PHASE II PM_{2.5} SPECIATION REPORT: ANALYSIS OF SPECIES DURING WINTER MONTHS

TABLE OF CONTENTS

1.0	Introduction1						
2.0	Liter	Literature Review					
	2.1	Background					
3.0	Mate	erials and Methods					
	3.1	Sample Collection					
	3.2	Gravimetric Analysis					
	3.3	Elemental X-ray Fluorescence Analysis					
	3.4	Carbon Analysis					
	3.5	Levoglucosan Analysis7					
	3.6	Soluble Ions Analysis					
	3.7	Particulate Carbon Determination					
	3.8	PM _{2.5} Fingerprinting Analysis					
	3.9	Quality Assurance and Data Reconciliation					
4.0	Resu	llts					
	4.1	Composition of PM _{2.5}					
	4.2	Changes in PM _{2.5} 11					
5.0	Disc	ussion14					
	5.1	Study Limitations					
	5.2	Unknown Component					
	5.3	Findings					
6.0	Cond	clusions					
	6.1	Recommendations and Report					
7.0	Refe	rences					

Appendix 1.....

LIST OF FIGURES

Figure 1. Composition of PM2.5 Separated into Major Components and Source Categories	10
Figure 2. Total Average Concentration of PM2.5 per Winter Season	11
Figure 3. Total Average Concentration of Biomass Burning Markers per Winter Season	12
Figure 4. Total Average Concentration of Combustion Pollutants per Winter Season.	12
Figure 5. Total Average Concentration of Mineral/Dust per Winter Season.	13
Figure 6. Total PM2.5 and Carbon Measurement Comparison, CSN vs. Phase II Study	15
Figure 7. Average Concentration Profile of PM2.5 vs. Elevated Sample	16
Figure 8. Correlation of Levoglucosan with BC and UVPM.	16
Figure 9. Correlation of Levoglucosan with Temperature Change.	17

LIST OF TABLES

Table 1. Statistical Summary of PM _{2.5} Concentrations (µg/m ³) (2015-2020)	1
Table 2. PM2.5 Pearson Correlation of DES PM2.5 Monitoring Sites	1
Table 3. Overview of PM _{2.5} Analyses	5
Table 4. Total Average Concentration of PM2.5 By Source Category at JM	

ACRONYMS

AAE	absorption Ångström exponent
ATN	attenuation
BC	black carbon
BrC	brown carbon
COC	chain-of-custody (sheet)
CSN	EPA's Chemical Speciation Network
DART	CSN Data Analysis and Reporting Tool
DES	Clark County Department of Environment and Sustainability
EC	elemental carbon
ED-XRF	energy dispersive x-ray fluorescence
EPA	U.S. Environmental Protection Agency
FRM	federal reference method
GV	Green Valley monitoring station
JM	Jerome Mack monitoring station
JN	Jean monitoring station
JO	Joe Neal monitoring station
LVV	Las Vegas Valley
NAAQS	National Ambient Air Quality Standards
NIOSH	National Institute for Occupational Safety and Health
NIST	National Institute of Standards and Technology
OC	organic carbon
PM	Paul Meyer monitoring station
PM _{2.5}	particulate matter ≤ 2.5 microns
RT	Rancho & Teddy monitoring station
SA	Sunrise Acres
SVOC	semi-volatile organic carbon
UVPM	ultraviolet absorbing particulate matter
VSCC	very-sharp-cut cyclone
WR	Walnut Recreation Center monitoring station
XRF	x-ray fluorescence

EXECUTIVE SUMMARY

This study investigates the composition of PM_{2.5} aerosols in the Las Vegas Valley during the winters of 2019 and 2022. Its primary aim was to identify major source contributors to elevated levels of particulate matter less than 2.5 microns in diameter (PM_{2.5}) and to create a mass balance of PM_{2.5} components to prepare for a potential designation of nonattainment of the National Ambient Air Quality Standard (NAAQS) for PM_{2.5}. Samples were collected from at Jerome Mack (JM), Sunrise Acres (SA), Green Valley (GV), and the Walnut Recreation Center (WRC). These samples were then analyzed for the chemical composition of PM_{2.5}, with a focus on carbon particulate matter, inorganic ions, mineral dust, and biomass burning markers (e.g., levoglucosan). Statistical analysis of the data revealed significant increases in PM_{2.5} during colder weather conditions, which typically favor temperature inversions that can lead to an accumulation of combustion-related pollutants. Specifically, residential biomass burning was identified as a major source of PM_{2.5} that could be regulated. Recommendations will therefore emphasize residential outreach and incentive programs, depending on whether the U.S. Environmental Protection Agency designates the Las Vegas Valley as being in nonattainment of the PM_{2.5} NAAQS.

1.0 INTRODUCTION

DES manages the Clark County air quality monitoring program. A PM_{2.5} "fingerprint study" was conducted to understand PM_{2.5} composition for potential reductions in National Ambient Air Quality Standards (NAAQS) pollutants, focusing on elevated wintertime concentrations. The study, which analyzed speciated PM_{2.5} data from Teflon® filters and the EPA Chemical Speciation Network (CSN), identified major PM_{2.5} components, including:

- Elemental carbon (EC)
- Black carbon (BC);
- Organic carbon (OC) (per CSN data);
- Inorganic cations (sodium (Na⁺), potassium (K⁺), and ammonium (NH4⁺));
- Inorganic anions (sulfate (SO₄²⁻), chloride (Cl⁻), and nitrate (NO₃⁻));
- Levoglucosan;
- Major elements, such as aluminum, magnesium, silicon, sulfur, potassium, calcium, iron, and sodium.
- Minor elements, such as barium, bromine, manganese, copper, tantalum, zirconium, strontium, and zinc.

DES reviewed available monitoring data from daily PM_{2.5} analyses, the CSN, the DES Annual Network Plan and Five-Year Network Assessment, and historical trends of monitored pollutants. Table 1 provides a statistical summary for seven PM_{2.5} monitoring sites from 2015 to 2020.

Variable	Mean	Standard Deviation	Minimum	Maximum
Paul Meyer	5.52	3.36	0.52	79.45
Joe Neal	4.86	3.70	0.32	111.61
Green Valley	5.38	3.44	0.39	86.82
Jerome Mack	8.44	7.69	0.00	74.36
Sunrise Acres	8.05	7.52	0.57	108,70
Jean	4.02	2.93	0.03	72.77
Rancho & Teddy	7.10	4.58	0.50	45.53

Table 1. Statistical Summary of $PM_{2.5}$ Concentrations (µg/m³) (2015-2020)

The highest average $PM_{2.5}$ concentrations were observed at Jerome Mack (JM) (8.44 µg/m³) and Sunrise Acres (SA) (8.05µg/m³). Rancho & Teddy (RT), situated near the busy interstate I-15, also exhibited elevated $PM_{2.5}$ values (7.10 µg/m³). Conversely, Jean (JN) registered the lowest $PM_{2.5}$ concentrations: 4.02 µg/m³ during the specified period.

Table 2. PM _{2.5} Pearson Correlation of DES PM _{2.5}	5 Monitoring Sites
---	--------------------

Site	Paul Meyer	Joe Neal	Green Valley	Jerome Mack	Sunrise Acres	Jean	Rancho & Teddy
Paul Meyer	1.0000	_					

Site	Paul Meyer	Joe Neal	Green Valley	Jerome Mack	Sunrise Acres	Jean	Rancho & Teddy
Joe Neal	0.9046	1.0000	—		_	—	
Green Valley	0.8385	0.8805	1.0000		_	—	
Jerome Mack	0.6496	0.6321	0.6263	1.0000			
Sunrise Acres	0.6402	0.5654	0.6847	0.8640	1.0000	_	
Jean	0.6928	0.7943	0.7514	0.2864	0.3552	1.0000	
Rancho & Teddy	0.6994	0.6175	0.6436	0.8425	0.8379	0.2934	1.000

Statistical analysis of PM_{2.5} in the "2020 5-Year Network Assessment" and a preliminary review of the monitoring data reveal:

- 1. JM, SA, and RT exhibit a high correlation ($\rho > 0.83$) and consistently show elevated PM_{2.5} levels from October through March annually. RT is a near-road site and thus subject to more mobile-source influence. These sites also have the highest mean PM_{2.5} values.
- 2. Monitoring data from JO, PV, and PM show similarity, suggesting little variation in PM_{2.5} emission levels along the west side of the Las Vegas Valley (LVV).
- 3. Monitoring data from SA, JM, and GV show similarity, suggesting little variation in PM_{2.5} emission levels along the east side of the LV.
- 4. JO, GV, and PM show a high correlation ($\rho > 0.84$).
- 5. JN exhibits the lowest correlation ($\rho < 0.35$) with JM, SA, and RT.
- 6. PM_{2.5} samples routinely collected and tested for chemical composition at JM show significant increases in ammonium nitrate (NH₄NO₃), total nitrates (NO₃⁻), OC, and EC during episodes of higher PM_{2.5} emissions from October through March, as shown in CSN speciation data.

DES has formulated a hypothesis to interpret the observed results:

- 1. A substantial portion of $PM_{2.5}$ emissions during winter in central-east parts of the LVV can be attributed to residential burning of wood in fireplaces, as well as the burning of charcoal and other biomasses.
- 2. Elevated levels of PM_{2.5} during winter in central-east parts of LVV are likely caused by emissions from increased commercial and residential heating.
- 3. Winter weather conditions, including winds and ambient temperature inversions, may contribute to or cause high PM_{2.5}. PM_{2.5} is not solely regional, and short-term impacts from blowing dust and mobile source emissions are evident.
- 4. The east side of LVV, characterized by its lower elevation, may function as a "PM_{2.5} sink" during stagnant atmospheric and inversion conditions.

To test the assumptions underlying these hypotheses, DES has designed a comprehensive study with the following experimental components:

- 1. Review and analyze historical data from federal reference method (FRM), CSN, and special studies samples to identify periods of high PM_{2.5} and the composition of PM_{2.5} during those periods.
- 2. Collect PM_{2.5} FRM samples at four monitoring sites (JM, SA, GV, and WR) during winter months (Dec–Feb) in the central-east parts of the LVV.
- 3. Analyze collected PM_{2.5} samples for trace elements using energy dispersive X-ray fluorescence (ED-XRF).
- 4. Analyze collected PM_{2.5} samples for levoglucosan using ion chromatography (IC).
- 5. Analyze collected PM_{2.5} samples by IC for soluble common cations and anions.
- 6. Analyze samples for carbon content using optical analysis.
- 7. Evaluate analytical results and determine potential chemical fingerprints of the significant sources and composition of PM_{2.5} in the LVV. These include at least (1) mineral dust, (2) road dust, (3) brake dust, (4) anthropogenic sources, (5) solid fuels such as wood, charcoal, and other biomasses, and (6) speciation of various vehicular exhaust emissions, including diesel.
- 8. Analyze $PM_{2.5}$ data at JN to identify a location to represent baseline emissions for $PM_{2.5}$.

This study was designed to provide a comprehensive understanding of the root cause(s) behind elevated $PM_{2.5}$ concentrations during winter months and to discern potential temporal and geographical patterns of $PM_{2.5}$ in the LVV.

2.0 LITERATURE REVIEW

2.1 <u>Background</u>

Speciation offers enhanced chemical resolution compared to standard mass measurements, providing insights into fine particulates' composition (Ahuja et al. 1989; Houck et al. 1989). Common emission sources contribute to suspended particles, with coarse particles coming mainly from such sources as soil, unpaved roads, construction, and evaporation; fine particulates can be formed secondarily from gases by chemical reaction or vaporization. Sources of fine particulates include the combustion of coal, oil, gasoline, diesel fuel, and wood, along with such high-temperature processes as steel mills. At various places and times, any one of three or four major components can dominate the mass of PM in a 24-hour sample (Luo 2024).

Major components of PM_{2.5} include primary aerosols (those from direct emission) and secondary aerosols (those formed through chemical transformation). Combustion-related primary aerosols originate from motor vehicles, burning practices, residential wood combustion, and industrial processes, emitting trace metals, sulfuric acid, sulfate, nitrate, particulate organic carbon, and ammonium. Urban and nonurban PM compositions are defined by a mix of the primary and secondary aerosols listed below.

Geological Material: Suspended dusts primarily comprise aluminum, silicon, calcium, titanium, iron, and other metal oxides, with composition varying based on local geology and industrial processes. Typically, 5–15% of PM_{2.5} consists of geological material, rising to 30–40% in central California during summer months.

Sulfate: Atmospheric sulfate mainly exists as ammonium sulfate, ammonium bisulfate, and sulfuric acid; it is water-soluble and resides exclusively in the PM fraction. Most fine sulfates originate from the oxidation of SO_2 gas emitted by coal-burning power plants and copper smelters. The eastern United States has a concentration of coal-burning power plants that emit significant amounts of SO_2 , but the western U.S. has relatively low SO_2 emission densities (Malm et al. 1994).

Nitrate: Ammonium nitrate, a product of reversible gas-to-particle equilibrium between ammonia gas and nitric acid gas, is the predominant nitrate compound in PM_{2.5}. NO_x emissions, mainly from fuel combustion, contribute to nitrate formation, with about 60% of NO_x coming from stationary sources and 40% from mobile sources (Zawacki et al. 2018).

Ammonium: Ammonium sulfate, ammonium bisulfate, and ammonium nitrate are common ammonium-containing compounds formed through reactions between sulfuric acid, ammonia gas, and nitric acid. Atmospheric ammonia (NH₃) arises from biological decay, either absorbing on surfaces or reacting to form ammonium nitrate.

Organic Carbon: Particulate OC, a complex mix of compounds with over 20 carbon atoms, originates from combustion, geological processes, road dust, and photochemistry. Various compounds make characterization challenging, requiring multiple analytical techniques.

Elemental Carbon: Particles from combustion sources contain light-absorbing EC, often called soot or BC. EC serves as a tracer for combustion-derived particles, distinguishing them from soil- and marine-derived aerosols. Geological material exhibits variable abundances of it. Since EC occurs with OC, discrimination of particulate EC from OC depends on the analytical method used.

Sodium and Potassium: These two cations trace wood-burning and ocean sources, respectively. Analyzing aqueous extracts of sample filters using ion chromatography reveals concentrations of potassium and sodium, along with other ions.

	Major Analyte/Species	Sampling/Analysis
Total Mass	Mass	PTFE (Teflon®) Filter/Gravimetric
Mineral dust (usually 5-15% of PM _{2.5})	Al Si Ca P Mn Fe	PTFE (Teflon) filter/EDXRF and gravimetric
Road dust (brake and tire dust)	Zn Cu Ni Pb Cr Cd	PTFE (Teflon) filter/EDXRF and gravimetric
Brake dust	Ti Fe Cu Zn Sb Ba	PTFE (Teflon) filter/EDXRF and gravimetric
SO ₂ from burning of coal/Cu smelters	Total S	PTFE (Teflon) filter/EDXRF and gravimetric
Solid fuels such as wood, charcoal, and other biomasses (cellulose based)	Levoglucosan	PTFE (Teflon) filter/IC and gravimetric
Pb-gasoline (Mexico)	Pb	PTFE (Teflon) filter/EDXRF and gravimetric
Gasoline-engines emissions (catalytic converters)	Pt Pd	PTFE (Teflon) filter/EDXRF and gravimetric
Fuel combustion/mobile and stationary	Nitrate	PTFE (Teflon) filter//IC
SO ₂ from burning of coal/Cu smelters	Sulfate by IC	PTFE (Teflon) filter//IC
Biological decay	Ammonia as NH ₄ +	PTFE (Teflon) filter//IC
Wood burning (pine) and ocean sources	K+ Na+	PTFE (Teflon) filter//IC
Combustion/geological processes/road dust/photochemistry	Total carbon = EC/OC/carbonates	Pre-fired quarts fiber filter/TOA (NIOSH 5040) ¹
Combustion/diesel	Elemental carbon	Pre-fired quarts fiber filter/TOA (NIOSH 5040)

Table 3. Overview of PM_{2.5} Analyses

¹ National Institute for Occupational Safety and Health: Method 5040, Issue 3 (2003).

XRF has been used extensively in the analysis of ambient aerosols (Dzubay and Stevens 1975; Goulding and Jaklevic 1977) because they are non-destructive, have multi-element capabilities, and cost relatively little. This technique is performed on Teflon® filters to determine the concentration of approximately 40 elements (from sodium to uranium); however, for typical atmospheres, XRF analysis is meaningful only for half these elements, such as aluminum, silicon, sulfur, chlorine, potassium, calcium, titanium, vanadium, chromium, manganese, iron, nickel, copper, zinc, arsenic, selenium, bromine, cadmium, and lead.

ED-XRF is a variation of XRF (Marguí et al. 2009) used in this study that utilizes a semiconductor detector with high intrinsic resolution. The detector allows the recording of an electric signal from a sample, which corresponds to the energy of the X-ray photons the sample emits. Xray emission profiles can then be used to identify the elemental composition of the sample.

3.0 MATERIALS AND METHODS

The elemental analysis of PM_{2.5} samples is pivotal for identifying particle sources and assessing their contributions to fine particle mass. Teflon®-membrane filters were used to examine major components in aerosol samples, revealing their prevalence in both anthropogenic and geological source profiles. This study focused on EC, vehicle and biomass combustion, metals, and trace metal salts (e.g., oxides, nitrates, sulfates) obtained from those filters.

3.1 <u>Sample Collection</u>

PM_{2.5} samples were collected from December 2021 to February 2022 at four monitoring sites (JM, SA, GV, and WR) in the central-east parts of LVV. Sequential FRM particulate sampler E-SEQ-FRM (MetOne Instruments) was employed for sample collection, using pre-weighed 47-mm Teflon filter discs in individual EPA-standardized cassettes.

Prior to sampling, both sample filters and quality control samples (i.e., blanks or duplicates) were preconditioned in stable conditions, i.e., maintained with a mean relative humidity (RH) of 35 \pm 5% and a mean temperature of 22°C \pm 2°C over a 24-hour period. Instrument flow was controlled to 16.67 LPM (1 m³/hr) and ambient air drawn through a BX-808 very-sharp-cut cyclone (VSCC) to selectively sample PM_{2.5} aerosols. The sampling duration was 24 hours, after which dust-laden filters were sent to a laboratory for equilibration and reweighing. Clean and dirty mass values for the filters were combined with the volume of air sampled to calculate the concentration of PM_{2.5} in µg/m³.

3.2 Gravimetric Analysis

Sample filters underwent conditioning and weighing in a controlled environment, with temperature and humidity carefully regulated. Gravimetric analysis was performed using a Sartorius Cubis MSE SG EE microbalance equipped with WinWedge Pro serial communication software (Sartorius Lab Instruments) with a readability of $\pm 1\mu g$ and a repeatability of $\pm 1\mu g$. The microbalance operated in the same controlled environment where the filters were conditioned.

To minimize dust contamination, precautionary measures included positive pressure, highefficiency particulate air filters, tacky mats, and powder-free gloves. Microbalance performance was verified using certified, National Institute for Science and Technology-traceable mass standards. Before sampling, all filters were conditioned and weighed, then packaged in cassettes alongside with chain-of-custody sheets (COC). After sampling, the filters underwent another round of conditioning and weighing. The recorded weights were used to determine mass and concentration values.

3.3 <u>Elemental X-ray Fluorescence Analysis</u>

ED-XRF was used for non-destructive analysis of Teflon®-membrane filters to determine the concentration of approximately 20 elements, including Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Cd, and Pb.

3.4 <u>Carbon Analysis</u>

The multi-wavelength OT21 Model 2015 carbon analyzer was used to measure optically absorbing BC and ultraviolet particulate matter (UVPM) as proxy for brown carbon (BrC) in aerosol particles collected on the 47-mm Teflon filters. The data generated by the OT21 was attenuation (ATN x 100) at 370 nm and 880 nm. Equation 1 was used to convert from ATN (unitless) to BC.

Eq. 1.
$$BC\left(\frac{\mu g}{m^3}\right) = \frac{ATN}{\sigma_{abs}(\frac{m^2}{g})} \times \frac{deposit\ area\ (m^2)}{sample\ volume\ (m^3)} \times 10^6\ \left(\frac{\mu g}{g}\right)$$

The factor σ_{abs} is the BC mass absorption efficiency, and a value of 16.6 m²/g is commonly used to convert ATN to BC for the 880-nm channel. The filters deposit area was 11.52 cm² and the sample volume was 24 m³.

Theoretically, BrC can be calculated in a similar way. However, there are two challenges: (1) the σ_{abs} for BrC is not known, and (2) the ultraviolet channel has more attenuation due to artifacts such as particle loading and multiple scattering. Consequently, no reliable correction algorithm has been developed; therefore, the BrC calculation by OT21 is not well defined. Calculated concentration of BrC or UVPM may overlap with concentration of BC causing a potential overestimation of carbon particulate matter in the data.

The absorption Ångström exponent (AAE), which describes the spectral dependence of light absorption by aerosol is determined to be approximately 1.1 for BC, although a value of 0.6–0.8 is often found in experiments. For BrC, the AAE value is typically larger than 1.1. The calculated AAE from the analyzed data varies from 0.48–0.88, indicating that BrC contribution is likely not significant.

3.5 <u>Levoglucosan Analysis</u>

Levoglucosan is a polysaccharide that originates solely from the pyrolysis of cellulose, making it a significant marker for biomass burning emissions (Bhattarai et al. 2019). Collected samples were analyzed for levoglucosan using gas chromatography-mass spectrometry.

3.6 Soluble Ions Analysis

Ion chromatography was used to analyze Cl⁻, SO_4^{2+} , NO_3^{-} , and NH_4^+ ions.

3.7 <u>Particulate Carbon Determination</u>

Methods to determine total particulate carbon require an accurate mass balance and effective quality assurance procedures. Differentiation of OC, EC, and carbonate carbon (Cc) provides useful characterization for trends analysis and source attribution. Total carbon (TC) is defined as TC = OC + EC + Cc. Semi-volatile organic carbon (SVOC) species compose a fraction of the organic carbon, which exists in the atmosphere in an equilibrium between the particle and gas phases. Despite limitations, the first and fundamental step of carbon speciation is the semi-

quantitative assessment of OC, EC, and Cc from a CSN quartz filter analyzed by thermal optical analysis (NIOSH 2003).

3.8 <u>PM2.5 Fingerprinting Analysis</u>

- 1. Review and analyze historical data of FRM, CSN, and special studies samples to specifically identify periods of high PM_{2.5} and the composition of PM_{2.5} during those periods.
- 2. Use the analytical results for chemical fingerprints of the significant sources and composition of $PM_{2.5}$ in the LVV. At a minimum, fingerprinting includes:
 - a. Mineral dust (ED-XRF: Al, Si, Ca, P, Mn, Fe);
 - b. Road dust from brakes and tires (ED-XRF: Zn, Cu, Ni, Pb, Cr, Cd);
 - c. Brake dust (ED-XRF: Ti, Fe, Cu, Zn, Sb, Ba);
 - d. Solid fuels, such as wood, charcoal, and other biomasses (levoglucosan); and
 - e. SO₂ from coal burning/Cu smelters (ED-XRF: total S), unlikely in the LVV.

3.9 **Quality Assurance and Data Reconciliation**

The data used was spot-checked and audited, verified against CSN Data Analysis and Reporting Tool (<u>DART</u>) data, compared against a master file, and subjected to other work verification techniques.

4.0 **RESULTS**

Table 4 and the figures in this section present the data collected during the winter seasons of 2019–2020, 2020–2021, and 2021–2022 across four sites within the LVV, with a focus on chemical speciation of $PM_{2.5}$. Particulates were grouped into their major source categories to better show the contributions sources make to $PM_{2.5}$. Some figures were supplemented by data from CSN and DART.

Component / Source Category	Average Concentration (µg/m³)	Error (µg/m³)	% of Total PM _{2.5}	Category Composition
BC	2.886	1	14.496%	BC
UVPM	1.736	1	8.720%	UVPM
Biomass burning markers	0.7837	± 0.08297	3.936%	Levoglucosan, K, Na
Minerals/dust	2.1235	± 0.08539	12.545%	Al, Si, Ca, P, Mn, Fe
Inorganic ions	2.5003	± 0.1432	12.559%	Cl ⁻ , SO4 ²⁺ , NO3 ⁻ , NH4 ⁺
Unknown	9.8797	—	49.624%	Unknown
Total	19.9092	_	—	—

Table 4. Total Average Concentration of PM_{2.5} By Source Category at JM

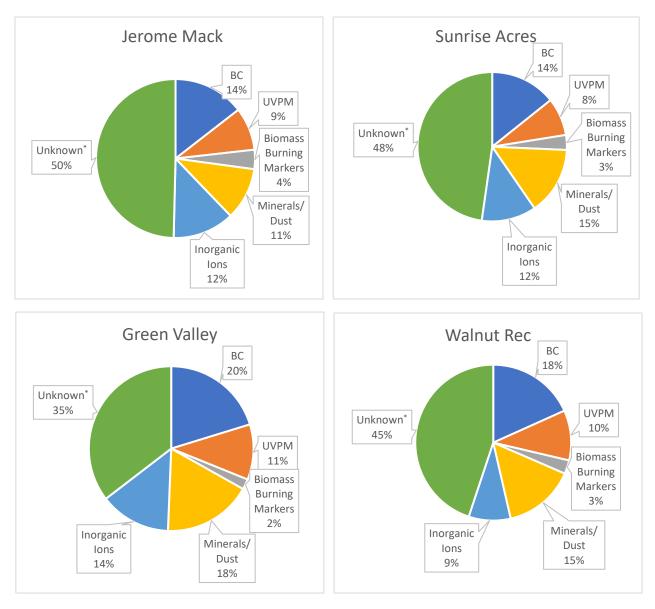
¹ Error for carbon particulate matter, including BC and UVPM, unquantifiable due to complex indirect analysis related to absorption of light.

4.1 <u>Composition of PM_{2.5}</u>

Table 4 shows the composition of $PM_{2.5}$, separated into major components and source categories, along with their average concentration and percentage contribution to total $PM_{2.5}$, collected at the site with the largest data set (JM) during the study period using the broadest set of data.

Carbon material, in the form of BC and UVPM, consistently made up the majority of measured $PM_{2.5}$, contributing 20–30% of the total mass. Minerals, in the form of various oxides from dust and debris, contributed 10–15% of measured $PM_{2.5}$. Inorganic ions originating from combustion and industrial processes contributed 10–15%. Biomass burning markers, composed primarily of levoglucosan, contributed 2–4%. However, a large proportion of $PM_{2.5}$ (35–50% of its concentration) was not measurable through the methods of this study.

These findings are consistent with previous studies on the composition of $PM_{2.5}$ and expected ratios, but included a significant unknown component (derived from the mass balance analysis) that may reduce the accuracy of this study's conclusions. A large portion of this unknown may include a form of carbon that does not absorb light and cannot be detected with the optical analysis method employed (Figure 1).



*Unknown component that was unquantifiable, most likely due to restrictions in optical analysis of carbon. Any material that does not absorb light could not be identified in this study.

Figure 1. Composition of PM_{2.5} Separated into Major Components and Source Categories.

Figure 1 shows the difference in the average composition of $PM_{2.5}$ as a percentage of the total mass measured per site at the four sites where data was collected. As expected, data from JM was highly correlative with SA data. GV and WR did not correlate as strongly with the other two sites, most probably due to a decrease in sample size and an increase in distance from the city center compared to the other two sites; however, both showed a significant increase in carbon and a decrease in the unknown as a percentage of the total mass measured.

4.2 <u>Changes in PM_{2.5}</u>

Comparing the average total concentration of $PM_{2.5}$ between winter seasons (Figure 2) shows significantly elevated levels of $PM_{2.5}$ in the winter of 2020. A further breakdown of components reveals potential sources of $PM_{2.5}$ elevation during the winter.

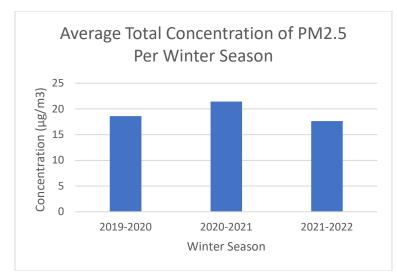


Figure 2. Total Average Concentration of PM_{2.5} per Winter Season.

Figures 3–5 show the changes in the major components of $PM_{2.5}$ between the winter seasons measured. Markers connected to biomass burning, like levoglucosan, potassium, and sodium, increased nearly 50% on average in the winter of 2020 compared to the previous year. General combustion pollutants like carbon and nitrates also showed significantly elevated levels during this period. Components of mineral dust, on the other hand, seemed to decrease on average in the winter of 2020. These figures suggest that the most significant components causing elevation of $PM_{2.5}$ during the winter season are those related to combustion (specifically, biomass or wood burning) due to the significant increases they show in markers like levoglucosan.

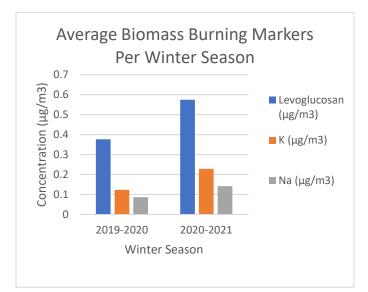


Figure 3. Total Average Concentration of Biomass Burning Markers per Winter Season.

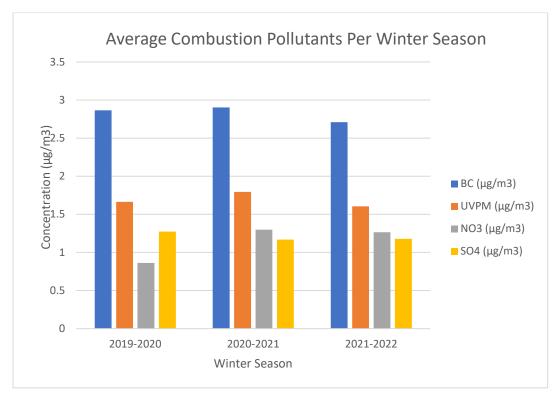


Figure 4. Total Average Concentration of Combustion Pollutants per Winter Season.

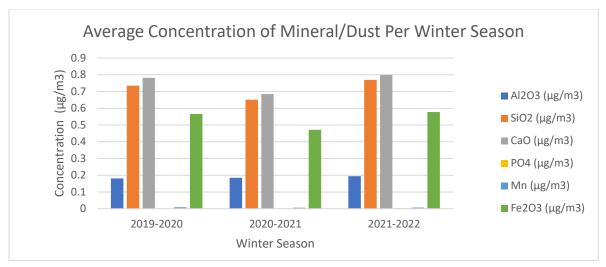


Figure 5. Total Average Concentration of Mineral/Dust per Winter Season.

5.0 **DISCUSSION**

This study sought out to break down the major components of $PM_{2.5}$ and identify major source categories, such as biomass burning or woodsmoke, that can be regulated to reduce overall $PM_{2.5.}$ Unfortunately, the data from the samples collected and measured for this study were in some ways incomplete.

5.1 <u>Study Limitations</u>

Due to legal and regulatory restrictions related to sample preservation, key components of $PM_{2.5}$ were only given a partial analysis, so there is no data for them in the winter of 2021. These include biomass burning markers (levoglucosan, potassium, and sodium) and inorganic ions (Cl⁻ and NH₄⁺). Also, most samples in this study came from JM, with GV and WR each contributing less than half the samples of JM and no samples at all from the winters of 2019 and 2020. Such limitations restricted the scope of this analysis in comparisons between sites and between components.

The mass and concentrations of pollutants included in the mineral/dust component of $PM_{2.5}$ were measured indirectly, by converting the elements measured into their respective oxides (e.g., silicon into silicon dioxide) that would be found in $PM_{2.5}$, adding mass not directly measured. This technique may introduce a level of error in the concentrations of mineral/dust particles.

5.2 <u>Unknown Component</u>

In this study, 35-50% of each sample could not be identified from the methods of measurement used. This unidentified material fluctuated significantly along with all the other components measured in this study and increased along with other components during elevated PM_{2.5} events. Having such a large component of PM_{2.5} unaccounted for limits the strength of the conclusions that can be drawn from this study's data.

The source of this unknown seems to be related to the indirect measurement of carbon and the formula used to derive a mass concentration of carbon. This was inferred by comparing carbon measurements from CSN data to those in this study, which showed a large discrepancy (Figure 6). The measurement of UVPM in this study was used to approximate the mass of BrC because there is no consistent way to make that calculation, but the level of error in this approximation is unclear. Additionally, there may exist within the samples a non-light absorbing "white carbon," identified in Chen et al. 2021 as representing roughly 40–60% of the total concentration of carbon. The light-absorption methods used in this study to measure carbon would be unable to identify such matter.

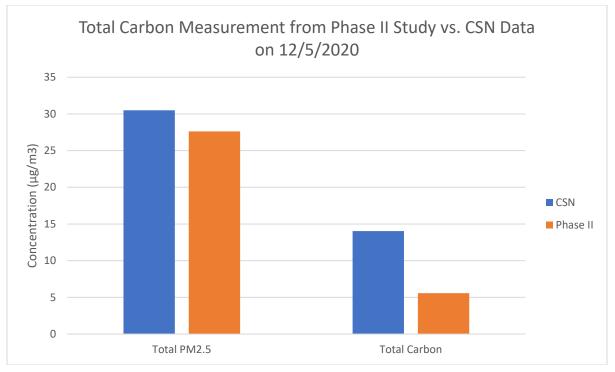


Figure 6. Total PM_{2.5} and Carbon Measurement Comparison, CSN vs. Phase II Study.

Figure 6 shows the measurement of total concentrations of $PM_{2.5}$ and carbon PM measured at JM on an example date of 12/5/2020 from both the CSN and this study. The difference in the measurement of total $PM_{2.5}$ is relatively small compared to the difference in the measurement of total carbon. In this report, carbon was identified in the form of BC and UVPM; in the CSN data, carbon is measured as EC and OC. These two different ways to quantify carbon overlap somewhat, which may have led to an incomplete measurement of carbon in this study, making it difficult to compare the two measurements.

5.3 <u>Findings</u>

Data from Phase II of this study and from the CSN suggested that woodsmoke, a pollutant source DES has some authority to regulate, may be a significant factor in increased $PM_{2.5}$ levels during the winter. The samples collected for this study seem to agree that increased levels of $PM_{2.5}$ during the winter are associated with biomass burning or woodsmoke.

Figures 3–5 of Section 4 shows that elevated levels of $PM_{2.5}$ in the winter of 2020 were due to an increase in combustion pollutants and shows that biomass burning markers increased nearly 50% compared to the winter of 2019.

Figure 7 compares the total sample average measurements of the components of $PM_{2.5}$ at JM and the sample with the highest measured concentration of $PM_{2.5}$ at Jerome Mack on 12/5/2020 and shows the percentage increase from that average. The most significant increase from the average is the concentration of biomass burning markers followed by all the other components related to combustion including the unknown, which is likely mostly carbon.

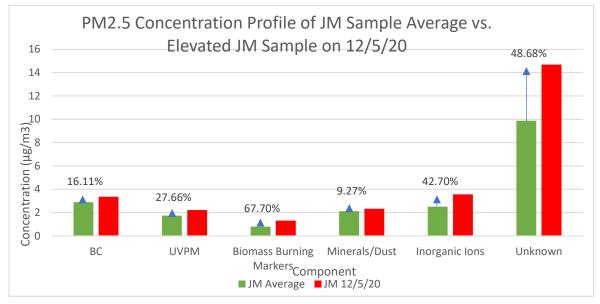


Figure 7. Average Concentration Profile of PM_{2.5} vs. Elevated Sample.

Further correlation analysis shows the relationship between increases in biomass burning and increases in $PM_{2.5}$ (Figures 8 and 9).

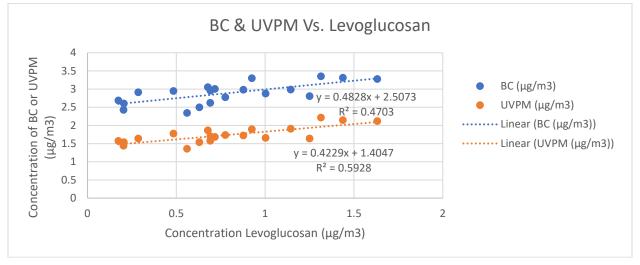


Figure 8. Correlation of Levoglucosan with BC and UVPM.

Figure 8 reinforces a known positive correlation between the biomass burning marker levoglucosan and carbon, but levoglucosan is more closely correlated with UVPM versus BC.

Figure 9 shows a strong negative correlation between levoglucosan and temperature, suggesting that increased levels of $PM_{2.5}$ during the winter can be correlated to lower temperatures.

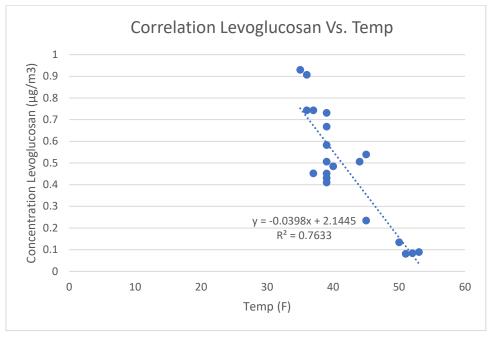


Figure 9. Correlation of Levoglucosan with Temperature Change.

Carbon particulate emissions and levoglucosan seem to correlate well, and levoglucosan correlates strongly with temperature. It is likely that a decrease in temperature generally influences PM_{2.5} positively through increased combustion emissions (more wood-burning) and reduced dispersion. Reduced temperatures tend to lead to stronger temperature inversions in the LVV. More specifically, biomass burning (woodsmoke) emissions containing levoglucosan are correlated with temperature/temperature inversions.

This correlation is further supported by the increase in $PM_{2.5}$ shown in Figures 3–5, which show an average increase in $PM_{2.5}$ in the winter of 2020 compared to the previous year due to combustion emissions. Additionally, the average temperature on the dates on which samples were collected was lowest in the winter of 2020, at 39°F; the winters of 2019 and 2021 had average temperatures of 46°F and 43°F, respectively.

6.0 CONCLUSIONS

Analyzing the mass balance and figures in this Phase II report leads to the conclusion that biomass burning, particularly wood combustion (assumed to be largely for residential heating), is a significant contributor to elevated levels of $PM_{2.5}$ during the winter season. The data shows a significant correlation between cold weather, temperature inversions, and elevated levels of $PM_{2.5}$, with biomass burning markers such as levoglucosan exhibiting a sharp increase during these periods. However, the unknown fraction of $PM_{2.5}$ in the data (accounting for 35–50% of the total PM mass) highlights the limitations of current optical analysis methods of measuring carbon, which do not allow a complete measurement of total carbon PM.

6.1 <u>Recommendations and Report</u>

The following recommendations are based on the identification of residential biomass burning as a major and regulatable source of increased levels of $PM_{2.5}$ during the winter season in Phases I and II of this study. Study recommendations will depend on the upcoming attainment designation of Clark County for the current $PM_{2.5}$ NAAQS.

If the county is designated attainment for the PM_{2.5} NAAQS, recommendations are to:

- Develop and implement a PM_{2.5} emissions reduction outreach program with a primary focus on residential wood burning.
- Develop and implement an incentive program to replace or upgrade residential woodburning appliances.

If the county is designated nonattainment for the PM_{2.5} NAAQS, recommendations are to:

- Promulgate a regulation to reduce and control residential wood-burning.
- Develop and implement a compliance program based on new regulation(s).
- Develop and implement a PM_{2.5} emissions reduction outreach program with a primary focus on residential wood-burning.
- Develop and implement an incentive program to replace or upgrade residential woodburning appliances.

7.0 REFERENCES

Ahuja, M.S., J. Paskind, J.E. Houck, and J.C. Chow. 1988. "Design of a Study for the Chemical and Size Characterization of Particulate Matter Emissions from Selected Sources in California." In Watson, J. G., J.C. Chow, and C.V. Mathai (eds.), "Receptor Models in Air Resources Management: A Summary of the APCA International Specialty Conference." *JAPCA* 39, vol. 4: 419–426. <u>https://doi.org/10.1080/08940630.1989.10466539</u>

Bhattarai, H., E. Saikawa, X. Wan, H. Zhu, K. Ram, S. Gao, S. Kang, Q. Zhang, Z. Zhang, G. Wu, X. Wang, K. Kawamura, P. Fu, and Z. Cong. 2019. "Levoglucosan as a Tracer of Biomass Burning: Recent Progress And Perspectives." *Atmospheric Research* 220: pp. 20–33. https://doi.org/10.1016/j.atmosres.2019.01.004.

Chen, L., J. Chow, X. Wang, J. Cao, J. Mao, and J. Watson. 2021. "Brownness of Organic Aerosol over the United States: Evidence for Seasonal Biomass Burning and Photobleaching Effects." *Environmental Science & Technology* 55, no. 13: 8561–8572. https://doi.org/10.1021/acs.est.0c08706.

Dzubay, T. and R. Stevens. 1975. "Ambient Air Analysis with Dichotomous Sampler and X-ray Fluorescence Spectrometer." *Environmental Science & Technology* 9, no. 7: 663–668. <u>https://doi.org/10.1021/es60105a011</u>.

Goulding, F., and J. Jaklevic. 1977. "XRF Analysis—Some Sensitivity Comparisons Between Charged-Particle and Photon Excitation." *Nuclear Instruments and Methods* 142, vol. 1–2: 323–332. <u>https://doi.org/10.1016/0029-554X(77)90846-1</u>.

Houck, J.E, J.C. Chow, J.G. Watson, C.A. Simons, L. C. Pritchett, J.M. Goulet, and C.A. Frazier. 1989. "Determination of Particle Size Distribution and Chemical Composition of Particulate Matter from Selected Sources in California." Report No. PB-89-232805/XAB. California Air Resources Board, Sacramento, California. <u>https://ww2.arb.ca.gov/sites/default/files/2023-12/a6-175-32a_i.pdf</u>.

Luo, X.-S., W. Huang, G. Shen, Y. Pang, M. Tang, W. Li, Z. Zhao, H. Li, Y. Wei, L. Xie, and T. Mehmood. 2024. "Source Differences in the Components and Cytotoxicity of PM_{2.5} from Automobile Exhaust, Coal Combustion, and Biomass Burning Contributing to Urban Aerosol Toxicity." *Atmospheric Chemistry and Physics* 24: 1345–1360. <u>https://doi.org/10.5194/acp-24-1345-2024</u>.

Malm, W. C., J.F. Sisler, D. Huffman, R.A. Eldred, T.A. Cahill. 1994. "Spatial and Seasonal Trends in Particle Concentration and Optical Extinction in the United States." *Journal of Geophysical Research* 99, no. D1: 1347–1370. <u>https://doi.org/10.1029/93JD02916</u>.

Marguí, E., I. Queralt, and M. Hidalgo. 2009. "Application of X-ray Fluorescence Spectrometry to Determination and Quantitation of Metals in Vegetal Material." *TrAC Trends in Analytical Chemistry* 3, no. 28: 362–372. <u>https://doi.org/10.1016/j.trac.2008.11.011</u>.

National Institute for Occupational Safety and Health. 2003. *NIOSH Manual of Analytical Methods (NMAM), Fourth Edition*. "Diesel Particulate Matter (as Elemental Carbon): Method 5040, Issue 3." Publication No. 2003-154. Atlanta, Georgia: Centers for Disease Control and Prevention. <u>https://www.cdc.gov/niosh/docs/2003-154/pdfs/5040.pdf</u>.

Zawacki, M., K.R. Baker, S. Phillips, S., K. Davidson, P. Wolfe. 2018. "Mobile Source Contributions to Ambient Ozone and Particulate Matter in 2025." *Atmospheric Environment* 188: 129–141. <u>https://doi.org/10.1016/j.atmosenv.2018.04.057</u>.