COMPARATIVE EVALUATION OF AMBIENT FINE PARTICULATE MATTER ($PM_{2.5}$) DATA OBTAINED FROM URBAN AND RURAL MONITORING SITES ALONG THE UPPER OHIO RIVER VALLEY

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Semi-Annual Technical Progress Report
Revision No. 1

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PRINCIPAL AUTHORS:	Robinson P. Khosah, Ph.D. John P. Shimshock, Ph.D. Advanced Technology Systems, Inc.
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CONTRACTOR:	Advanced Technology Systems, Inc. 639 Alpha Drive – RIDC Park Pittsburgh, PA 15238-2819
SUBCONTRACTORS:	Ohio University E317 Grover Athens, OH 45701 Desert Research Institute 2215 Raggio Parkway Reno, NV 89512
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ABSTRACT

Advanced Technology Systems, Inc. (***ATS***), with Desert Research Institute (DRI) and Ohio University as subcontractors, was contracted by the NETL in September 1998 to manage the *Upper Ohio River Valley Project* (UORVP), with a goal of characterizing the ambient fine particulate in this region, including examination of urban/rural variations, correlations between $PM_{2.5}$ and gaseous pollutants, and influences of artifacts on $PM_{2.5}$ measurements in this region. Two urban and two rural monitoring sites were included in the UORVP. The four sites selected were all part of existing local and/or state air quality programs. One urban site was located in the Lawrenceville section of Pittsburgh, Pennsylvania at an air quality monitoring station operated by the Allegheny County Health Department. A second urban site was collocated at a West Virginia Division of Environmental Protection (WVDEP) monitoring station at the airport in Morgantown, West Virginia. One rural site was collocated with the Pennsylvania Department of Environmental Protection (PADEP) at a former NARSTO-Northeast site near Holbrook, Greene County, Pennsylvania. The other rural site was collocated at a site operated by the Ohio Environmental Protection Agency (OHEPA) and managed by the Ohio State Forestry Division in Gifford State Forest near Athens, Ohio. Previous Semi-Annual Technical Progress Reports presented the following: (1) the median mass and composition of $PM_{2.5}$ are similar for both Lawrenceville and Holbrook, suggesting that the sites are impacted more by the regional than by local effects; (2) there was no significant differences in the particulate trending and levels observed at both sites within seasons; (3) sulfate levels predominate at both sites and (4) $PM_{2.5}$ and PM_{10} mass concentration levels are consistently higher in summer than in winter, with intermediate levels being observed in the fall and spring. Analyses of data conducted during the period from April 1, 2003 through September 30, 2003 are presented in this Semi-Annual Technical Progress Report. Report Revision No. 1 includes the additions or removals of text presented in the previous version of this report.

TABLE OF CONTENTS

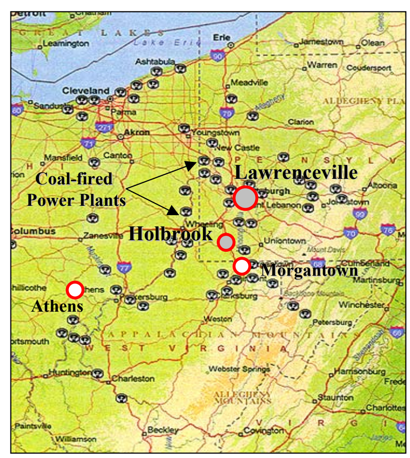
Page No.

EXECUTIVE SUMMARY

Analyses of data conducted during this semi-annual reporting period focused on the results generated using the sampling equipment supplied by Desert Research Institute, Inc. (DRI). Between one and five different DRI samplers were deployed at the Lawrenceville (LW), Holbrook (HB) and Morgantown (MO) sites. A summary of the sampling and analytical laboratory analyses schedule for each of the DRI samplers is presented. The frequency of sampling varied throughout the study period. “Intensive” sampling periods were defined as periods in which samples were collected on a relatively frequently basis (ranged from 6-hour integrated samples collected round-the-clock to one 24-hour integrated sample collected every third day). “Background” sampling periods were defined as periods in which 24-hour integrated samples were collected every sixth day. For each sampling period, all appropriate samples were analyzed for $PM_{2.5}$ or PM_{10} mass concentrations. For each sampling period, a subset of selected samples was analyzed for targeted elements, ions or compounds. Very few samples were collected during the background sampling periods that were analyzed for targeted elements, ions or compounds. As such, discussions regarding the chemical composition of the collected samples will be limited to samples collected during the intensive sampling periods. The results of these analyses conducted to date are summarized in this report.

INTRODUCTION

As part of its ambient fine particulate program, the U.S. Department of Energy’s-National Energy Technology Laboratory (NETL), in cooperation with key stakeholders including the U. S. Environmental Protection Agency (EPA), local and state environmental agencies, industry, and academia, established and operated several $PM_{2.5}$ speciation sites in the Upper Ohio River Valley.



The overall goal of this program, called the *Upper Ohio River Valley Project* (UORVP) was to investigate the nature and composition of fine particulate ($PM_{2.5}$) and its precursor gases in the Upper Ohio River valley and provide a better understanding of the relationship between coal-based power system emissions and ambient air quality in this region. The combustion of coal to generate electricity can produce primary ambient fine particulate matter ($PM_{2.5}$) as well as the gaseous precursors (e.g., SO_2 and NO_X) to the formation of secondary fine particles (e.g., ammonium sulfates and nitrates), and condensible species such as ammonia and nitric acid vapor. The Upper Ohio River Valley (UORV) was chosen for this extensive fine particulate research because it is representative of areas in the eastern half of the continental United States that are not well characterized but have a high density of coal-fired electric utility, heavy industry (e.g., coke and steel making), light industry and transportation emission sources. The UORV is also in the center of the ozone transport region, which provides a platform to study interstate pollution transport issues.

Advanced Technology Systems, Inc. (***ATS***), with Desert Research Institute (DRI) as the subcontractor, was contracted by the NETL in September 1998 to manage the *Upper Ohio River Valley Project* (UORVP). The location of the monitoring sites along with neighboring coal-fired plants are as shown in the map.

Two urban and two rural monitoring sites were included in the UORVP. The four sites selected were all part of existing local and/or state air quality programs. One urban site was located in the Lawrenceville section of Pittsburgh, Pennsylvania. This site is an air quality monitoring station operated by the Allegheny County Health Department. A second urban site was collocated at a West Virginia Division of Environmental Protection (WVDEP) monitoring station at the airport in Morgantown, West Virginia. One rural site was collocated with the Pennsylvania Department of Environmental Protection (PADEP) at a former NARSTO-Northeast site near Holbrook, Greene County, Pennsylvania. The other rural site was collocated at a site operated by the Ohio Environmental Protection Agency (OHEPA) and managed by the Ohio State Forestry Division in Gifford State Forest near Athens, Ohio.

Project Goal and Objectives

As stated above, the overall goal of this project was to investigate the nature and composition of fine particulate matter ($PM_{2.5}$) and its precursor gases in the Upper Ohio River Valley; however, in the process, the UORVP was intended to address the following four key scientific questions related to ambient fine particulate matter:

- Are sulfates a major or minor component of $PM_{2.5}$ mass in the eastern half of the continental USA?
- Is there a correlation between O_3 and $PM_{2.5}$ levels?
- Is there a significant variation in $PM_{2.5}$ composition/concentration between urban and rural sites impacted by similar regional emission sources?
- Does the Federal Reference Method (FRM) performance provide an accurate/realistic measurement of $PM_{2.5}$ mass?
  (What, if any, are the influences of artifacts on measurement?)

EXPERIMENTAL

Between one and five different Sequential Filter Samplers designed and built by Desert Research Institute (DRI-SFSs) were deployed at the Lawrenceville (LW), Holbrook (HB) and Morgantown (MO) sites. Additionally, one or two Federal Reference Method samplers (FRMs) were deployed at the LW and HB sites.

A summary of the sampling and analytical laboratory analyses schedules for each of the DRI-SFS is presented in Table 1 through 5.

The frequency of sampling varied throughout the study period and was as follows:

- "Intensive" sampling periods were defined as periods in which samples were collected on a relatively frequent basis (ranged from 6-hour integrated samples collected round-the-clock to one 24-hour integrated sample collected every third day).
- "Background" sampling periods were defined as periods in which 24-hour integrated samples were collected every sixth day.

For each sampling period, all appropriate samples were analyzed for $PM_{2.5}$ or PM_{10} mass concentration. For each sampling period, a subset of selected samples was analyzed for targeted elements, ions or compounds.

As outlined in Tables 1 though 5, there were very few samples collected during the background sampling periods that were analyzed for targeted elements, ions or compounds. As such, discussions regarding the chemical composition of the collected samples will be limited to samples collected during the intensive sampling periods.

RESULTS AND DISCUSSION

The data presented below summarizes efforts from discrete filter sampling at the three sampling sites (LW, HB & MO). As much as was possible, comparisons were drawn, noting observed similarities or differences between the rural and urban sites for both $PM_{2.5}$ and PM_{10} species.

It should be noted that DRI provided an extensive summary of the $PM_{2.5}$ and PM_{10} ambient air concentrations measured using DRI's sampling equipment at the HB, LW and MO sites. Per DRI's standard operating procedures (SOPs), $PM_{2.5}$ and PM_{10} ambient air concentrations were flagged (using a variety of descriptors) as appropriate if (i) nonstandard procedures were utilized in the field or in the laboratory or (ii) peculiar observations of the samples were noted. DRI voided some samples as appropriate (occurred primarily due to field equipment failures) and elected to report the remainder of the sample concentrations either with or without data flags. DRI's SOPs reserve the right for the end user of the data to accept or reject flagged data entries. ATS adopted a fairly conservative approach for filtering DRI's data prior to conducting the analyses presented in this report (i.e., ATS excluded many, but not all, of the flagged data entries – depended on the nature of the flag). In addition, ATS filtered the DRI data set sets for the HB and LW sites to exclude samples (paired observations) that satisfied the following criteria:

- PM_{10} concentration < $PM_{2.5}$ concentration; and
- The associated error bars for the $PM_{2.5}$ and PM_{10} concentrations did not overlap

If both criteria were satisfied, then both the $PM_{2.5}$ and PM_{10} concentrations were voided.

1.0 SAMPLES COLLECTED DURING THE BACKGROUND SAMPLING PERIODS

1.1 $PM_{2.5}$ Mass Concentrations – Site Comparisons - DRI Sampling Equipment

For the LW, HB and MO sites, examine the 24-hour integrated $PM_{2.5}$ mass concentrations (samples were collected every sixth day) – composite data were generated that sorted the concentrations by the common sample date (not examining seasonal variations in $PM_{2.5}$ mass concentrations here) -

(i) Calculate the Spearman Rank Correlation Coefficient (r_s) for each pairing (LW/HB, LW/MO and HB/MO) – the results are as follows:

Pairing ($PM_{2.5}$ DRI)	r_s value	Conclusion
LW / HB	0.70	Reasonably good positive correlation between LW and HB
LW / MO	0.71	Reasonably good positive correlation between LW and MO
HB / MO	0.65	Reasonably good positive correlation between HB and MO

A scatter plot for each pairing also confirms the positive correlations.

(ii) Calculate the differences for each pairing (LW/HB, LW/MO and HB/MO) – Run a statistical hypothesis test to determine if the average difference for each pairing is significantly different from zero at the 95 percent confidence level – the results are as follows:

Pairing ($PM_{2.5}$ DRI)	Conclusion
LW / HB	Insufficient data to conclude that the average difference is significantly different from zero
LW / MO	Ibid.
HB / MO	Ibid.

Essentially, the data collected during the background sampling periods suggests that $PM_{2.5}$ mass concentrations are statistically the same at the LW, HB and MO sites.

(iii) Compare the $PM_{2.5}$ mass concentrations measured at the LW, HB and MO sites with the promulgated $PM_{2.5}$ mass concentration standards –

<u>24-hour standard</u> = 65 μg/m^3 measured as the 98th percentile of the 24-hour $PM_{2.5}$ mass concentrations in a year (averaged over three years)

<u>Annual standard</u> = 15 μg/m^3 measured as the three year average of the annual arithmetic mean

The results are as follows:

Site	Overall Average $PM_{2.5}$ Conc. (DRI)	50th Percentile $PM_{2.5}$ Conc. (DRI)	98th Percentile $PM_{2.5}$ Conc. (DRI)
LW	14.4 μg/m^3	12.5 μg/m^3	32.7 μg/m^3
HB	13.0 μg/m^3	10.4 μg/m^3	35.0 μg/m^3
MO	16.3 μg/m^3	15.6 μg/m^3	34.6 μg/m^3

The results show that the overall average $PM_{2.5}$ mass concentrations measured at the HB, LW and MO sites are very nearly equal to the promulgated annual standard of 15 μg/m^3 but far less than the 24-hour standard of 65 μg/m^3.

1.2 PM_{10} Mass Concentrations – Site Comparisons - DRI Sampling Equipment

For the LW and HB sites, examine the 24-hour integrated PM_{10} mass concentrations (samples were collected every sixth day) – composite data were generated that sorted the concentrations by the common sample date (not examining seasonal variations in PM_{10} mass concentrations here) -

(i) Calculate the Spearman Rank Correlation Coefficient (r_s) for the LW/HB pairing – the results are as follows:

Pairing (PM_{10} DRI)	r_s value	Conclusion
LW / HB	0.80	Good positive correlation between LW and HB

A scatter plot for the pairing also confirms the positive correlations.

(ii) Calculate the differences for the LW/HB pairing – Run a statistical hypothesis test to determine if the average difference for the pairing is significantly different from zero at the 95 percent confidence level – the results are as follows:

Pairing (PM_{10} DRI)	**Conclusion**
LW / HB	The average difference is significantly different from zero (LW > HB)

The data collected during the background sampling periods suggests that there is a larger number of PM_{10} sources that impact the LW site as compared with the HB site.

(iii) Compare the PM_{10} mass concentrations measured at the LW and HB sites with the promulgated PM_{10} mass concentration standards –

24-hour standard = 150 $\mu g/m^3$ measured as the 99th percentile of the 24-hour $PM_{2.5}$ mass concentrations in a year (averaged over three years)

Annual standard = 50 $\mu g/m^3$ measured as an annual arithmetic mean

The results are as follows:

Site	**Overall Average PM_{10} Conc. (DRI)**	**50th Percentile PM_{10} Conc. (DRI)**	**99th Percentile PM_{10} Conc. (DRI)**
LW	22.3 $\mu g/m^3$	20.4 $\mu g/m^3$	52.6 $\mu g/m^3$
HB	17.0 $\mu g/m^3$	14.2 $\mu g/m^3$	49.0 $\mu g/m^3$

The results show that the overall average PM_{10} mass concentrations measured at the HB and LW sites are far less than the promulgated annual standard of 50 $\mu g/m^3$ and the 24-hour standard of 150 $\mu g/m^3$.

1.3 Comparison of $PM_{2.5}$ with PM_{10} Mass Concentrations – DRI Sampling Equipment

For the LW and HB sites, examine the 24-hour integrated $PM_{2.5}$ and PM_{10} mass concentrations (samples were collected every sixth day) – composite data were generated that sorted the concentrations by the common sample date (not examining seasonal variations in $PM_{2.5}$ and PM_{10} mass concentrations here) -

(i) For the LW and HB sites, calculate the Spearman Rank Correlation Coefficient (r_s) for each $PM_{2.5}$ / PM_{10} pairing – the results are as follows:

Pairing (DRI)	r_s value	Conclusion
LW $PM_{2.5}$ / PM_{10}	0.85	Very good positive correlation at the LW site
HB $PM_{2.5}$ / PM_{10}	0.84	Very good positive correlation at the HB site

A scatter plot for each pairing also confirms the positive correlation.

(ii) For the LW and HB sites, calculate the differences for each $PM_{2.5}$ / PM_{10} pairing – Run a statistical hypothesis test to determine if the average difference for each pairing is significantly different from zero at the 95 percent confidence level – the results are as follows:

Pairing (DRI)	Conclusion
LW $PM_{2.5}$ / PM_{10}	The average difference is significantly different from zero at the LW site ($PM_{10} > PM_{2.5}$)
HB $PM_{2.5}$ / PM_{10}	The average difference is significantly different from zero at the HB site ($PM_{10} > PM_{2.5}$)

If the sampling equipment is operating properly, then these are the expected results.

1.4 Comparison of $PM_{2.5}$ Mass Concentrations – DRI Sampling Equipment with $PM_{2.5}$ Mass Concentrations – FRM Sampling Equipment

For the LW and HB sites, examine the 24-hour integrated $PM_{2.5}$ mass concentrations (samples were collected every sixth day) that were measured using the DRI and the FRM sampling equipment – composite data were generated that sorted the concentrations by the common sample date (not examining seasonal variations in $PM_{2.5}$ mass concentrations here) -

(i) For the LW and HB sites, calculate the Spearman Rank Correlation Coefficient (r_s) for each DRI / FRM pairing - the results are as follows:

Pairing ($PM_{2.5}$)	r_s value	Conclusion
LW DRI / FRM	0.92	Very good positive correlation at the LW site
HB DRI / FRM	0.90	Very good positive correlation at the HB site

A scatter plot for each pairing also confirms the positive correlation.

(ii) For the LW and HB sites, calculate the differences for each DRI / FRM pairing - Run a statistical hypothesis test to determine if the average difference for each pairing is significantly different from zero at the 95 percent confidence level – the results are as follows:

Pairing ($PM_{2.5}$)	Conclusion
LW DRI / FRM	Insufficient data to conclude that the average difference is significantly different from zero
HB DRI / FRM	The average difference is significantly different from zero at the HB site (DRI > FRM)

The results summarized above present different conclusions for identical tests performed at two separate sites. To further understand these conclusions, an additional statistical hypothesis test was run in a manner similar to the test described in Section 1.1(ii). Calculate the differences for the LW/HB FRM pairings - Run a statistical hypothesis test to determine if the average difference for the pairing is significantly different from zero at the 95 percent confidence level – the results are as follows:

Pairing ($PM_{2.5}$)	Conclusion
FRM LW / HB	The average difference is significantly different from zero (LW > HB)

The result summarized above does not match the result summarized in Section 1.1 using the DRI sampling equipment ($PM_{2.5}$ DRI LW / HB). As such, we conclude that the $PM_{2.5}$ data generated with the FRM sampling equipment at the HB site may be suspect.

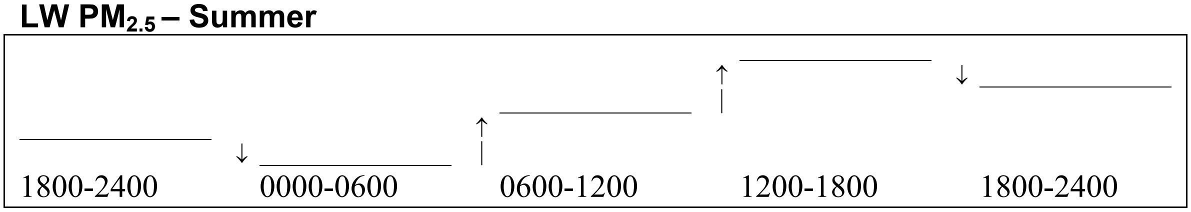
2.0 SAMPLES COLLECTED DURING THE INTENSIVE SAMPLING PERIODS

2.1 Diurnal Variations of LW $PM_{2.5}$ and PM_{10} Mass Concentrations – DRI Sampling Equipment

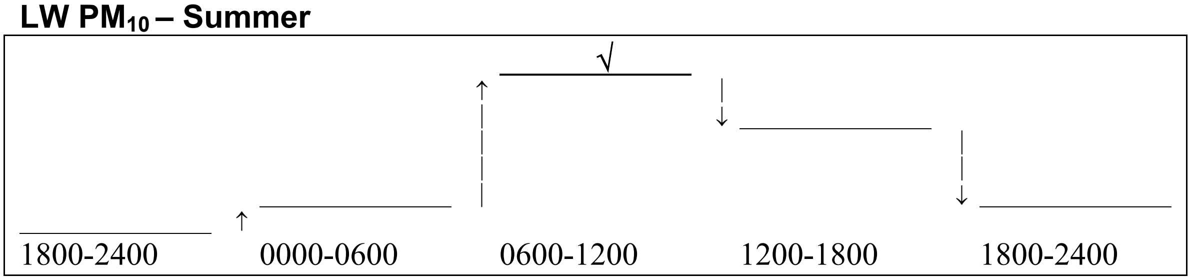
For the LW site, examine the 6-hour integrated $PM_{2.5}$ and PM_{10} mass concentrations to determine the presence of diurnal variations of these concentrations – For $PM_{2.5}$ and PM_{10}, calculate the difference in the concentrations for each consecutive 6-hour sampling period (i.e., concentration for [0600 to 1200] time period minus the concentration for the [0000 to 0600] time period) - composite data were generated that sorted the differences by the common sampling comparison period and the season of the year (summer or winter) – Run a statistical hypothesis test to determine if the average difference for each seasonal sampling comparison period is significantly different from zero at the 95 percent confidence level – the results are as follows:

Legend
↑ Average difference in concentration for consecutive 6-hour sampling periods > 0
↓ Average difference in concentration for consecutive 6-hour sampling periods < 0
(size of ↑ and ↓ approximates the value of the average difference)
√ Average difference is significantly different from zero

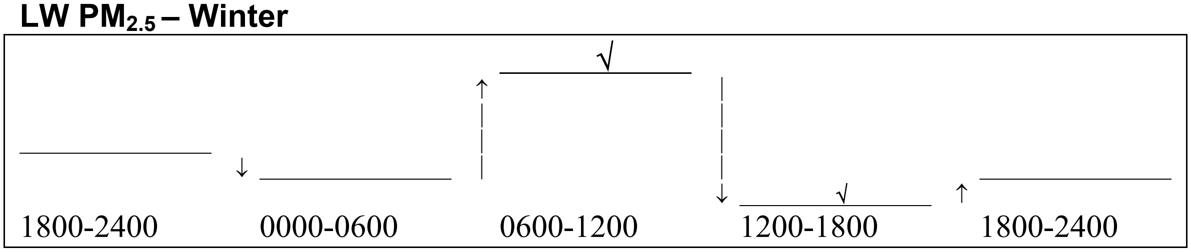
LW $PM_{2.5}$ – Summer



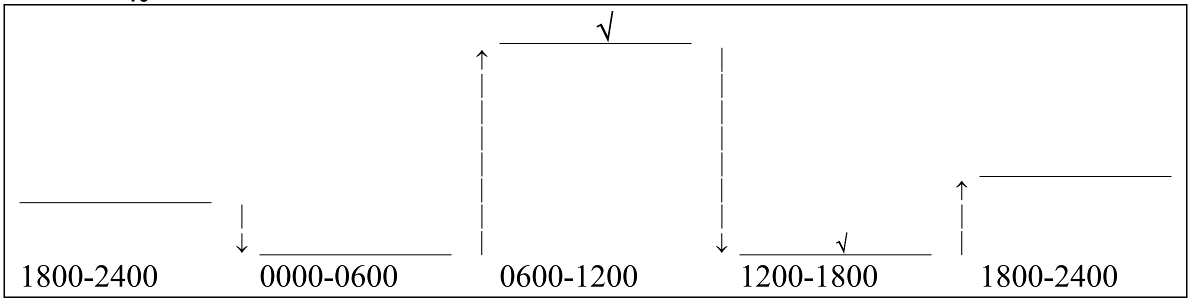
LW PM_{10} – Summer



LW $PM_{2.5}$ – Winter



LW PM_{10} – Winter



During the winter season, the changes in $PM_{2.5}$ and PM_{10} mass concentrations are likely due to (i) inputs from automotive sources during the morning hours and (ii) increases and decreases in the atmospheric mixing height during daytime and nighttime hours, respectively. During the summer season, the changes in $PM_{2.5}$ and PM_{10} mass concentrations are likely due to the factors outlined above and to the occurrence of atmospheric photochemical activity (especially for $PM_{2.5}$).

2.2 Seasonal Variations of $PM_{2.5}$ Mass Concentrations – Site Comparisons - DRI Sampling Equipment

Compare the $PM_{2.5}$ mass concentrations measured at the LW, HB and MO sites with the promulgated $PM_{2.5}$ mass concentration standards for each sampling period – the results are as follows:

24-hour standard = 65 μg/m^3 measured as the 98th percentile of the 24-hour $PM_{2.5}$ mass concentrations in a year (averaged over three years)

LW $PM_{2.5}$ (DRI)

Season	Sampling Dates	50th Percentile $PM_{2.5}$ Conc. (DRI)	98th Percentile $PM_{2.5}$ Conc. (DRI)
Winter	02/17/1999 – 02/28/1999 *	12.6 μg/m^3	34.2 μg/m^3
Summer	08/03/1999 – 09/11/1999 *	15.2 μg/m^3	36.0 μg/m^3
Winter	01/12/2000 – 02/18/2000 *	13.7 μg/m^3	32.5 μg/m^3
Summer	07/17/2000 – 08/25/2000 *	15.0 μg/m^3	38.8 μg/m^3
Summer	06/30/2001 – 08/08/2001 *	18.8 μg/m^3	52.8 μg/m^3
Winter	01/02/2002 – 01/22/2002	15.8 μg/m^3	20.5 μg/m^3
Fall & Winter	10/01/2002 – 02/27/2003	9.9 μg/m^3	27.1 μg/m^3

*: 6-hour integrated samples rather than 24-hour integrated samples

HB $PM_{2.5}$ (DRI)

Season	Sampling Dates	50th Percentile $PM_{2.5}$ Conc. (DRI)	98th Percentile $PM_{2.5}$ Conc. (DRI)
Winter	02/17/1999 – 02/28/1999	N/A – less than 20 samples available	N/A – less than 20 samples available
Summer	08/03/1999 – 09/11/1999	15.8 $\mu g/m^3$	29.6 $\mu g/m^3$
Winter	01/12/2000 – 02/17/2000	8.4 $\mu g/m^3$	16.0 $\mu g/m^3$
Summer	07/17/2000 – 08/25/2000	18.0 $\mu g/m^3$	36.9 $\mu g/m^3$
Summer	07/02/2001 – 08/08/2001	27.5 $\mu g/m^3$	55.9 $\mu g/m^3$
Winter	01/02/2002 – 01/22/2002	9.7 $\mu g/m^3$	15.4 $\mu g/m^3$

MO $PM_{2.5}$ (DRI)

Season	Sampling Dates	50th Percentile $PM_{2.5}$ Conc. (DRI)	98th Percentile $PM_{2.5}$ Conc. (DRI)
Winter	01/13/2000 – 02/18/2000	N/A – less than 20 samples available	N/A – less than 20 samples available
Summer	08/21/1999 – 08/05/2001	20.3 $\mu g/m^3$ (29 samples available)	38.3 $\mu g/m^3$ (29 samples available)

At the LW site, the data suggests that $PM_{2.5}$ mass concentrations are usually higher during the summer season as compared with the winter season, although other factors (e.g., local sources and weather) apparently contribute in a manner sufficient to obfuscate the seasonal pattern.

At the HB site, the data strongly suggests that $PM_{2.5}$ mass concentrations are higher during the summer season as compared with the winter season, which is likely due to the occurrence of photochemical activity. There is insufficient quantity of data from the MO site to deduce any seasonal variations in $PM_{2.5}$ mass concentrations at this site.

2.3 Seasonal Variations of PM_{10} Mass Concentrations – Site Comparisons - DRI Sampling Equipment

Compare the PM_{10} mass concentrations measured at the LW and HB sites with the promulgated PM_{10} mass concentration standards for each sampling period – the results are as follows:

24-hour standard = 150 $\mu g/m^3$ measured as the 99th percentile of the 24-hour PM_{10} mass concentrations in a year (averaged over three years)

LW PM_{10} (DRI)

Season	Sampling Dates	50^{th} Percentile $PM_{2.5}$ Conc. (DRI)	99^{th} Percentile $PM_{2.5}$ Conc. (DRI)
Winter	02/17/1999 – 02/28/1999 *	16.6 $\mu g/m^3$	48.9 $\mu g/m^3$
Summer	08/03/1999 – 09/11/1999 *	22.9 $\mu g/m^3$	53.7 $\mu g/m^3$
Winter	01/12/2000 – 02/18/2000 *	19.4 $\mu g/m^3$	56.5 $\mu g/m^3$
Summer	07/17/2000 – 08/25/2000 *	20.5 $\mu g/m^3$	48.8 $\mu g/m^3$
Summer	07/02/2001 – 08/07/2001 *	25.8 $\mu g/m^3$	70.3 $\mu g/m^3$

*: 6-hour integrated samples rather than 24-hour integrated samples

HB PM_{10} (DRI)

Season	Sampling Dates	50^{th} Percentile $PM_{2.5}$ Conc. (DRI)	99^{th} Percentile $PM_{2.5}$ Conc. (DRI)
Winter	02/17/1999 – 02/28/1999	N/A – less than 20 samples available	N/A – less than 20 samples available
Summer	08/03/1999 – 09/11/1999	20.0 $\mu g/m^3$	45.8 $\mu g/m^3$
Winter	01/13/2000 – 02/18/2000	12.7 $\mu g/m^3$	23.6 $\mu g/m^3$
Summer	07/17/2000 – 08/25/2000	19.9 $\mu g/m^3$	42.5 $\mu g/m^3$
Summer	06/30/2001 – 08/08/2001	24.0 $\mu g/m^3$	57.5 $\mu g/m^3$

At the LW site, the data suggests that there are no seasonal variations in PM_{10} mass concentrations at this site. At the HB site, the data suggests that PM_{10} mass concentrations may be higher during the summer season as compared with the winter season. However, the quantity of data from the HB site is not sufficient to strongly defend this conclusion.

2.4 Presence of Trace Elements in $PM_{2.5}$ and PM_{10} Samples – DRI Sampling Equipment – Site and Particle Size Comparisons

For the $PM_{2.5}$ and PM_{10} samples collected at the LW and HB sites with the DRI sampling equipment, calculate the "relative error" (defined as the ratio of the uncertainty value to the concentration) for each trace element – For comparison purposes, all HB $PM_{2.5}$, HB PM_{10} and LW PM_{10} mass concentrations had a "relative error" of 0.2 or less; For comparison purposes, 99 percent of the LW $PM_{2.5}$ mass concentrations had a "relative error" of 0.2 or less

√ = At least 80 percent of the samples classified in a particular category (HB $PM_{2.5}$, LW $PM_{2.5}$, HB PM_{10} or LW PM_{10}) had a "relative error" (defined as the ratio of the uncertainty value to the concentration) of 0.2 or less –

Trace Element	HB $PM_{2.5}$ (58 samples)	LW $PM_{2.5}$ (387 samples)	HB PM_{10} (8 samples)	LW PM_{10} (34 samples)
Na				
Mg				
Al				
Si				
P				
S	√	√	√	√
Cl	√	√		
K	√	√		
Ca			√	√
Ti				
V				
Cr				
Mn				
Fe	√	√	√	√
Co				
Ni				
Cu				
Zn			√	√
Ga			√	
As				
Se				
Br				
Rb				
Sr				
Y				
Zr				
Mo				
Pd			√	
Ag				
Cd				
In				
Sn				
Sb				
Ba				
La				
Au			√	
Hg			√	
Tl				
Pb				
U				

CONCLUSIONS

The following can be concluded from the findings discussed above:

<u>Samples Collected During the Background Sampling Periods</u>

- The data collected during the background sampling periods suggests that $PM_{2.5}$ mass concentrations are statistically the same at the LW, HB and MO sites
- The data collected during the background sampling periods show that the overall average $PM_{2.5}$ mass concentrations measured at the HB, LW and MO sites are very nearly equal to the promulgated annual standard of 15 $\mu g/m^3$ but far less than the 24-hour standard of 65 $\mu g/m^3$.
- The data collected during the background sampling periods suggests that LW PM_{10} mass concentrations are statistically greater than the HB PM_{10} mass concentrations
- The data collected during the background sampling periods show that the overall average PM_{10} mass concentrations measured at the HB and LW sites are far less than the promulgated annual standard of 50 $\mu g/m^3$ and the 24-hour standard of 150 $\mu g/m^3$.

<u>Samples Collected During the Intensive Sampling Periods</u>

- During the summer months, diurnal variations of LW $PM_{2.5}$ and PM_{10} mass concentrations were observed. The changes in concentrations from one 6-hour measurement period to the following 6-hour measurement period were not statistically significant except for PM_{10} (increase from 0000-0600 to 0600-1200, likely due to inputs from automotive sources during the morning hours)
- During the winter months, diurnal variations of LW $PM_{2.5}$ and PM_{10} mass concentrations were observed. The changes in concentrations from one 6-hour measurement period to the following 6-hour measurement period were not statistically significant except for (i) $PM_{2.5}$ and PM_{10} (increase from 0000-0600 to 0600-1200, likely due to inputs from automotive sources during the morning hours and decreases in the atmospheric mixing height during nighttime hours) and (ii) $PM_{2.5}$ and PM_{10} (decrease from 0600-1200 to 1200-1800, likely due to increases in the atmospheric mixing height during daytime hours).
- At the LW site, the data suggests that $PM_{2.5}$ mass concentrations are usually higher during the summer season as compared with the winter season, although other factors (e.g., local sources and weather) apparently contribute in a manner sufficient to obfuscate the seasonal pattern. At the HB site, the data strongly suggests that $PM_{2.5}$ mass concentrations are higher during the summer season as compared with the winter season, which is likely due to the occurrence of photochemical activity. There is insufficient quantity of data from the MO site to deduce any seasonal variations in $PM_{2.5}$ mass concentrations at this site.
- At the LW site, the data suggests that there are no seasonal variations in PM_{10} mass concentrations at this site. At the HB site, the data suggests that PM_{10} mass concentrations may be higher during the summer season as compared with the

winter season. However, the quantity of data from the HB site is not sufficient to strongly defend this conclusion.

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TABLE 1 - DRI SFS PM2.5 - NUMBER OF SAMPLES COLLECTED AND ANALYZED

05-Mar-04 Site ID FTQnnn & FQNnnn

Sampling Period Type	Site ID	Start Date	Stop Date	Sampling Frequency	Nominal Sampling Duration (hrs)	No. of Samples Collected *	No. of Valid Analyses **					
							Mass	38 Elements	Artifact Organic C	Elemental & Organic C	Inorganic Ions	Volatilized NO_3^-
Intensive (winter)	LW	2/17/1999	2/28/1999	4 times per day	6	48	46	36	36	36	36	36
	HB	2/17/1999	2/28/1999	Once per day	24	12	11	8	8	8	8	8
Background	LW	3/1/1999	7/29/1999	Every 6th Day	24	26	26	5	5	5	5	5
	HB	3/1/1999	7/29/1999	Every 6th Day	24	26	26	5	5	5	5	5
Intensive (summer)	LW	8/3/1999	9/11/1999	4 times per day	6	160	154	39	39	39	39	39
	HB	8/3/1999	9/11/1999	Once per day	24	40	39	10	10	10	10	10
	MO	8/21/1999	9/11/1999	Every 3rd Day	24	8	5	0	0	0	0	0
Background	LW	9/15/1999	1/7/2000	Every 6th Day	24	20	20	0	0	0	0	0
	HB	9/15/1999	1/7/2000	Every 6th Day	24	20	17	0	0	0	0	0
	MO	9/15/1999	1/7/2000	Every 6th Day	24	21	20	0	0	0	0	0
Intensive (winter)	LW	1/12/2000	2/18/2000	4 times per day	6	152	140	35	35	35	35	35
	HB	1/12/2000	2/18/2000	Once per day	24	38	35	9	9	9	9	9
	MO	1/13/2000	2/18/2000	Every 3rd Day	24	13	8	0	0	0	0	0
Background	LW	2/24/2000	7/11/2000	Every 6th Day	24	23	22	2	2	2	2	2
	HB	2/24/2000	7/11/2000	Every 6th Day	24	23	16	1	1	1	1	1
	MO	2/24/2000	7/11/2000	Every 6th Day	24	21	19	0	0	0	0	0
Intensive (summer)	LW	7/17/2000	8/25/2000	4 times per day	6	160	149	54	54	54	54	54
	HB	7/17/2000	8/25/2000	Once per day	24	40	39	13	13	13	13	13
	MO	7/17/2000	8/25/2000	Every 3rd Day	24	14	12	0	0	0	0	0
Background	LW	8/28/2000	6/24/2001	Every 6th Day	24	51	50	2	2	2	2	2
	HB	8/28/2000	6/24/2001	Every 6th Day	24	51	38	2	2	2	2	2
	MO	8/28/2000	6/24/2001	Every 6th Day	24	50	43	0	0	0	0	0
Intensive (summer)	LW	6/30/2001	8/8/2001	4 times per day	6	160	156	75	75	75	75	75
	HB	6/30/2001	8/8/2001	Once per day	24	40	36	18	18	18	18	18
	MO	6/30/2001	8/5/2001	Every 3rd Day	24	14	12	0	0	0	0	0
Intensive (winter)	LW	1/2/2002	1/22/2002	Once per day	24	21	21	0	0	0	0	0
	HB	1/2/2002	1/22/2002	Once per day	24	21	21	0	0	0	0	0
Intensive	LW	10/1/2002	2/28/2003	Once per day	24	151	148	148	148	148	148	148
(fall & winter)												

*: Excludes Field Blanks and Missing Data

**: Excludes Field and Laboratory Blanks

TABLE 2 - DRI SFS PM10 - NUMBER OF SAMPLES COLLECTED AND ANALYZED

05-Mar-04 Site ID TTQnnn & TQNnnn

Sampling Period Type	Site ID	Start Date	Stop Date	Sampling Frequency	Nominal Sampling Duration (hrs)	No. of Samples Collected *	No. of Valid Analyses **					
							Mass	38 Elements	Artifact Organic C	Elemental & Organic C	Inorganic Ions	Volatilized NO_3^-
Intensive (winter)	LW	2/17/1999	2/28/1999	4 times per day	6	48	45	34	34	34	34	34
	HB	2/17/1999	2/28/1999	Once per day	24	12	11	8	8	8	8	8
Background	LW	3/1/1999	7/29/1999	Every 6th Day	24	26	25	5	5	5	5	5
	HB	3/1/1999	7/29/1999	Every 6th Day	24	26	26	5	5	5	5	5
Intensive (summer)	LW	8/3/1999	9/11/1999	4 times per day	6	160	155	0	0	0	0	0
	HB	8/3/1999	9/11/1999	Once per day	24	40	40	0	0	0	0	0
Background	LW	9/15/1999	1/7/2000	Every 6th Day	24	20	20	0	0	0	0	0
	HB	9/15/1999	1/7/2000	Every 6th Day	24	19	19	0	0	0	0	0
Intensive (winter)	LW	1/12/2000	2/18/2000	4 times per day	6	147	132	0	0	0	0	0
	HB	1/12/2000	2/18/2000	Once per day	24	38	35	0	0	0	0	0
Background	LW	2/24/2000	7/11/2000	Every 6th Day	24	23	21	0	0	0	0	0
	HB	2/24/2000	7/11/2000	Every 6th Day	24	22	20	0	0	0	0	0
Intensive (summer)	LW	7/17/2000	8/25/2000	4 times per day	6	160	153	0	0	0	0	0
	HB	7/17/2000	8/25/2000	Once per day	24	40	39	0	0	0	0	0
Background	LW	8/28/2000	6/24/2001	Every 6th Day	24	51	46	0	0	0	0	0
	HB	8/28/2000	6/24/2001	Every 6th Day	24	51	51	0	0	0	0	0
Intensive (summer)	LW	6/30/2001	8/8/2001	4 times per day	6	160	145	0	0	0	0	0
	HB	6/30/2001	8/8/2001	Once per day	24	40	40	0	0	0	0	0
Intensive (winter)	LW	1/2/2002	1/22/2002	Once per day	24	0	0	0	0	0	0	0
	HB	1/2/2002	1/22/2002	Once per day	24	0	0	0	0	0	0	0
Intensive (fall & winter)	LW	10/1/2002	2/28/2003	Once per day	24	0	0	0	0	0	0	0

*: Excludes Field Blanks and Missing Data

**: Excludes Field and Laboratory Blanks

TABLE 3 - DRI SGS TP - NUMBER OF SAMPLES COLLECTED AND ANALYZED

05-Mar-04 Site ID OQN & DQNnnn

Sampling Period Type	Site ID	Start Date	Stop Date	Sampling Frequency	Nominal Sampling Duration (hrs)	No. of Samples Collected *	No. of Valid Analyses **	
							HNO_3 (g) & NO_3^- (p)	NO_3^- (p)
Intensive (winter)	LW	2/17/1999	2/28/1999	4 times per day	6	48	34	34
	HB	2/17/1999	2/28/1999	Once per day	24	12	9	9
Background	LW	3/1/1999	7/29/1999	Every 6th Day	24	26	5	5
	HB	3/1/1999	7/29/1999	Every 6th Day	24	26	5	5
Intensive (summer)	LW	8/3/1999	9/11/1999	4 times per day	6	160	39	39
	HB	8/3/1999	9/11/1999	Once per day	24	40	10	10
Background	LW	9/15/1999	1/7/2000	Every 6th Day	24	20	0	0
	HB	9/15/1999	1/7/2000	Every 6th Day	24	20	0	0
Intensive (winter)	LW	1/12/2000	2/18/2000	4 times per day	6	152	0	0
	HB	1/12/2000	2/18/2000	Once per day	24	38	0	0
Background	LW	2/24/2000	7/11/2000	Every 6th Day	24	24	0	0
	HB	2/24/2000	7/11/2000	Every 6th Day	24	24	0	0
Intensive (summer)	LW	7/17/2000	8/25/2000	4 times per day	6	160	0	0
	HB	7/17/2000	8/25/2000	Once per day	24	40	0	0
Background	LW	8/28/2000	6/24/2001	Every 6th Day	24	51	0	0
	HB	8/28/2000	6/24/2001	Every 6th Day	24	51	0	0
Intensive (summer)	LW	6/30/2001	8/8/2001	4 times per day	6	160	0	0
	HB	6/30/2001	8/8/2001	Once per day	24	40	0	0
Intensive (winter)	LW	1/2/2002	1/22/2002	Once per day	24	21	0	0
	HB	1/2/2002	1/22/2002	Once per day	24	21	0	0
Intensive (fall & winter)	LW	10/1/2002	2/28/2003	Once per day	24	0	0	0

*: Excludes Field Blanks

**: Excludes Field and Laboratory Blanks

TABLE 4 - DRI SGS PM2.5 - NUMBER OF SAMPLES COLLECTED AND ANALYZED

05-Mar-04 Site IDOQC & DQCnnn

Sampling Period Type	Site ID	Start Date	Stop Date	Sampling Frequency	Nominal Sampling Duration (hrs)	No. of Samples Collected *	No. of Valid Analyses **	
							NH_3 (g) & NH_4^+ (p)	NH_4^+ (p)
Intensive (winter)	LW	2/17/1999	2/28/1999	4 times per day	6	48	34	34
	HB	2/17/1999	2/28/1999	Once per day	24	12	4	4
Background	LW	3/1/1999	7/29/1999	Every 6th Day	24	26	5	5
	HB	3/1/1999	7/29/1999	Every 6th Day	24	26	5	5
Intensive (summer)	LW	8/3/1999	9/11/1999	4 times per day	6	160	39	39
	HB	8/3/1999	9/11/1999	Once per day	24	40	6	6
Background	LW	9/15/1999	1/7/2000	Every 6th Day	24	20	0	0
	HB	9/15/1999	1/7/2000	Every 6th Day	24	20	0	0
Intensive (winter)	LW	1/12/2000	2/18/2000	4 times per day	6	152	42	42
	HB	1/12/2000	2/18/2000	Once per day	24	38	11	11
Background	LW	2/24/2000	7/11/2000	Every 6th Day	24	24	2	2
	HB	2/24/2000	7/11/2000	Every 6th Day	24	24	1	1
Intensive (summer)	LW	7/17/2000	8/25/2000	4 times per day	6	160	57	57
	HB	7/17/2000	8/25/2000	Once per day	24	40	16	16
Background	LW	8/28/2000	6/24/2001	Every 6th Day	24	51	2	2
	HB	8/28/2000	6/24/2001	Every 6th Day	24	51	3	3
Intensive (summer)	LW	6/30/2001	8/8/2001	4 times per day	6	160	72	72
	HB	6/30/2001	8/8/2001	Once per day	24	40	16	16
Intensive (winter)	LW	1/2/2002	1/22/2002	Once per day	24	0	0	0
	HB	1/2/2002	1/22/2002	Once per day	24	0	0	0
Intensive (fall & winter)	LW	10/1/2002	2/28/2003	Once per day	24	0	0	0

*: Excludes Field Blanks

**: Excludes Field and Laboratory Blanks

TABLE 5 - DRI PORTABLE PM2.5 - NUMBER OF SAMPLES COLLECTED AND ANALYZED

05-Mar-04

Sampling Period Type	Site ID	Start Date	Stop Date	Sampling Frequency	Nominal Sampling Duration (hrs)	No. of Samples Collected *	No. of Valid Analyses ** CCSEM
Intensive (winter)	LW	2/17/1999	2/28/1999	4 times per day	6	48	0
	HB	2/17/1999	2/28/1999	Once per day	24	12	0
Background	LW	3/1/1999	7/29/1999	Every 6th Day	24	26	0
	HB	3/1/1999	7/29/1999	Every 6th Day	24	26	0
Intensive (summer)	LW	8/3/1999	9/11/1999	4 times per day	6	160	0
	HB	8/3/1999	9/11/1999	Once per day	24	40	0
Background	LW	9/15/1999	1/7/2000	Every 6th Day	24	20	0
	HB	9/15/1999	1/7/2000	Every 6th Day	24	20	0
Intensive (winter)	LW	1/12/2000	2/18/2000	4 times per day	6	152	0
	HB	1/12/2000	2/18/2000	Once per day	24	38	0
Background	LW	2/24/2000	7/11/2000	Every 6th Day	24	24	0
	HB	2/24/2000	7/11/2000	Every 6th Day	24	24	0
Intensive (summer)	LW	7/17/2000	8/25/2000	4 times per day	6	160	0
	HB	7/17/2000	8/24/2000	Once per day	24	39	0
Background	LW	8/28/2000	6/24/2001	Every 6th Day	24	51	0
	HB	8/28/2000	6/24/2001	Every 6th Day	24	51	0
Intensive (summer)	LW	6/30/2001	8/8/2001	4 times per day	6	160	0
	HB	6/30/2001	8/8/2001	Once per day	24	40	0
Intensive (winter)	LW	1/2/2002	1/22/2002	Once per day	24	21	0
	HB	1/2/2002	1/22/2002	Once per day	24	21	0
Intensive (fall & winter)	LW	10/1/2002	2/28/2003	Once per day	24	0	0

*: Excludes Field Blanks

**: Excludes Field and Laboratory Blanks