5	В	230	4	ND
10/25/08	11/12/08	0.5-1.0	С	230	3	ND
10/25/08	11/12/08	0.25-0.5	D	230	4	ND
10/25/08	11/12/08	< 0.25	F	230	8	ND
11/12/08	12/10/08	2.5-10.0	А	352899	6	ND
11/12/08	12/11/08	1.0-2.5	В	352899	2	ND
11/12/08	12/12/08	0.5-1.0	С	352899	1	ND
11/12/08	12/13/08	0.25-0.5	D	352899	4	ND
11/12/08	12/14/08	< 0.25	F	352899	5	ND
1/14/09	1/19/09	2.5-10.0	А	6	0.1	ND
1/14/09	1/19/09	1.0-2.5	В	6	0.2	ND
1/14/09	1/19/09	0.5-1.0	С	6	0.3	ND
1/14/09	1/19/09	0.25-0.5	D	6	0.2	ND
1/14/09	1/19/09	< 0.25	F	6	0.2	ND

Table 8. PAH and Particulate Matter Level Collected by Sioutas Cascade Impactor

This Impactor did not work as expected. We performed different kinds of tests and worked with the manufacturer to resolve the problem. Last month the repaired equipment was returned by SKC Inc. We have deployed the Impactor for collecting more data.

## **Polycyclic Aromatic Hydrocarbons:**

PAHs represent a group of organic compounds consisting of carbon and hydrogen with two or more rings. A large number of PAH species are formed in most combustion processes. In this study, 16-EPA recommended PAHs and one biodiesel marker have been studied. All the values of PAH concentration were below the detection limit. It is confirmed that indoor air is free of any carcinogenic substance.

## **<u>5. Knowledge Dissemination</u>**

The results of this project are being transferred into the educational environment by incorporating the findings into the undergraduate course, "Introduction of Air Pollution Engineering," and the graduate course, "Indoor Air Quality." The results have been posted on our website "Alternative Fuels" (under construction) for use by entities such as state departments of transportation and public transport systems. The papers are being presented at various conferences and submitted to various journals for possible publications. A list of the published papers and conference presentation from the present grant is given on the next page.

## **<u>6. List of Published Papers/Presentations From the Grant</u>**

- Shandilya, Kaushik K., Kumar, A., 2010, Qualitative Evaluation of Particulate Matter inside Public Transit Buses Operated by Biodiesel, The Open Environmental Engineering Journal, 3, 13-20.<sup>4</sup>
- Shandilya, Kaushik K., Kumar, A., 2010, 'Morphology of Single Inhalable Particle inside Public Transit Biodiesel Fueled Bus', Journal of Environmental Sciences, 22(2) 263–270.<sup>2</sup>
- Paper under review in Environmental Progress, "Physical Characterization of Fine Particulate Matter Inside the Public Transit Buses Fueled by Biodiesel in Toledo, Ohio", Kaushik K. Shandilya and Ashok Kumar.<sup>5</sup>
- Presented in Poster Presentation in UT Graduate Research Symposium, April 10, 2009 in Toledo, Ohio; Morphology of Inhalable particles Inside Urban Transit Bus in the City of Toledo, Ohio, USA, Shandilya, Kaushik K. and Kumar, A. (Received Second Prize)<sup>6</sup>.
- Presented in 2009 Alternative Energy Technology Transfer Forum on April 8, 2009, in Detroit, Michigan on Characterization of Indoor Air Pollutants and Emissions from Public Transport Buses Using Biodiesel, Kumar Ashok, A. Kadiyala, K. Shandyla, V. Nerrala<sup>7</sup>.
- Poster Presentation in 102nd Annual Conference & Exhibition, AWMA, June 16-19, 2009 in Detroit, Michigan; Investigation of Scanning Electron Microscopy as a Sustainable Analytical Technique for Particulate Matter in a Public Transit Bus Fueled by Sustainable Biodiesel Fuel, Shandilya, Kaushik K. and Kumar, A.<sup>8</sup>

<sup>&</sup>lt;sup>2</sup> Shandilya, Kaushik K., Kumar, A., 2010, 'Morphology of Single Inhalable Particle inside Public Transit Biodiesel Fueled Bus', Journal of Environmental Sciences, 22(2) 263–270.

<sup>&</sup>lt;sup>4</sup> Shandilya, Kaushik K., Kumar, A., 2010, Qualitative Evaluation of Particulate Matter inside Public Transit Buses Operated by Biodiesel, The Open Environmental Engineering Journal, 3, 13-20.

<sup>&</sup>lt;sup>5</sup> Paper under review in Environmental Progress, "Physical Characterization of Fine Particulate Matter Inside the Public Transit Buses Fueled by Biodiesel in Toledo, Ohio", Kaushik K. Shandilya and Ashok Kumar.

<sup>&</sup>lt;sup>6</sup> Presented in Poster Presentation in UT Graduate Research Symposium, April 10, 2009 in Toledo, Ohio; Morphology of inhalable particleS inside urban transit bus in the city of Toledo, Ohio, USA, Shandilya, K.K. and Kumar, A.

<sup>&</sup>lt;sup>7</sup> Presented in 2009 Alternative Energy Technology Transfer Forum on Wednesday, April 8, 2009, at Detroit, MI on *Characterization of Indoor Air Pollutants and Emissions from Public Transport Buses using Biodiesel*, Kumar A., Kadiyala, A., Shandilya Kaushik K., Nerella, V.V.K.

<sup>&</sup>lt;sup>8</sup> Poster Presentation in 102<sup>nd</sup> Annual Conference & Exhibition, AWMA, June 16-19, 2009 in Detroit, MI; Investigation of Scanning Electron Microscopy as a sustainable analytical technique for particulate matter in a public transit bus fueled by sustainable biodiesel fuel, *Student Poster #62*, **Shandilya, Kaushik K.** 

## 7. Key Published Findings

- 1. SEM methodology is a valuable tool for studying the distribution of particulate pollutants.
- 2. Agglomerate particles were found in abundance.
- 3. The surface of most particles was coarse with a fractal edge that can provide a suitable chemical reaction bed in the polluted atmospheric environment.
- 4. The three sorts of surface patterns of squares were smooth, semi-smooth, and coarse. The three sorts of square surface patterns represented the morphological characteristics of single inhalable particles in the air inside the bus in Toledo.
- 5. The size distribution was generally multi-modal for the ULSD but uni-modal for the B20-fueled bus.
- 6. The aspect ratio found for different filters collected inside the bus fueled by both the B20 blend and ULSD ranged 2.4-3.6 and 2.3-2.9 in average value with standard deviation range 0.9-7.4 and 1-7.3, respectively.
- 7. The square and oblong-shaped particles represented the single inhalable particle's morphology characteristics in the air of a Toledo transit bus.
- 8. The indoor air inside the bus is free of any carcinogenic substance.

## 8. Conclusions

This project was focused on monitoring, analyzing, and assessing the particulate matter inside the buses. For this purpose, two buses in the TARTA fleet were chosen. The sampling was performed with the help of the GRIMM sampler and Sioutas Cascade Impactor. The study profile included the above two buses, two seasons, and varying types of fuel usage. Results of particulate matter level suggest that air quality is healthful in terms of carcinogenic potential of PAHs. Scanning electron microscope analysis was helpful in understanding the origin of particulate matter level. The interpretations of results bring attention to several noteworthy issues.

These issues are briefly presented:

- 1. The levels of particulate matter are well below the guideline values.
- 2. There is a definite distinction between particulate pollution level inside and outside of the buses.
- 3. When PAH levels are absent in particulate phase, this ensures healthful air inside the bus.
- 4. SEM analysis helped us determine the possible sources of particulate matter inside the bus.
- 5. The shape, size distribution analysis, and aspect ratio will help in determining the potential particle deposition in the lungs, as well as understanding particle dynamics inside the bus.

## 9. Future Work

Further work was not done due to limited time and resources, however, several recommendations emerged from this study as listed:

A. Further characterization of fine particulates should be continued. The different analyses are:

1. Analyzing the X-ray diffraction (XRD) data collected during the project year.

2. Analyzing the Fourier Transform Infrared Spectroscopy (FTIR) data collected during the project year.

3. Analyzing the Magnetic Susceptibility (MS) data collected during the project year.

4. Analyzing the PM collected during the project year for Thermogravimetric analysis.

5. Analyzing the PM collected during the project year for Differential Scanning Calorimetry analysis.

- 6. Analyzing the PM collected during the project year for Ionic analysis.
- 7. Analyzing the PM collected during the project year for Metals analysis.
- 8. Analyzing the PM collected during the project year for Raman Spectroscopy analysis.
- 9. Analyzing the PM collected during the project year for Transmission electron microscope (TEM) and SEM analysis.
- B. Conduct a comprehensive field study using the Cascade Impactor to collect more samples in different particle size ranges.
- C. Conduct field studies using Dust track and GRIMM to collect more samples for refining source-receptor relationships.
- D. Refine the current air pollution emission inventory for Toledo including non-point sources and unorganized sources.
- E. Conduct laboratory studies using different blends of biodiesel fuels to understand the characteristics of the exhaust from the buses.

The Michigan-Ohio (MIOH) University Transportation Center (UTC) is a coalition of five regional universities improving transportation. The MIOH UTC partner institutions are the University of Detroit Mercy (UDM), Bowling Green State University (BGSU), Grand Valley State University (GVSU), The University of Toledo (UT), and Wayne State University (WSU).

The coalition addresses the transportation capabilities and competitive position of the region and the nation. A focus on environmental stewardship promotes the reduction of pollutants and other adverse effects not only by decreasing fossilfuel dependence but also by developing congestion avoidance systems. UDM is leading the effort with Dr. Leo E. Hanifin, Dean of the College of Engineering & Science, serving as the MIOH UTC Director.

In addition to a four-year commitment from the U.S. DOT, support is also coming from the Michigan DOT, local and regional government organizations, as well as, partner universities and corporations.



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