Summary of Findings Report for the RARE
Pinal County Source Apportionment Study

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INTRODUCTION

Pinal County, located in the Arizona Sonoran Desert South of Phoenix, has historically measured elevated particulate matter (PM) levels in excess of the National Ambient Air Quality Standard (NAAQS) for PM$_{10}$ at monitoring locations within the agricultural basin, which occupies roughly the western third of the county. The elevated concentrations are some of the highest in the country and frequently exceed the NAAQS. In this region, PMc (PM$_{10-2.5}$) is the dominant fraction of PM$_{10}$, and is highly influenced by the entrainment of crustal material from sources including dust from paved roads, unpaved roads, agricultural fields, and arid desert land as well as dust generated from earth moving activities and bulk material handling. Dust control strategies may be improved with a greater understanding of the strength of each type of source but, distinguishing the relative impact of these sources requires chemical fingerprinting and modeling. This project was undertaken to measure PM concentrations, conduct the chemical analysis, and to model the sources and the relative strength of each in an effort to help the county, and in turn the state, find better ways to reach attainment of the federal PM$_{10}$ NAAQS.
OVERVIEW

This report details the ambient particle composition and source apportionment findings of the year-long field sampling campaign conducted in Pinal County, AZ between February 2009 and February 2010. Characterization of PMc (PM_{10-2.5}, particles with an aerodynamic diameter (AD) between 2.5 μm and 10 μm) and PMf (PM_{2.5}, particles with an AD less than 2.5 μm) in terms of mass, bulk organic and elemental carbon (OC/EC), ions, and elements were conducted at one-in-six day resolution from low-volume filter samples collected at three different sampling sites. These data were then used to determine the sources of PMc, PMf, PM_{10} and their relative impact using positive matrix factorization (PMF). The sources and relative impact were compared between the two fractions and across each of the sampling sites.

Differentiation between several fugitive dust sources was facilitated by the collection of bulk samples from several known sources of fugitive dust within the region. These crustal materials were resuspended in the laboratory environment and chemically analyzed to create fingerprint profiles for each source, representative of particles that could be suspended as PM_{10} (particles with an AD less than 10 μm) and PM_{2.5}. These source signatures were compared to the source profiles generated by PMF modeling for validation of the modeled results.
STUDY APPROACH

Field Sampling Collection Program

Ambient Sampling

Between February 2009 and February 2010, ambient PM samples were collected at three monitoring locations in Pinal County, AZ in and around the vicinity of the town of Casa Grande, which is located to the south of Phoenix, AZ and approximately half way between the major metropolitan areas of Phoenix and Tucson. The three sites were within the Pinal County Air Quality District’s existing network and are shown in Figure 1.

Figure 1: Sampling Site Locations Within Pinal County, AZ
The Casa Grande (CG) site (401 Marshall St.), denoted by A in Figure 1, is on the roof of a one-
story building located within the town of Casa Grande, AZ, a small city with a population of
roughly 50,000. The site is situated within a local business district and is immediately
surrounded by buildings, paved roads, parking lots, and is more distantly surrounded by
residential neighborhoods with trees which are slightly taller than the height of the building.
Local emissions from railroad traffic, paved roadway traffic, and a few light industries are
potentially contributing to air quality at this site.

The Cowtown (CWTN) site (37580 W. Maricopa-Casa Grande Hwy.), denoted by B in Figure 1,
is located approximately 27 km to the northwest of the city of Casa Grande. It is a rural location
located along a two lane highway connecting Casa Grande with the city of Maricopa, 35 km
northwest of Casa Grande. The CWTN site is about 8 km southeast of the center of Maricopa.
Agricultural cropping fields, in various stages of rotation or lying fallow, are located in all
directions, extending 4 km east and west and 10 km north and south, of the CWTN site.
Superimposed on the general agricultural fields surrounding the site are a large cattle feedlot
(within 0.5 km south and southeast), a grain processing operation (0.7 km southwest), railroad
traffic (tracks <0.5 km south), and traffic on unpaved (adjacent and various distances) and paved
(adjacent) roads. The cattle feedlot underwent several changes during the last month and a half
of the study period characterized by the relocation of a substantial number of animals, the
removal of some metal structures, and displacement of the top layers of crustal material. These
localized sources in the immediate vicinity of this sampling site likely contributed to the poor air
quality that regularly registered 24-hour exceedances of the PM$_{10}$ standard on regulatory air
quality monitoring equipment at the site.
The Pinal County Housing (PCH) site (970 N. Eleven Mile Corner Rd), denoted by C in Figure 1, is located approximately 17 km to the east of the city of Casa Grande. The site is located in native desert, about 0.2 km west of the Pinal County Housing Projects and about 0.2 km east-southeast of a small wastewater treatment pond that treats sewage for the complex. Air quality at this site is influenced by agricultural fields (within 1 km in all directions), vehicle traffic from the housing project, and traffic over the native desert and unpaved (adjacent and at various distances) and paved roads (0.3 km to the east), and a dairy and cotton gin (located within 3 km).

Four dichotomous samplers (Sierra-Anderson, Model 241) were deployed at each of the three sites. Each unit collected 24-hour composite samples on a 1-in-6 day schedule for the period of one year. Three of the four samplers were run concurrently, two collecting particulate samples on Teflon substrates which were subsequently used for mass and ion and elemental composition analysis, the third collecting aerosols on quartz fiber substrates which were subsequently used for bulk OC and EC concentrations. The fourth sampler deployed at each site was used periodically for a variety of measurements including blank and replicate sampling.

The model 241 dichot sampler collects two different PM size fractions at 16.7 lpm total flow. An FRM PM$_{10}$ inlet collects particles with AD less than 10 μm at a 50% collection efficiency. A virtual impactor then separates fine particles and coarse particles by directing ten percent of the flow to the coarse particle side and the remainder to the fine side.
Source Sampling

A number of crustal sources within the region potentially contribute to ambient PM concentrations. ASU investigators collected samples from eleven sites located within close proximity (<2 km) to one of the ambient sampling site were used to collect representative material for source characterization. These samples represented native soils (collected from unaltered desert land), agricultural soils (collected from within agricultural fields in various stages of rotation or lying fallow), road dusts (collected from unpaved and paved roads), and feedlot material (collected near a cattle feeding operation).

Native and agricultural soil, unpaved road dust, and material representative of local feedlots was sampled using a garden trowel. Only the top layer (approximately 15 cm thick) was sampled. Paved road dust samples were swept from the surface using a small brush and collected using a dust pan. Once collected, each sample was placed in a pre-cleaned glass jar, returned to the laboratory, and stored in a freezer until analysis.

Samples were collected from all 11 sites a total of three times representing different seasons. Additionally, two other samples were collected from a cotton field to provide a greater variety in the samples representing agricultural cropping dust sources, and three additional samples were collected from the cattle feedlot after operations at the feedlot were altered, including sampling closer to the cattle and from the mounds of former top layer crustal material.

Sample Analysis - Target Compounds
Gravimetric Mass

Analysis

Mass concentrations of atmospheric particles were determined gravimetrically using flow rates measured in the field and the mass of material collected on Teflon filters. Teflon filters were weighed pre- and post-field sampling under controlled environmental conditions including temperature between 21.5-24.5°C and relative humidity between 40-50% on a Cahn microbalance. Filters were allowed to equilibrate to the controlled temperature and relative humidity conditions for approximately 24 hours prior to weighing. Filters were weighed one-by-one in groups of ten starting and ending with a reading of the zero as well as a small calibration weight as quality control. Both readings were required to be within 0.005 mg of the prescribed weight and within 0.002 mg of the starting weight at the end of the batch. The mass of each filter was recorded when the weight of the filter was stable at the last digit for at least 20 seconds.

Sample Validation

In addition to the zero and calibration weight checks, the performance of the balance while measuring ambient filters was challenged using three “weigh tracking” filters. These filters were stored with the ambient filters and were measured each time a batch of filters was weighed on the microbalance. The measurements were compared to all pervious weighing session and differences greater than 0.015 mg were flagged for quality assurance purposes and investigated.
Chemical Composition

The complex mixture of ambient particles is made up of a number of different constituents. Some components are present at relatively high concentrations and are relatively easy to detect and quantify using current analytical techniques. Others are present at trace concentrations and may not be detected at all. Because particle composition has been linked to the severity and types of human health effects caused by particles independent of the level of particle exposure, much effort has been aimed at more accurately determining the composition of ambient PM, augmenting the routine measurement of mass with chemical specificity, and closing the gap between the total measured PM mass and the portion that can be quantified by analytical techniques.

Ions

The concentrations of ions present in PM samples are often quantified as they compose a significant fraction of ambient PM, a number of ions indicated the role of air pollution in acid-rain formation, and others serve as the main base to neutralize aerosol acidity. Ion chromatography (IC) is the most widely used tool for quantification of ions because ambient concentrations are usually sufficiently above instrument detection limits and a wide range of ions can be determined simultaneously by this method [1]. A suite of cation and anion species are often quantified, including cations ammonium ($\text{NH}_4^+$), potassium ($\text{K}^+$), and sodium ($\text{Na}^+$) and anions sulfate ($\text{SO}_4^{2-}$), nitrate ($\text{NO}_3^-$), and chloride ($\text{Cl}^-$).
Extraction

For ambient samples, quantification of ionic material was analyzed for samples collected on Teflon filters. Sampled filters were removed from storage in freezers and allowed to defrost to ambient temperatures prior to extraction. Filters were placed upside down in plastic sample cups and 200 μL aliquot of ethanol (Fisher Scientific) was added to each filter to improve wetting of the Teflon surface of the filter. Subsequently, 7.5 mL of ultrapure water was added to each cup which was then sealed and sonicated for 15 minutes. The liquid extract was removed using a new, clean, 10 mL, plastic syringe (BD Biosciences) using a new stainless needle (BD Biosciences). The extract was then filtered through a 0.22 μm syringe filter (Millex GP PES Membrane) into a 10 mL Dionex polyvial.

Ion analysis of resuspended crustal material representing source samples was conducted from quartz fiber filters. Two 1 cm x 1.5 cm filter punches were removed from the sampled area of the filter. The filters punches were placed into a 10 ml Dionex polyvial along with 7.5 mL of ultrapure water. The sonication, filtration, and subsequent analysis were conducted in the same manner as they were for Teflon filters.

Analysis

Atmospheric particulate ion concentrations were determined using flow rates measured in the field and ion concentrations determined from the liquid extracts. Ion levels in source samples for the resuspended crustal materials were determined using the mass of the material collected for each resuspension experiment and the ion concentration of the liquid extracts.
Each liquid extract was analyzed twice on a Dionex IC20 system with an AS50 autosampler used for sample injection. The Dionex IC20 is a dual channel system but the channels cannot be run simultaneously and eluent changes must be done manually resulting in separate ion runs for cations and anions.

Anions were measured using the Dionex IonPac AG12A guard column (4×50 mm) with AS12A analytical column (4×200 mm) using a 2.7 mM sodium carbonate/0.3mM sodium bicarbonate eluent running at 1.5 mL/min. This column is a carbonate-based, anion-exchange resin designed for the isocratic separation of inorganic anions including fluoride (F⁻), chlorite (ClO⁻), bromate (BrO₃⁻), chloride (Cl⁻), nitrite (NO₂⁻), bromide (Br⁻), nitrate (NO₃⁻), phosphate (PO₄³⁻), and sulfate (SO₄²⁻). Ions quantified from ambient and source samples during this project included Cl⁻, NO₃⁻, PO₄³⁻ and SO₄²⁻ as few other species are present at concentrations above the detection limit. Analysis time was roughly 20 minutes.

Cations were measured using the Dionex IonPac CG12A guard column (4x50 mm) with CS12A analytical column (4x250 mm) using a 11 mM methylsulfonic acid eluent running at 1.00 mL/min. This column is a cation-exchange resin designed for isocratic separation of lithium (Li⁺), sodium (Na⁺), ammonium (NH₄⁺), potassium (K⁺), magnesium (Mg²⁺), and calcium (Ca²⁺). Samples analyzed during this project were characterized in terms of all species except Li⁺, which was not found in atmospheric samples at concentrations above the detection limit. Analysis time was roughly 15 minutes.

**Sample Validation**

The instrument was calibrated using standard dilutions of a concentrated certified standard stock solution that was purchased from Dionex. Each stock solution was traceable to NIST Standard
Reference Materials and was shipped with a certificate of analysis verifying the concentration.

The anion standard solution (P/N 056933) contained fluoride (20 mg/L), chloride (30 mg/L), nitrite (100 mg/L), bromide (100 mg/L), nitrate (100 mg/L), phosphate (150 mg/L), and sulfate (150 mg/L). The cation standard solution (P/N 046070) contained lithium (50 mg/L), sodium (200 mg/L), ammonium (250 mg/L), potassium (500 mg/L), magnesium (250 mg/L), and calcium (500 mg/L). Standard stock solutions were refrigerated during storage and were discarded after the expiration date prescribed by the manufacturer for each solution. A calibration curve consisting of a series of least 10 standard dilutions of the concentrated standard stock solutions was measured prior to sample analysis, each time the system was switched between cations and anion analysis, and each time the instrument was stopped for more than 24 hours. In addition, interspersed periodically with sample runs, different standard dilutions were run for quality assurance and precision purposes.

A series of blanks were included with each batch of 18 ambient samples, which included one solvent blank and one filter blank. Two separate types of filters were used for the filter blank analysis. The lab blank filters were on and off-weighed in the laboratory and were transported to the field and back in sealed petri dishes. The trip blank filter were on and off-weighed in the laboratory, transported to the field and back in sealed petri dishes, and opened briefly and exposed to the ambient environment at one of the field sampling locations. These trip blank filters were never loaded into the field samplers themselves. Analysis showed no distinguishable difference between the lab blank filters and the trip blank filters and only a slight difference, if any, with the solvent blank. A blank correction was applied to each sample from a given batch based on the solvent blank measurements which typically only had very low concentrations of sodium and chloride.
A series of replicate analyses were conducted within each batch representing approximately 40% of the samples. The standard deviation of replicate samples was used as the basis for estimating the precision of measurement associated with this analytical instrument.

Artifact and Concerns

A variety of artifacts can impact the results of the ion chromatography measurement, including positive and negative artifacts that arise from the filter-based collection of ambient PM. Absorption of gas phase compounds like nitric acid (HNO₃) can inflate measured nitrate concentrations creating a positive artifact. Volatile losses of species like nitrate (NO₃⁻) can occur when filters experience large temperature fluctuation following collection leading to negative artifacts. Furthermore, ion measurement by IC requires that PM samples be extracted into water and the extraction process may not be 100% efficient. The method used in this work wets the Teflon filter with ethanol to increase the surface contact between the Teflon filter and the extracting solution with the goal of making the extraction process more efficient.

Source Tracer Species

The conversion of primary gas-phase air pollutants such as SO₂ and NOₓ into condensable oxidized products is an important contribution to the atmospheric levels of anion species, including SO₄²⁻ and NO₃⁻ [2]. The gas-to-particle conversion of gas phase NH₃ can result in particle-bound NH₄⁺ [3]. Na⁺ and Cl⁻ commonly come from sea salt [4], while mineral forms of CaCO₃ result in high Ca²⁺ concentrations in airborne particles [5]. Other common constituents of soils include Mg²⁺, Na⁺, and K⁺ [6]. NH₄⁺, SO₄²⁻, NO₃⁻, Cl⁻, and Na⁺ have all been associated with entrainment of agricultural soils [7]. K⁺ has been shown to be a good tracer for biomass burning [8].
Elements

The concentrations of elements, including metals, in PM samples often comprise a significant fraction of the mass of ambient PM when aggregated as a group. Some individual compounds, including those associated with crustal material, have significant concentrations while others are found at only trace concentrations and may not be detected by routine analytical methods. Some individual metal species have been found to be tracer species for specific PM sources, while others, including the crustal minerals, are more ubiquitous and represent a suite of potential sources rather than one individual process.

Digestion

For ambient samples and resuspended crustal material samples, elemental analysis was conducted on off-weighted Teflon filter samples. First, the support ring was removed and discarded prior to digestion using a ceramic cutting blade and Teflon forceps on a Teflon acid-cleaned cutting board. The Teflon filter material and the associated particulate matter sample were then placed in a 20 mL Teflon microwave digestion vial along with a mixture of 4 mL nitric acid, 0.9 mL hydrochloric acid, and 0.1 mL hydrofluoric acid (Fisher). The vials are capped with Teflon plugs and Teflon screw caps and placed in the turret which was placed in the microwave (MARS 5, CEM Corp) for digestion which proceeded by applying heat. Over the course of 6 minutes, the temperature was ramped to 140°C where it was held for 2 minutes followed by a 5 minute temperature ramp to 165°C which was held for 6 minutes. The temperature was further increased to 180°C and held for 15 minutes. The cooled digestion solution was diluted to 25 mL using ultrapure water and subsequently, a 1.25 ml aliquot was transferred to a 15 mL centrifuge vial and diluted to 5 mL using ultrapure water for analysis.
**Analysis**

Each batch of 34 ambient samples was analyzed for 52 trace elements including, but not limited to, P, Na, Fe, Al, Ti, Mo, Ni, Sb, Pb, Cr, U, W, Zn, Y, Se, As, Cs, Sr, Co, Cd, Cu, Rb, V, Ba, Mn, Ca, Mg, K, and Ag using high-resolution inductively coupled plasma mass spectrometry (ThermoFinnigan ELEMENT 2, HR-ICP-MS, herein referred to as ICPMS). High-resolution was used to separately quantify sodium and potassium.

**Sample Validation**

Instrument performance in measuring each sample was verified using an internal indium standard. The instrument was calibrated using a multi-element standard commercially available from SPEX Certiprep Inc. Quality control was maintained by analyzing laboratory and field blanks which represented approximately 10% of the sample. Additionally, replicate analyses were conducted on approximately 7% of the samples. Each batch included six additional vials for analysis, two containing reagent blanks and four containing reference materials from the National Institute of Standards and Technology (NIST) including two vials containing extracted material from San Joaquin Soil (#2709) and two vials containing extracted material from Urban Dust (#1649a). The SRM samples are digested and analyzed in using the same procedures outlines for ambient samples.

**Artifacts**

The method used to quantify elemental composition in this work involves the acid-digestion of Teflon filter samples followed by quantification of metals by inductively coupled plasma mass spectrometry (ICPMS). Analytical uncertainty comes from matrix effects and spectral interferences. Matrix effects are characterized by artifacts that arise when a co-material is
dissolved with acids and filter material not representative of the native aerosol deposit are introduced into solution. Matrix effects are usually quantified by the analysis of blank solutions and internal standards. Spectral interferences occur for different elements with the same mass, species that have the same mass to charge ratio, and elements that become poly-charged or form novel agglomerations in solution (May 1998). Because of these uncertainties, detection limits for individual metal species are determined from blank measurements.

**Tracer Species**

Aluminum (Al), calcium (Ca), iron (Fe), potassium (K), magnesium (Mg), silica (Si), and titanium (Ti) are all common elements of crustal material. Barium (Ba), copper (Cu), lead (Pb), and zinc (Zn) have been associated with mechanical brake wear and engine combustion in motor vehicles [9]. Vanadium (V) has been used as a tracer species for emissions from the shipping industry due to the heavy crude burned for fuel [10] while rare earth metals have been shown to result from petroleum refining operations [11]. Based on understanding local emission sources in Pinal County, neither of these sources is expected to contribute significantly to local air quality, and these representative metals are not expected to be found above trace concentrations during this sampling campaign. Smelting operations can emit significant concentrations of Pb, Zn and other heavy metals [12]. At present, Pinal County has one working copper smelter. However, this smelter is in a different air shed and emissions from this source are not expected impact concentrations observed during this study, but will be monitored as potential source tracers.
Bulk OC/EC

Carbon makes up a significant fraction of atmospheric PM and is comprised of many thousands of individual species with variable chemical and physical properties [13]. Elemental carbon is representative of the graphitic form of carbon, while organic carbon constitutes many compounds present at trace concentrations. With the variety of structures of organic molecules, it is virtually impossible to determine the chemical identity and concentration of them all. Because current methods quantify only certain species or classes of compounds, a determination of the bulk mass concentration is helpful for mass closure calculations and in determining the fraction of the overall mass can be attributed to organic material. Fractions of the evolved organic carbon (OC) and elemental carbon (EC), based on the volatility of the components and whether the material volatilizes in an inert atmosphere or only via oxidation in an oxygen rich atmosphere, have been used in source apportionment studies.

Analysis

Bulk elemental and organic carbon concentrations were determined for ambient samples and resuspended crustal material from quartz fiber filters samples using a Sunset Laboratories thermal –optical OC/EC instrument. A 1 cm x 1.5 cm punch was removed from sampled filter area, placed on a quartz spoon, and inserted into the quartz oven which was then sealed, purged with helium, and heated in a step-wise fashion to thermally desorb organic compounds. As the evolved carbon flowed through the manganese dioxide oxidizing oven, it was quantitatively converted to CO₂ gas. The CO₂ gas was swept out of the oxidizing oven by the helium stream, mixed with hydrogen gas, and sent through a heated nickel catalyst where it was quantitatively converted to methane. The methane was then measured using a flame ionization detector.
After the initial temperature ramp in the quartz oven is complete, the oven is cooled to 550°C and the flow stream is switched to an oxidizing helium/oxygen carrier gas mixture. A second temperature ramp is then initiated in the oxidizing gas stream and any elemental carbon is oxidized off the filter and into the oxidization oven. The elemental carbon is then detected in the same manner as the organic carbon.

The optical component of the instrument, a red diode laser, is used to correct for organic material that undergoes pyrolysis during the initial inert heating of the sample and is converted to elemental carbon. By separating the native elemental carbon that is naturally present in the ambient sample from the elemental carbon formed from the charring of organic carbon that was pyrolyzed during the initial temperature ramp, the pyrolyzed material is quantified as organic carbon and not elemental carbon. To do this, the instrument can monitor either laser transmittance or reflectance from the sample continuously during the heating steps. As organic carbon chars, the transmittance (or reflectance) of the laser incident on the sample will decrease. Once the charred material is oxidized and released during the second temperature ramp in an oxidizing atmosphere, the laser reading will return to a background level. The split point between the two different types of elemental carbon is determined by the point in the second phase oxidizing ramp at which the laser reading returns to the initial reading. This particular model contains sensors to determine this optical correction based on reflectance or transmittance. Transmittance is the preferred optical measurement for consistency with other air quality monitoring programs and was used for all analyses presented here.
Sample Validation

During instrument start-up at the beginning of each day, instrument performance is verified by testing the instrument blank and a set of two sucrose standard spikes. The sucrose spike tests the instrument response to known carbon concentration (10 µl of a 3.06 µgC/µl solution prepared by Sunset Laboratories). Blank levels and sucrose concentrations must be within the reported error estimate of the actual concentration (0 µg and 30.6 µg) in order to proceed to sample analysis.

Blank samples were extremely important for the analysis of organic carbon content of collected material as clean quartz fiber filters can absorb organic vapors from the environment during storage and handling that are then released upon heating. Several different types of blank filters were analyzed including laboratory blanks (pre-cleaned and then stored under freezing conditions until analysis), travel blanks (pre-cleaned, transported to the field and back, and then stored in the freezer), exposed travel blanks (pre-cleaned, transported to the field, opened briefly at the field site, transported back and frozen), and field blanks (pre-cleaned, transported to the field, installed in a sampler and left to sit for 6 days, and transported back and frozen). The analysis of laboratory, travel, and exposed travel blanks did not lead to statistically different blank organic carbon content of the sampling media. A blank value representing the mean measured blank level over the entire campaign was determined and then the blank value was subtracted from the measured organic carbon content of ambient samples. The correction was at most 20% of the measurement of the ambient filters that contained the lowest aerosol loadings (i.e. the cleanest ambient samples) but generally much less than 10%. Field blanks were excluded from the blank average because concentrations were generally higher and more variable in this category but the measurement was less than 20% of the measurement on the ambient filters.
Replicate analysis could not be conducted on regular ambient filters because after removing the punch for this analysis, the remainder of the filter was reserved for quantification of individual organic compounds through aggregating multiple samples to obtain enough organic carbon mass for speciation. Quartz fiber filters were collected on the fourth sampler running at each site during approximately 10% of the sample days and these filters were used for sample validation in two ways. First, ambient concentrations as measured by two independent instruments were compared. Second, filters collected on the fourth sampler were not used for subsequent analyses so multiple punches from the same filter were analyzed. Both comparisons yielded ambient concentrations that were statistically equivalent within the instrument reported error estimate.

**Caveats**

Thermal desorption does not allow for the distinct differentiation of carbonate carbon from organic carbon directly. The prescribed method for the determination of carbonate involves a two step process. First, a sample is analyzed in its native state. Second, a portion of the same sample is subjected to fuming with HCl which reacts with the carbonate, and the sample is then reanalyzed. The difference in organic carbon as measured in these two otherwise equivalent samples provides the carbonate carbon concentration. Because only one filter punch was available for bulk carbon analysis, carbonate was left un-quantified in this study. If carbonate carbon is a significant contributor to ambient particle levels, then the measured organic carbon concentrations could be biased slightly high. Investigation into the contribution of carbonate carbon in samples of fine particles collected in locations in the southwestern US [14], concluded that carbonate does not cause significant biases in total carbon (TC), organic carbon (OC), and elemental carbon (EC) concentrations measured by the thermal optical method. However, carbonate concentrations are likely more significant in coarse particles than in fine particles.
Artifact and Concerns

The measurement method used in this study involves a commercially available OC/EC analyzer built by Sunset Laboratory which determines the bulk carbon concentrations based on a thermal optical method [15, 16]. Analyzers that use a similar approach for quantification are available from other vendors but, more importantly, the temperature profiles used by various investigators and across different monitoring networks vary making data comparison across studies difficult [16, 17].

Sample artifacts are of concern with the quantification of organic and elemental carbon method because gas phase organic compounds readily absorb to the quartz fiber filter substrate causing positive artifacts and sampling conditions or handling procedures can also cause volatile loss of some compounds [18]. Filter media must be pre-baked, handled with care, and stored properly after sampling to ensure these artifacts are minimized. Blank correction of data representing the quantity of gaseous organic carbon sorbed to the filter media is often necessary.

By this method, OC and EC concentrations are expressed in terms of the carbon concentration while any associated oxygen, nitrogen, sulfur or hydrogen is left unquantified. A conversion factor, investigated by several different studies under a number of conditions, must be applied to estimate the mass of the organic matter (OM) concentration of the sample [19] leading to uncertainty in determining the OM concentration.

Tracers

Because this measurement is a characterization of the bulk carbonaceous material, no unique organic tracers are available. At most, information about the volatility of fractions of the organic
carbon can be determined during the analysis and compared to known sources and the volatility of different source categories. Elemental carbon however, is often associated with combustion processes and has been used as a non-specific tracer for various combustion processes.

**Soil Characterization/Resuspension**

**Resuspension**

Bulk crustal samples collected during the source characterization program were resuspended using an apparatus assembled in our laboratory to perform appropriate size selection for representative characterization. The resuspended soil material was size selected for collection of particles in the PM$_{10}$ and PM$_{2.5}$ size range on Teflon membrane and quartz fiber filters for appropriate comparison to particles that would be found in air quality samples collected in similar size ranges.

After collection in the field, samples of crustal material were stored in sealed glass jars at freezing temperatures. At least 24 hours prior to resuspension, samples were removed from the freezer and thawed to room temperature. Once thawed, the entire sample was loosely wrapped in a double layer of aluminum foil, placed in a muffle furnace, and heated to 110°C for 24 hours to remove moisture from the sample. Once cool, approximately half of the sample was transferred to a mortar and a pastel was used to gently break up the large aggregates within the sample. The force on the soil sample was minimal resulting in less pressure than would be exerted by walking on the crustal surface. Although the force exerted was minimal, it is not
unlike a mechanical force, such as vehicle traffic or agricultural harvesting efforts, that lead to dust resuspension through disturbance of the soil surface.

The loose material was then deposited into the resuspension chamber, a 1L heavy wall filtering flask. HEPA filtered air entered the chamber through a stainless steel tube which directed the air flow over the loose material. Small particles were entrained into the air in the resuspension chamber and then drawn through a cyclone separator. Two different cyclone separators may be used in the set-up, one which will separate into PM$_{10}$ (URG-2000-30EA requires 28 lpm) and another into PM$_{2.5}$ (URG-2000-30EC requires 42 lpm). Following the cyclone separator, flow was divided into three separate channels, one loaded with a 47mm Teflon filter and the other two loaded with pre-baked 47mm quartz fiber filters. The flow through each channel was regulated by critical vacuum orifice. Flows through the first and second filter holders are held constant at 10.15 lpm and 12.14 lpm, respectively. Because PM$_{10}$ and PM$_{2.5}$ sampling require different flow rates, the flow through the third filter holder will vary from 6.55 lpm for PM$_{10}$ sampling to 24.8 lpm for PM$_{2.5}$ sampling. The entire apparatus was disassembled and cleaned thoroughly between resuspension of different soil samples.

The mass collected during the resuspension process was measured from the Teflon filter using the procedures outlined in the following section. The total sampling time was based on the time necessary to collect approximately 10mg of material on the quartz fiber filter with the highest flow rate which was variable based on the material type. The mass collected on a quartz fiber filter cannot be measured with the same level of accuracy as is possible for a Teflon membrane filter, and thus mass deposited on the quartz filter was determined based on the mass measured from the Teflon filter and the ratio of flow through each channel.
Sample Validation

Flow rates through each channel were measured prior to each batch of sampling using a bubble flow meter (Gilian Inc, Gilibrator Primary Air Flow Calibration System). Roughly 50 measurements were recorded for each channel using both types of filter media each time the flow rates were determined.

A set of blank filters were collected by pulling HEPA filtered air through a clean apparatus. These filters were analyzed in the same fashion as each of the collected source samples.

Source Apportionment

Source apportionment techniques elucidate source categories based on analysis of ambient air quality data and can quantitatively determine the relative contribution of each to the measured ambient concentrations.

Positive matrix factorization (PMF) is a modeling approach that uses the measurements of chemical constituents made at air quality sampling sites and statistical correlations within the time-series data to isolate common factors of co-varying components [20]. Each isolated factor represents a source and the relative contribution of each factor can be determined through comparison of source factor strength and ambient PM mass data. One strength of PMF analysis is that no information about the suspected sources is input into the model. This makes the technique very useful in isolating sources where profiles are not readily available, not representative of the area or conditions, or contain significant uncertainty and could also isolate sources that are unexpected or unknown at the start of analysis. Although source profiles are not
input into the model, some knowledge regarding the appropriate chemical composition of source emissions is required to accurately identify each isolated source.

The application of any source apportionment method results in a certain degree of uncertainty often related to co-linearity between emission sources and difficulty in determining the sources based on resolved profiles. In particular, the ability to isolate appropriate markers for similar sources (i.e. for entrainment of native soil versus agricultural processes emitting crustal material) can produce large uncertainty. For modeling purposes, only species with concentrations above the method detection limit were used, compounds measured by more than one analytical method were reduced to only one measure, and compounds with very poor modeling results were eliminated one by one and retained if the model fit to the overall variable was not significantly improved by their absence. The number of isolated factors was increased step-wise while monitoring the residual measure. A minimum number of factors were determined based on a comparison between residual measures while the optimal number of factors was determined when no significant decrease in the residual measure was observed with an increase in the number of modeled factors.

**Ambient Data Summary**

**Mass Comparison**

The temporal variation of PMc mass at each of the sampling sites as measured by gravimetric filter analysis is shown in Figure 2. Measured 24-hour average PMc concentrations ranged from 5 to 180 µg/m³. The lowest PMc concentrations were observed at CG, which is an urban site
less influenced by resuspension of crustal material from agricultural or native desert sources. Because of the relatively small size of the urban area, local sources impacting this site have a moderate influence resulting in common trends in PMc mass concentration measurements at the CG and PCH sites. PMc mass concentrations at PCH were, on average, approximately 10 µg/m³ (approximately 35%) higher than those measured at CG, indicating the influence of nearby sources potentially including native desert dust, unpaved roads, and agricultural soil re-entrainment. PMc mass concentrations at CWTN were quite variable, based on the 1-in-6 day sampling schedule, and often significantly exceeded concentrations measured at the other two sites, which is consistent with previously reported observations at this location. The localized effect of substantial emissions in the vicinity of the CWTN site resulted in elevated PMc mass concentrations of 5 to 90 µg/m³ over levels at the other two sites, as well as different temporal variations relative to GC and PCH, especially during spring. Concentrations measured at the various sampling locations become much more uniform in January and February 2010 signaling a marked decrease in the impact from local sources. Local rain events, determined by accumulations of at least 0.2 inches at the monitoring station in the town of Maricopa, are denoted by vertical dotted lines in this figure. Sampling days in close proximity to these events show a decrease in ambient particle mass concentrations.
Fine particle mass concentrations are shown in Figure 3. Measured 24-hour average PMf concentrations ranged from 2 to 22 µg/m³. As expected, PMf mass concentrations are much lower than PMc concentrations but often follow similar temporal and spatial trends.

As was observed for PMc, PMf concentrations at CWTN are higher and more variable than those measured at PCH and CG. During peak periods, the concentration difference can be between 5 and 10 µg/m³ or 1.5 to 2 times the concentration measured at either of the other sites. These results indicate that local sources also likely impact the fine fraction at the CWTN site. This is in agreement with a 2003 study which found that up to 50% of the mass concentration measured at CWTN may be apportioned to the local feedlot source during winter periods where stagnation and inversions are common. When compared, fine particle concentrations were 10-30% of the coarse particle concentrations at any one time. Local rain events, determined by accumulations of at least 0.2 inches at the monitoring station in the town of Maricopa, are denoted by vertical dotted lines in this figure but, no significant change in particle mass concentration is observed.
Figure 3: Fine Particle Mass Concentration Time Series

Coarse Particle Composition

The average aerosol composition of coarse particles collected at each of the sampling sites is shown in Table 1. Coarse particle mass is highest at the rural sampling locations. The average coarse mass at CWTN measured $67 \mu g/m^3$ and concentrations at PCH measured $45 \mu g/m^3$ while the more urban CG site measured an average concentration of $31 \mu g/m^3$. The composition at these sampling sites shows some similarities. Crustal material, determined as mass attributed to common oxide forms of the elements Fe, Al, Ca, Ti, and Si, makes up the bulk of the coarse particle composition with a contribution between 42 and 49%. Organic material, determined as 2 times the measured organic carbon concentration, again comprises a significant portion of the collected aerosol contributing between 9 and 25%. The ions and elements are minor contributors. A large portion of the coarse particle mass remains unidentified and is likely, at
least partially, comprised of large biological particles (pollen, etc.) and particle bound water which was not directly measured during analysis.

Table 1: Coarse Particle Chemical Composition

<table>
<thead>
<tr>
<th></th>
<th>Casa Grande</th>
<th>Cowtown</th>
<th>Pinal County Housing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coarse Particle Mass</td>
<td>31 μg/m³</td>
<td>67 μg/m³</td>
<td>45 μg/m³</td>
</tr>
<tr>
<td>Crustal</td>
<td>48%</td>
<td>42%</td>
<td>49%</td>
</tr>
<tr>
<td>Organic</td>
<td>12%</td>
<td>25%</td>
<td>9%</td>
</tr>
<tr>
<td>Nitrate</td>
<td>2%</td>
<td>1%</td>
<td>2%</td>
</tr>
<tr>
<td>Sulfate</td>
<td>1%</td>
<td>1%</td>
<td>1%</td>
</tr>
<tr>
<td>Ammonium</td>
<td>0.2%</td>
<td>0.2%</td>
<td>0.1%</td>
</tr>
<tr>
<td>Other Measured Species</td>
<td>9%</td>
<td>11%</td>
<td>8%</td>
</tr>
<tr>
<td>Unidentified</td>
<td>28%</td>
<td>20%</td>
<td>31%</td>
</tr>
</tbody>
</table>

_Casa Grande_

_Average PMc Composition_

The average aerosol composition of coarse particles collected at Casa Grande is shown in Figure 4. Approximately 48% of the particles are categorized as crustal material, or in other words fugitive dust. This portion of the aerosol was reconstructed from the elemental composition and the common metal oxides found in dust sources. Fugitive dust at this sampling site could be attributed to the combination of roads (paved and unpaved road dust), agricultural fields, and uncultivated desert. Of the remaining mass, 12% is organic material, 4% is comprised on the major soluble ions of ammonium, nitrate, and sulfate, 9% of the mass was measured and characterized as other ions or trace elements. 28% of the mass remains uncharacterized. The
unknown fraction in this size range might be associated with biological material such as pollen, spores, and fungi which may not be properly accounted for by the OM conversion factor from the OC measurement, as well as potentially particle-bound liquid water.

Figure 4: Average Coarse Particle Composition Measured at Casa Grande

PMc Composition Time Series

The one-in-six day time series graph is shown in Figure 5. The Casa Grande monitoring location is situated in a small urban area but the influence of crustal sources is still pronounced. Concentrations are highly variable day to day. Mass closure is roughly within 28% but is near zero in late December and early January.
Figure 5: Coarse Particle Composition Time Series Measured at Casa Grande

Cowtown

Average PMc Composition

The average aerosol composition of coarse particles collected at Cowtown is shown in Figure 6. The fugitive dust concentrations at the CWTN sites are still significant with approximately 42% of the particle mass attributed to this source. Organic material concentrations are more pronounced at this site comprising 25% or the coarse particle mass. Additionally, 2% is attributed to the major ions, 11% is attributed to other measured ions and elements, and 20% remains uncharacterized. The unknown fraction in this size range might be associated with biological material such as pollen, spores, and fungi which may not be properly accounted for by the OM conversation factor from the OC measurement, as well as potentially particle-bound liquid water.
Figure 6: Average Coarse Particle Composition Measured at Cowtown

**PMc Composition Time Series**

The coarse particle composition measured at Cowtown is shown in Figure 7. In this size fraction, the organic material signature is most pronounced at this site. Again, the mass concentrations, as measured on the one-in-six day schedule, are highly variable. Mass closure appears to be best during the winter period.
Pinal County Housing

Average PMc Composition

Coarse particles collected at PCH are comprised of approximately 49% crustal material, 9% organic material, 3% major ions, 8% characterized ions and elements, and 31% remains uncharacterized. The uncharacterized fraction at this location is larger than the estimated unknown mass at the other sampling locations. It is highly likely that this unknown mass contains biological material such as pollen, spores, and fungi which may not be properly accounted for by the OM conversation factor from the OC measurement. Because this site is located in closer proximity to active agricultural field, higher concentration of these materials is expected to be collected at this site.
PMc Composition Time Series

Figure 9 shows the one-in-six time series graph of particle composition measured at the PCH monitoring location. Mass concentrations measured here are more moderate with occasional severe spikes.
The average aerosol composition of fine particles collected at each of the sampling sites is shown in Table 2. The average fine particle mass is highest at the CWTN sampling site. The composition at these sampling sites show some similarities. Organic material comprises the largest portion of the collected aerosol contributing 31-45% with crustal material contributing another major portion ranging from 17%-30%. The organic material contribution is highest at the CG site which is most influenced by motor vehicle emission while the PCH, a more rural monitoring location, shows the most significant influence from crustal material.
In comparison to the coarse particle mass, fine particle mass concentrations are significantly lower. In terms of composition, the contribution of crustal material is about 60% lower and organic material is about 2 to 4 times higher than in coarse particles. Additionally, the major ions become more significant and the unidentified portion of the aerosol is much lower in the fine particles.

### Table 2: Fine Particle Chemical Composition

<table>
<thead>
<tr>
<th></th>
<th>Casa Grande</th>
<th>Cowtown</th>
<th>Pinal County Housing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fine Particle Mass</td>
<td>10 μg/m³</td>
<td>11 μg/m³</td>
<td>9 μg/m³</td>
</tr>
<tr>
<td>Crustal</td>
<td>17%</td>
<td>22%</td>
<td>30%</td>
</tr>
<tr>
<td>Organic</td>
<td>45%</td>
<td>45%</td>
<td>31%</td>
</tr>
<tr>
<td>Nitrate</td>
<td>3%</td>
<td>8%</td>
<td>6%</td>
</tr>
<tr>
<td>Sulfate</td>
<td>10%</td>
<td>9%</td>
<td>10%</td>
</tr>
<tr>
<td>Ammonium</td>
<td>4%</td>
<td>5%</td>
<td>4%</td>
</tr>
<tr>
<td>Other Measured Species</td>
<td>7%</td>
<td>8%</td>
<td>9%</td>
</tr>
<tr>
<td>Unidentified</td>
<td>14%</td>
<td>3%</td>
<td>10%</td>
</tr>
</tbody>
</table>

**Casa Grande**

**Average PMf Composition**

The average aerosol composition of coarse particles collected at Casa Grande is shown in Figure 10. Within the fine particles, carbon is the most significant fraction comprising 45% of the particle mass. Of the remaining mass, 17% of the particles are categorized as crustal, 17% as the major soluble ions species, 7% as other ions or trace elements, with 14% remaining uncharacterized.
PMf Composition Time Series

The composition time series is shown in Figure 11. Highest concentrations are measured in winter due to inversions. The highest measured mass concentrations are accompanied by increases in the crustal component.
The average aerosol composition of fine particles collected at Cowtown is shown in Figure 12. Approximately 22% of the particles are categorized as fugitive dust, 45% as organic material, 22% as the major soluble ions, 8% other measured ions and elements, with only about 3% remaining uncharacterized.
PMf Composition Time Series

The fine particle composition measured at CWTN is shown in Figure 13. Many of the concentration spikes are accompanied by significant increased in the crustal component of the aerosol. The winter and spring 2010 composition shows significant increases in major ion concentrations at this site with significant increases in the measured nitrate.
At PCH, the average aerosol composition of fine particles consists of 30% crustal material, 31% organic material, 20% major ion species, 9% other measured ions and elements, and 10% remains uncharacterized. The organic fraction observed at the PCH location is smaller than that observed at the other monitoring locations.
Figure 14: Average Fine Particle Chemical Composition at Pinal County Housing

PMf Composition Time Series

Fine particle composition as measured on the one-in-six day schedule at PCH is shown in Figure 15. Many of the concentration spikes are accompanied by increases in the crustal component of the aerosol while other contributing species remain relatively constant. The winter mass concentrations and crustal components are most significant in winter when inversion layers emissions prevent dilution.
PM$_{10}$ Particle Composition

Table 3 details the aerosol composition of the fine, coarse, and PM$_{10}$ particle size fractions collected at each site. The average PM$_{10}$ composition (determined by summing the measured PMc and PMf concentrations) closely resembles the coarse particle composition because the coarse particle mass is such a large fraction of the PM$_{10}$ mass; roughly 3 to 6 times the fine particle mass concentration. Fine particles showed several differences from the coarse particles in that they contain higher concentrations of ion and organic species. The crustal fraction is the dominant fraction in both coarse and PM$_{10}$ particle size fractions and the unidentified portion remains between 17 and 25%.
The highest PM$_{10}$ particle mass concentration is highest at the CWTN sampling site, followed by PCH and then CG. Organic material also comprises a considerable portion of the PM$_{10}$ aerosol contributing 13-27% with the highest concentrations observed at CWTN.

### Table 3: Particle Composition for Fine, Coarse, and PM$_{10}$ Size Fractions by Sampling Site

<table>
<thead>
<tr>
<th></th>
<th>PMc</th>
<th>PMf</th>
<th>PM$_{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Casa Grande</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Particle Mass</td>
<td>31 µg/m$^3$</td>
<td>10 µg/m$^3$</td>
<td>38 µg/m$^3$</td>
</tr>
<tr>
<td>Crustal</td>
<td>48%</td>
<td>17%</td>
<td>46%</td>
</tr>
<tr>
<td>Organic</td>
<td>12%</td>
<td>45%</td>
<td>21%</td>
</tr>
<tr>
<td>Nitrate</td>
<td>2%</td>
<td>3%</td>
<td>3%</td>
</tr>
<tr>
<td>Sulfate</td>
<td>1%</td>
<td>10%</td>
<td>3%</td>
</tr>
<tr>
<td>Ammonium</td>
<td>0.2%</td>
<td>4%</td>
<td>1%</td>
</tr>
<tr>
<td>Other Measured Species</td>
<td>9%</td>
<td>7%</td>
<td>8%</td>
</tr>
<tr>
<td>Unidentified</td>
<td>28%</td>
<td>14%</td>
<td>18%</td>
</tr>
<tr>
<td><strong>Cowtown</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Particle Mass</td>
<td>67 µg/m$^3$</td>
<td>11 µg/m$^3$</td>
<td>77 µg/m$^3$</td>
</tr>
<tr>
<td>Crustal</td>
<td>42%</td>
<td>22%</td>
<td>43%</td>
</tr>
<tr>
<td>Organic</td>
<td>25%</td>
<td>45%</td>
<td>27%</td>
</tr>
<tr>
<td>Nitrate</td>
<td>1%</td>
<td>8%</td>
<td>3%</td>
</tr>
<tr>
<td>Sulfate</td>
<td>1%</td>
<td>9%</td>
<td>2%</td>
</tr>
<tr>
<td>Ammonium</td>
<td>0.2%</td>
<td>5%</td>
<td>1%</td>
</tr>
<tr>
<td>Other Measured Species</td>
<td>11%</td>
<td>8%</td>
<td>7%</td>
</tr>
<tr>
<td>Unidentified</td>
<td>20%</td>
<td>3%</td>
<td>17%</td>
</tr>
<tr>
<td><strong>Pinal County Housing</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Particle Mass</td>
<td>45 µg/m$^3$</td>
<td>9 µg/m$^3$</td>
<td>54 µg/m$^3$</td>
</tr>
<tr>
<td>Crustal</td>
<td>49%</td>
<td>30%</td>
<td>49%</td>
</tr>
<tr>
<td>Organic</td>
<td>9%</td>
<td>31%</td>
<td>13%</td>
</tr>
<tr>
<td>Nitrate</td>
<td>2%</td>
<td>6%</td>
<td>3%</td>
</tr>
<tr>
<td>Sulfate</td>
<td>1%</td>
<td>10%</td>
<td>2%</td>
</tr>
<tr>
<td>Ammonium</td>
<td>0.1%</td>
<td>4%</td>
<td>1%</td>
</tr>
<tr>
<td>Other Measured Species</td>
<td>8%</td>
<td>9%</td>
<td>7%</td>
</tr>
<tr>
<td>Unidentified</td>
<td>31%</td>
<td>10%</td>
<td>25%</td>
</tr>
</tbody>
</table>

*Casa Grande*

Average PM$_{10}$ Composition
The average aerosol composition of PM$_{10}$ particles collected at Casa Grande is shown in Figure 16. Within the PM$_{10}$ size fraction, crustal material is the largest fraction 46% of the particle mass. Of the remaining mass, 21% of the particles are categorized as organic, 7% as the major soluble ions species, 8% as other ions or trace elements (not considered crustal in nature), with 18% remaining uncharacterized.

![Pie chart showing PM$_{10}$ composition](image)

**Figure 16: Average PM$_{10}$ Chemical Composition Measured at Casa Grande**

**PM$_{10}$ Composition Time Series**

The composition time series is shown in Figure 17. Highest concentrations are measured in winter due to inversions causing reduced vertical mixing. Concentrations spikes correspond to similar spikes in the coarse particle time series but carbon concentrations are much higher than those found in that time series graph.
The average aerosol composition of PM$_{10}$ particles collected at Cowtown is shown in Figure 18. Approximately 43% of the particles are categorized as fugitive dust, 27% as organic material, 6% as the major soluble ions, 7% other measured ions and elements, with about 17% remaining uncharacterized.

**Cowtown**

**Average PM$_{10}$ Composition**

The average aerosol composition of PM$_{10}$ particles collected at Cowtown is shown in Figure 18. Approximately 43% of the particles are categorized as fugitive dust, 27% as organic material, 6% as the major soluble ions, 7% other measured ions and elements, with about 17% remaining uncharacterized.
**PM\textsubscript{10} Composition Time Series**

The PM\textsubscript{10} particle chemical composition time series measured at CWTN is shown in Figure 19. Many of the concentration spikes are accompanied by significant increases in the crustal component of the aerosol. The winter and spring 2010 composition shows significant increases in major ion concentrations at this site with significant increases in the measured nitrate. Much like in the coarse particle time series, these increases correspond to changes in the cattle feeding operations in close proximity to the site.
**Pinal County Housing**

**Average PM$_{10}$ Composition**

At PCH, the average PM$_{10}$ aerosol composition consists of 49% crustal material, 13% organic material, 6% major ion species, 7% other measured ions and elements, and 25% remains uncharacterized. The organic fraction within these particles is smaller than it is in the particles collected at the other monitoring locations but the unidentified fraction is larger.
Figure 20: Average PM$_{10}$ Chemical Composition as Measured at Pinal County Housing

**PM$_{10}$ Composition Time Series**

PM$_{10}$ particle composition as measured on the one-in-six day schedule at PCH is shown in Figure 21. Many of the concentration spikes are accompanied by increases in the crustal component of the aerosol while other contributing species remain relatively constant. The winter mass concentrations and crustal components are most significant in winter when inversion layers emissions and prevent dilution.
SOURCE CONTRIBUTION

Coarse Particle Sources

PMF analysis of the coarse particle fraction measured at each of the sites resulted in the isolation of nine factors which have been related to sources impacting each of the sampling sites. Mass and composition data for these particles as measured at each of the sites were combined for this analysis. Figure 22 illustrates the profiles of each of the isolated factors. Each factor is labeled with the factor number as described by the PMF analysis as well as the named description. The order in which the factors are presented are roughly in order of their abundance as averaged among the sites.
Many of the crustal components are found in abundance in these particles and four factors contain the abundance of crustal components including a factor with composition consistent of resuspended crustal material (contains all elemental crustal components), a factor with composition consistent with resuspended road dust (paved and unpaved road dust would both be included in this factor – characterized by crustal components and elevated copper and zinc concentrations), a factor possibly identified as transported soil (contains elemental crustal components and sulfate and chloride ions which were likely condensed onto the crustal material during transport), as well as a factor characterized by elevated boron concentrations (these crustal components co-vary with the boron element). The primary biological aerosol particle (PBAP) factor was among the most abundant factors at most locations. This source identification was made based on the comparison of ion and element concentrations to reported concentrations from aerosol samples collected in Amazonia which are dominated by primary biological material, primarily pollen and fungi [21-23]. Additionally, previous work on samples within the region has shown that PBAPs are an important and sometimes dominant source [24]. Secondary particles were isolated into factor 2 which is approximately the fourth most abundant component in coarse particles. A feedlot factor was isolated in this analysis as well and ammonium nitrate and sodium chloride were isolated as separate factors.
The most significant factors at each of the sampling sites were found to be the primary biological aerosol particles (PBAPs) and crustal factors. Two factors show significant variation between sites including the feedlot factor which is significant only at the CWTN site, and the road dust factor which is more significant at the urban CG site.

Figure 22: Coarse Particle Source Factor Profiles
Table 4: Average Coarse Particle Source Contribution at Each Sampling Site

<table>
<thead>
<tr>
<th>Source</th>
<th>Casa Grande</th>
<th>Cowtown</th>
<th>Pinal County Housing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary Biological</td>
<td>23%</td>
<td>30%</td>
<td>22%</td>
</tr>
<tr>
<td>Crustal</td>
<td>16%</td>
<td>20%</td>
<td>24%</td>
</tr>
<tr>
<td>Road Dust</td>
<td>20%</td>
<td>7%</td>
<td>7%</td>
</tr>
<tr>
<td>Feed Lot</td>
<td>1%</td>
<td>11%</td>
<td>1%</td>
</tr>
<tr>
<td>Secondary</td>
<td>10%</td>
<td>7%</td>
<td>10%</td>
</tr>
<tr>
<td>Boron-Rich</td>
<td>9%</td>
<td>6%</td>
<td>15%</td>
</tr>
<tr>
<td>Transported Soil</td>
<td>5%</td>
<td>7%</td>
<td>6%</td>
</tr>
<tr>
<td>Ammonium Nitrate</td>
<td>4%</td>
<td>4%</td>
<td>3%</td>
</tr>
<tr>
<td>Salt</td>
<td>3%</td>
<td>2%</td>
<td>2%</td>
</tr>
<tr>
<td>Unidentified</td>
<td>9%</td>
<td>6%</td>
<td>10%</td>
</tr>
</tbody>
</table>

Seasonal Variability

Several of the modeled factors show seasonal variability that elucidates differences in source contributions over the year. Factor 2 is a secondary aerosol source characterized by nitrate and sulfate. As shown in Figure 23, the contribution of this factor is highest in summer, when photochemical activity is highest, with a slight elevation in winter when the inversion layer prevents vertical mixing and dilution.

Figure 23: Seasonal Contribution of the Coarse Particle Secondary Aerosol Source Factor
Factor 3 is the ammonium nitrate factor which is presumed to be associated with fertilizers which are applied to agricultural fields. Figure 24 shows that the relative contribution of this source factor is lowest during summer. High temperatures lead to volatilization of ammonium nitrate predominantly into the gas phase.

![Seasonal Contributions](image)

**Figure 24: Seasonal Contribution of the Coarse Particle Ammonium Nitrate Source Factor**

PBAPs (Factor 7) show a strong seasonal variation in the relative contribution with the smallest influences during the winter and highest contribution in spring which is consistent with the growing season.

![Seasonal Contributions](image)

**Figure 25: Seasonal Contribution of the Coarse Particle PBAP Source Factor**

Salt is represented by factor 9. The relative contribution from this factor is highest in summer when the monsoon brings in moist air from the Gulf of Mexico. High sea salt concentrations are expected and high humidity is experienced during this time of year.
Factor 4 represents the feedlot source which is local to the CWTN sampling site. The source contribution of this source at only the CWTN monitoring location is shown in Figure 27. The contribution from this source is shown to be lowest in winter. However, this representation is likely skewed by the previously mentioned relocation of some of the cattle which influenced the final winter of this sampling campaign. This observation is consistent with marked decreases in particle mass and many of the chemical marker species for this source including phosphate, potassium, and magnesium.

*Casa Grande*

*Model Performance*
The PMF model was able to reasonably predict the observed coarse particle concentrations at the CG site. The highest concentrations, often observed as spikes, are the most difficult to predict.

Figure 28: Coarse Particle Mass Concentration Model Performance for Casa Grande
Figure 29: Model Predicted Coarse Particle Mass Concentration Time Series for Casa Grande

Average Source Contribution

At CG, the PBAPs and road dust factors each comprise nearly 23% of the coarse particles mass. The crustal component contributes approximately 16% with the boron-rich crustal factor, secondary aerosol factor, and the unidentified fraction making up approximately 9% of the average composition. The remaining factors, ammonium nitrate (4%), feedlot material (1%), transported soil (5%), and salt (3%) components round out the composition description.
Figure 30: Average Source Category Contributions to Coarse Particles at Casa Grande

Cowtown

Model Performance

The modeled coarse particle concentrations more closely matched the measured mass concentration at the CWTN sampling site. A couple of samples were not well modeled but there was no consistent under or over prediction of particle concentrations.
Figure 31: Coarse Particle Mass Concentration Model Performance for Cowtown
Figure 32: Model Predicted Coarse Particle Mass Concentration Time Series for Cowtown

Average Source Contribution

At CWTN, the PBAPs and crustal factors together comprise 50% of the coarse particles mass at this sampling site. The feedlot is expected to be a significant contributor at this site and the factor, which does not contain a lot of the crustal material that accompanies these emissions, contributes 11% to the observed mass. The remaining factors, boron enriched crustal material (6%), secondary particles (7%), ammonium nitrate (4%), road dust (7%), transported soil (7%), and salt (2%) components round out the composition description with approximate 6% remaining unattributed.
Figure 33: Average Source Category Contributions to Coarse Particles at Cowtown

**Pinal County Housing**

**Model Performance**

The model performance at the PCH site more closely resembled the performance at the CG site where high particle concentrations were more poorly modeled.
Figure 34: Coarse Particle Mass Concentration Model Performance for Pinal County Housing
Average Source Contribution

At the PCH site, the PBAPs and crustal factors again comprise 46% of the coarse particles mass at this sampling site when combined. The boron enriched crustal material was significant contributing 15% to the observed mass. The remaining factors, including secondary particles (10%), ammonium nitrate (3%), feedlot (1%), road dust (7%), transported soil (6%), and salt (2%) components round out the composition description with approximate 10% remaining unattributed.
Figure 36: Average Source Category Contributions to Coarse Particles at Pinal County Housing

Fine Particle Sources

PMF analysis of the fine particle fraction measured at each of the sites resulted in the isolation of six factors which have been related to sources impacting each of the sampling sites. Mass and composition data for these particles as measured at each of the sites were combined for this analysis. Figure 37 illustrates the profiles of each of the isolated factors. Each factor is labeled with the factor number as described by the PMF analysis as well as the named description. The order in which the factors are presented are roughly in order of their abundance as averaged among the sites.
One of the major factors appears to represent motor vehicle related emissions with elevated elemental and organic carbon content as well as a bit of the Cu and Zn elements associated with brake wear. This factor likely contains not only the light duty road traffic by also heavy duty...
diesel and train emissions as well. A separate brake wear factor was also isolated accounting for the majority of the measured Cu and Zn elements. Separately, a road dust featuring both organic carbon and crustal material was also isolated. Pb was isolated into a separate factor associated with a minor amount of crustal and vehicle (elemental carbon) components. This factor indicates that the Pb concentrations do not co-vary with many other components and were thus isolated into a separate factor. The exact source of Pb is unknown at this time. Also, one factor was isolated that is specific to the crustal components (contains the common crustal elements) and another was isolated as salt.

The factors with the most significant influence at all sites are the motor vehicle and road dust factors. The PCH site is more removed from roadways and is closest to uncultivated native soil sources yielding the smallest contribution from the motor vehicle source and the largest contribution from the crustal source.

**Table 5: Average Fine Particle Source Contribution at Each Sampling Site**

<table>
<thead>
<tr>
<th>Source</th>
<th>Casa Grande</th>
<th>Cowtown</th>
<th>Pinal County Housing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Motor Vehicle</td>
<td>45%</td>
<td>41%</td>
<td>25%</td>
</tr>
<tr>
<td>Road Dust</td>
<td>30%</td>
<td>29%</td>
<td>29%</td>
</tr>
<tr>
<td>Lead-rich</td>
<td>12%</td>
<td>8%</td>
<td>11%</td>
</tr>
<tr>
<td>Brake Wear</td>
<td>4%</td>
<td>3%</td>
<td>8%</td>
</tr>
<tr>
<td>Crustal</td>
<td>2%</td>
<td>3%</td>
<td>7%</td>
</tr>
<tr>
<td>Salt</td>
<td>3%</td>
<td>2%</td>
<td>3%</td>
</tr>
<tr>
<td>Unidentified</td>
<td>4%</td>
<td>14%</td>
<td>17%</td>
</tr>
</tbody>
</table>
**Seasonal Variability**

The seasonal variability of the factors was investigated for consistency with the factor identification. Factor 1, the lead-rich source, had the highest relative contribution during the winter season when the inversion layer prevents mixing trapping higher concentrations near the surface.

![Seasonal Contributions](image)

**Figure 38: Seasonal Contribution of the Fine Particle Lead-Rich Source Factor**

The motor vehicle factor, labeled factor 3, shows a very similar seasonal pattern with the highest contributions observed during period of decreased ventilation, namely winter and fall. However, the overall relative contribution of the motor vehicle emissions is higher which is consistent with this being a major source of particles within this size range.

![Seasonal Contributions](image)

**Figure 39: Seasonal Contribution of the Fine Particle Motor Vehicle Source Factor**
Factor 5 represents the road dust component of the aerosol. This factor actually shows the smallest relative contribution during the winter period. Rather than suggesting that emissions from this source are reduced during this period, it might actually suggest that concentrations stay consistent but that the relative contribution from this source goes down because emissions from other sources actually increase.

![Figure 40: Seasonal Contribution of the Fine Particle Road Dust Source Factor](image)

Finally, factor 6 has been identified as the salt factor. As seen in the coarse particle fraction, the relative contribution from this factor is highest in summer when the monsoon brings in moist air from the Gulf of Mexico.

![Figure 41: Seasonal Contribution of the Fine Particle Salt Source Factor](image)
**Casa Grande**

**Model Performance**

The PMF model was able to reasonably predict the observed fine particle concentrations at the CG site. The overall concentration trends were modeled appropriately however, the highest mass concentrations were slightly over-predicted.

![Figure 42: Fine Particle Mass Contribution Model Performance for Casa Grande](image)

\[ y = 1.0827x \]
\[ R^2 = 0.6773 \]
At CG, the motor vehicle factor is pronounced with 45% of the fine particle mass attributed to this single factor. The road dust factor is another significant contributor representing 30% of the measured mass. The remaining factors, lead rich (12%), brake wear (4%), crustal (2%), salt (3%), and unattributed (4%) components, round out the composition description.
Cowtown

Model Performance

The PMF model was able to reasonably predict the observed fine particle concentrations at the CWTN site but tended to slightly underestimate the measured mass. Model agreement appears worst during the winter months.
Figure 45: Fine Particle Mass Concentration Model Performance for Cowtown

Figure 46: Model Predicted Fine Particle Mass Concentration Time Series for Cowtown
Average Source Contribution

The motor vehicle factor is still the largest contributor to fine particle mass at the CWTN site representing approximate 41% of the mass. As at CG, the road dust component is the second largest component representing 29% of the mass. The remaining factors, lead-rich (8%), brake wear (3%), crustal (3%), and salt (2%) components round out the composition description. The unattributed mass is rather high at this monitoring location representing 14% of the mass.

Figure 47: Average Source Category Contributions to Fine Particles at Cowtown
Pinal County Housing

Model Performance

The fine particle mass measured at PCH is modeled reasonably well by the modeled reconstructed mass however, the modeled mass is in general lower than the observed mass and the agreement is worst for transient high particle concentrations.

Figure 48: Fine Particle Mass Concentration Model Performance for Pinal County Housing
Figure 49: Model Predicted Fine Particle Mass Concentration Time Series for Pinal County Housing

Average Source Contribution

Being a location more removed from roadways, the contribution of motor vehicles to fine particles at the PCH site is lower representing approximately 25% of the particle mass. The road dust factor remains significant at 29% of the particle mass and could be representative of the fine nature of the road dust in close proximity to this site. The remaining factors, lead-rich (11%), brake wear (8%), crustal (7%), and salt (3%) factors are significant components of the fine particle mass. The unattributed mass is also significant at this rural site representing 17% of the particle mass.
PM$_{10}$ Particle Sources

PMF analysis of the PM$_{10}$ size fraction resulted in the isolation of eight factors which have been related to sources impacting each of the sampling sites. Seven factors closely resemble the factors isolated during analysis of the coarse fraction which is expected as coarse particles make up at least 75% of the PM$_{10}$ mass. The additional factor, labeled traffic, closely resembles the traffic factor from the fine particle analysis and represents the most unique factor from the fine fraction.
Figure 51 illustrates the profiles of each of the isolated factors. Each factor is labeled with the factor number as described by the PMF analysis as well as the named description. The order in which the factors are presented are roughly in order of their abundance as averaged among the sites.

Many of the crustal components are found in abundance in these particles and two factors contain the abundance of crustal components including a factor with composition consistent with the resuspended crustal material and transported soil factors isolated during coarse particle analysis. A road dust factor was previously isolated from the coarse particle fraction and is not isolated in the analysis of the PM$_{10}$ data. The fraction has likely been divided between the two crustal components because the key features were isolated into the new traffic factor. The boron-rich factor which was isolated from the coarse particle fraction is still present in the PM$_{10}$ profiles but has now been effectively decoupled from the elemental components which make up a dominating fraction of the coarse particles. The isolation of this element points to a unique source for boron which does not co-vary with other chemical components. The exact source for this element remains unknown.

The primary biological aerosol particle (PBAP) factor was among the most abundant factors at most locations as it was in the coarse particle analysis. Again, this source identification was made based on the comparison of ion and element concentrations to reported concentrations from aerosol samples collected in Amazonia which are dominated by primary biological material.
Figure 51: PMF Isolated Source Profiles for the PM$_{10}$
The secondary factor isolated in this analysis combined two a set of factors isolated in the coarse and fine fraction analysis. In the PM$_{10}$ analysis, this factor is characterized by both ammonium nitrate and ammonium sulfate. The feedlot factor closely resembles the feedlot factor isolated for coarse particles but the ion species have been decoupled from the crustal elements which are thought to also be present in emissions from this source. The salt factor is closely resembled to the salt factors isolated for both coarse and fine particles. The traffic factor most closely resembles the traffic factor from the fine particle analysis.

Table 6 shows the modeled sources and their relative contribution at each of the sampling sites. The factors with the most significant influence at all sites are the primary biological and crustal (crustal and transported soil) factors. These factors alone account for 43% or more of the PM$_{10}$ particle mass. The feedlot factor is most significant at the CWTN site which is the only site in close proximity to this type of source. The traffic factor is the most significant factor at the CG site which is located in the urban center. The other factors are minor contributors to particle mass leaving between 5 and 8% unattributed.

Table 6: PM$_{10}$ Source Factors and Relative Contribution to Each Site

<table>
<thead>
<tr>
<th></th>
<th>Casa Grande</th>
<th>Cowtown</th>
<th>Pinal County Housing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary Biological</td>
<td>27%</td>
<td>16%</td>
<td>35%</td>
</tr>
<tr>
<td>Crustal</td>
<td>10%</td>
<td>12%</td>
<td>23%</td>
</tr>
<tr>
<td>Transported Soil</td>
<td>22%</td>
<td>15%</td>
<td>9%</td>
</tr>
<tr>
<td>Feed Lot</td>
<td>5%</td>
<td>32%</td>
<td>4%</td>
</tr>
<tr>
<td>Traffic</td>
<td>15%</td>
<td>8%</td>
<td>8%</td>
</tr>
<tr>
<td>Secondary</td>
<td>8%</td>
<td>5%</td>
<td>7%</td>
</tr>
<tr>
<td>Salt</td>
<td>4%</td>
<td>2%</td>
<td>4%</td>
</tr>
<tr>
<td>Boron-Rich</td>
<td>4%</td>
<td>2%</td>
<td>3%</td>
</tr>
<tr>
<td>Unidentified</td>
<td>5%</td>
<td>8%</td>
<td>7%</td>
</tr>
</tbody>
</table>
**Seasonal Variability**

Several of the modeled factors show seasonal variability that elucidate differences in source contributions over the year and in every case they are consistent with the coarse or fine particle factors they most closely resemble. Primary biological particles show a strong seasonal variation consistent with the factor isolated from coarse particle analysis. The relative contribution is smallest during the winter and highest during spring which is consistent with the growing season. The feedlot source, which is local to the CWTN sampling site, has the smallest contribution during winter. This is consistent with the observations in the corresponding coarse fraction factor and both are likely influenced by the relocation of cattle during the final winter of the sampling campaign. The traffic factor, consistent with the similar fine particle factor, shows a seasonal pattern with the highest contributions observed during winter and fall, which is consistent with decreased ventilation trapping emissions and increasing concentrations but, also with the decrease of traffic during summer because of seasonal residents. Secondary aerosol contributes the most in summer, when photochemical activity is highest, with a slight elevation in winter when the inversion layer prevents vertical mixing and dilution. Finally, the salt factor has the highest contribution during summer when the monsoon brings in moist air from the Gulf of Mexico. This is consistent with the salt factors isolated from the coarse and fine fractions, separately.

**Casa Grande**

**Model Performance**
The PMF model was able to closely predict the observed PM$_{10}$ particle concentrations at the CG site even though the concentration was considerably smaller than those observed at the other sampling sites. The overall concentration trends were modeled appropriately with small under predictions of peak concentrations.

Figure 52: PM$_{10}$ Mass Concentration Model Performance at Casa Grande
Figure 53: Model Predicted PM$_{10}$ Mass Concentration Time Series at Casa Grande

Average Source Contribution

The CG sampling site represents the urban area and therefore has the most significant contribution from traffic (15%). The primary biological (27%) and crustal factors (crustal-10% and transported soil-22%) remains significant together representing 59% of the particle mass. The remaining factors, feedlot (5%), secondary (8%), boron-rich (4%), and salt (4%) factors are significant components of the PM$_{10}$ particle mass. The unattributed mass remains at 5% of the particle mass.
The PMF model was able to reasonably predict the observed PM$_{10}$ particle concentrations at the CWTN site. The overall concentration trends were modeled appropriately however, there was a slight over prediction in general but two more severe under-predictions and one more severe over-predictions at peak concentrations.

Figure 54: Average Source Category Contribution for PM$_{10}$ at Casa Grande

Cowtown

Model Performance
Figure 55: PM$_{10}$ Mass Concentration Model Prediction for Cowtown

Figure 56: Model Predicted PM$_{10}$ Mass Concentration Time Series at Cowtown
Average Source Contribution

The CWTN sampling site is located in close proximity to cattle feeding operations and therefore the feedlot has the most significant contribution at this site (32%). The primary biological (16%) and crustal factors (crustal-12% and transported soil-15%) remains significant together representing 43% of the particle mass. The remaining factors, traffic (8%), secondary (5%), boron-rich (2%), and salt (2%) factors are significant components of the PM$_{10}$ particle mass. The unattributed mass remains at 8% of the particle mass.

![Figure 57: Average Source Category Contribution to PM$_{10}$ at Cowtown](image)

_Pinal County Housing_

_Model Performance_
The PMF model was able to reasonably predict the observed PM$_{10}$ particle concentrations at the PCH site. The overall concentration trends were modeled appropriately. However, there were two more severe under-predictions of peak measured concentrations.

Figure 58: PM$_{10}$ Mass Concentration Model Performance at Pinal County Housing
Average Source Contribution

The PCH sampling site is closely situated near agricultural fields. The influence of biological material is represented by the primary biological factor which dominates the source profile for this site representing 35% of the PM$_{10}$ particle mass. The crustal factors (crustal-23% and transported soil-9%) remain significant representing an additional 32% of the particle mass. The remaining factors, traffic (8%), feedlot (4%), secondary (7%), boron-rich (3%), and salt (4%) factors are significant components of the PM$_{10}$ particle mass. The unattributed mass remains at 7% of the particle mass.
CRUSTAL SOURCE SAMPLING

PM$_{10}$ Particle Sources

A number of samples were collected by ASU personnel from crustal sources in close proximity to the sampling sites. These samples represent a variety of source types including uncultivated native soil, agricultural soils, from dirt roads in close proximity to agricultural sources, paved road dust, a dirt road near the cattle feedlots, and from the feedlots. The PM$_{10}$ chemical composition of resuspended dust from these source categories is shown in Figure 45. Mass closure is within 20%. The feedlot samples contain the highest percentage of organic material. Dirt roads near the agricultural field shows measureable ammonium and nitrate concentrations.
consistent with the deposition of fertilizers that were not used as nutrients by the agricultural crop. Elevated sulfate concentrations were found in the feedlot samples and more so in the samples from the dirt roads adjacent to the feedlots. This is consistent with the deposition of liquid feed supplements which may be used in these feeding operations.
Figure 61: PM$_{10}$ Resuspended Soil Composition

PM$_{2.5}$ Particle Sources

The PM$_{2.5}$ chemical composition of resuspended dust from these source categories is shown in Figure 46. Mass closure for the uncultivated native soil, the agricultural soil, and the road dust is within 20%. The feedlot samples, marked with a star, were collected from the dirt road adjacent to the feedlot and from within the feedlot itself. These samples show an over prediction of reconstructed mass. The largest contributor to the reconstructed mass is the crustal component which was reconstructed as they were for the ambient aerosol samples from the measured
elemental composition assuming the common oxides. It is hypothesized the assumptions regarding the dominant mineral forms of Al, Ca, Mg, Ti, and Si are do not hold for these sites. As an example, calcium can be included in liquid finishers for cattle feed and thus, calcium may not be exclusively present in the carbonate form.

![Figure 62: PM$_{2.5}$ Resuspended Soil Composition](image)

SUMMARY AND CONCLUSIONS
This report details the ambient particle composition and source apportionment findings of the year-long field sampling campaign conducted in Pinal County, AZ between February 2009 and February 2010. Characterization of PMc and PMf in terms of mass, bulk organic and elemental carbon, ions, and elements were conducted at one-in-six day resolution from low-volume filter samples collected at three different sampling sites. These data were then used to determine the sources of PMc and PMf and their relative impact using positive matrix factorization. The sources and relative impact were compared between the two fractions and across each of the sampling sites.

Measured one-in-six day 24-hour average PMc concentrations ranged from 5 to 180 µg/m³. The average coarse mass concentrations were lowest at the CG (31 µg/m³). Concentrations at PCH were approximately 14 µg/m³ higher on average while concentrations at CWTN were much more variable with concentrations ranging between 5-90 µg/m³ higher than at the other two sites (average of 22 µg/m³ higher than the other two sites). The highly variable concentrations at CWTN indicate the influence of local sources.

In comparison, PMf concentrations measured at the three sampling sites ranged between 2 and 22 µg/m³. Again, the influence of local sources near CWTN is seen in higher (between 5 and 10 µg/m³) and more variable concentrations.

For both coarse and fine particles, crustal and organic material are the major components representing on average 45% and 15% of coarse particles and 25% and 40% of fine particles, respectively.

Coarse particles have been attributed to 9 different sources including a source tentatively identified as primary biological aerosol particles (PBAPs) based on composition and relevant
recent studies of organic speciation in the region, crustal material, road dust, secondary particles, transported soil, a boron-rich factor, feedlots, ammonium nitrate, and salt. The dust factors, when combined together, agree well with the reconstructed mass calculations representing on average about 45% of the coarse particles. The road dust factor had its strongest influence at the CG site consistent with increased nearby vehicle traffic while the feedlot factor is significant at the CWTN site which is closest proximity to this unique source.

Fine particles have been attributed to 6 different sources including motor vehicles, road dust, brake wear, crustal material, salt, and a lead-rich factor. The road dust and crustal factors combined make up approximately 35% of the fine particle mass. The motor vehicle factor had its strongest influence at the CG site which is again consistent with increased nearby vehicle traffic.

To complete the analysis, fine and coarse particle data were combined to examine the data in terms of PM$_{10}$ mass and composition. PM$_{10}$ particles were attributed to 8 different source factors including several factors closely resembling factors isolated during analysis of the coarse fraction and a couple of factors isolated from analysis of the fine fraction. As the coarse fraction makes up about 75% of the PM$_{10}$ mass and because the fine fraction contains some very unique factors, this result is expected. The primary biological aerosol particles were again isolated as a major source contributing between 17 and 36% of the particle mass. Also isolated were two crustal factors including crustal and transported soil. Other sources included feedlot material, traffic, secondary particles, salt, and a boron-rich factor. The traffic source was strongest at the CG site consistent with nearby vehicle traffic in the urban center. The feedlot factor is most significant at the CWTN site which is closest proximity to this unique source. The primary biological aerosol source was most significant at the PCH site consistent with nearby agricultural activity.
Differentiation between several fugitive dust sources was facilitated by the collection of bulk samples (by ASU personnel) from several known sources of fugitive dust within the region. These crustal materials were resuspended in the laboratory environment and chemically analyzed to create fingerprint profiles for each source, representative of particles that could be suspended as PM$_{10}$ and PM$_{2.5}$. These source signatures were compared to the source profiles generated by PMF modeling for validation purposes. Additionally, analysis of the feedlot samples revealed that crustal elements such as Al, Ca, Mg, Ti, and Si may not all be present in their dominant oxide forms in these samples thereby making reconstruction of the associated crustal mass an overestimation of what is found in these samples.
REFERENCES


