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Mass, Composition, Source Identification and Impact Assessment for Fine and Coarse Atmospheric Particles in the Desert Southwest

by

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Abstract

A year-long study was conducted in Pinal County, Arizona to characterize fine and coarse particulate matter as a means of furthering our understanding of ambient concentrations and composition in rural, arid environments. Detailed measurement of ambient fine and coarse mass, ion, metal, and carbon concentrations at one-in-six day resolution was conducted at three sites from February 2009 to February 2010. Detailed organic carbon speciation was collected at 5-week resolution. A series of samples representing native soil, agricultural soil, road dust, and cattle feed lot material was collected, resuspended in the laboratory, and analyzed to provide a chemical source profile for each soil type yielding insights into unique source signatures.

Observations within the chemical speciation data and subsequent modeling analysis show a strong impact from local sources at the Cowtown site where mass concentrations are highest. Source apportionment results confirm the significant impact from the cattle feedlot adjacent to the site. Chemical analysis of ambient particles and local feedlot material shows the presence of chemical marker species including phosphate, which is unique to this source.

Fugitive dust is a significant contributor to ambient particulate matter concentrations at all monitoring locations. Seasonal observations show higher concentrations during tilling and harvesting, indicating the large role agricultural sources play on particle concentrations in this area. Chemical characterization and modeling show that re-entrained road dust is a significant factor.
Fine particle modeling results indicate that concentrations are influenced significantly by motor vehicles including impacts from direct emissions including brake wear and indirect emissions including resuspended road dust. A significant fraction is also associated with crustal sources, while about 5 µg/m³ appears to be transported into the region from beyond the air shed.

Detailed analysis of the local monsoon season indicates that monsoon rains serve to clean the atmosphere, resulting in a marked decrease in ambient coarse mass and a period where local coarse particulate matter (PM) concentrations measured at all sites became more uniform. The monsoon season also featured localized high wind events which severely increased coarse PM concentrations and often caused exceedences of the PM National Ambient Air Quality Standard.
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Chapter 1: Introduction

1.1 Project Overview

This work details the year-long field sampling campaign conducted in Pinal County, AZ characterizing 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) as a means of furthering our understanding of ambient concentrations and composition in rural, arid environments. Detailed measurements of ambient fine and coarse mass, ions, elements, and carbon concentrations at one-in-six day resolution were conducted at three sites within the region between February 2009 and February 2010.

Additionally, samples were collected 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\(_{2.5}\) with the goal of identifying key differences in chemical composition that could be used for source apportionment studies.

Finally, two different modeling approaches were used to determine the sources of PMc and PMf and their relative impact. The sources and relative impact were compared between the two fractions and across each of the sampling sites. The results of each modeling approach were compared and used to evaluate these methods.
1.2 Research Questions

The research approach described above was designed to address the following questions:

• What are ambient coarse and fine particulate matter (PM) concentrations in Pinal County, AZ and how much do they vary spatially and temporally?

• In comparing the more widely studied chemical composition of fine particulate matter, does the composition of coarse particles reveal something unique?

• What are the sources of fine and coarse particles and how do they differ based on particle size and sampling location?

• Are there chemical species which can be used as markers to differentiate between various routes of entrainment of crustal material into the atmosphere?

1.3 Motivation

PM concentrations in the desert Southwest, and Pinal County in particular, are elevated. Much of the desert southwest is designated non-attainment of the federal 24-hour National Ambient Air Quality Standard (NAAQS) for PM$_{10}$. Parts of six Arizona counties are designated moderate non-attainment (Cochise, Gila, Pima, Pinal, Santa Cruz, and Yuma) and parts of two counties are designated serious non-attainment (Maricopa and Pinal) of the PM$_{10}$ standard (U.S. EPA 2008). Pinal County regularly experiences exceedances of the NAAQS at multiple monitors and measures some of the highest PM$_{10}$ concentrations in the country. According to the US EPA Airdata database, Pinal County registered the second highest 24-hour averaged concentration, the highest number of 24-hour averaged concentration exceedances, and the highest annual averaged PM$_{10}$
concentration in the nation in 2007 (U.S. EPA AirData 2012). Violations are not isolated with six monitoring locations within the county registering exceedences between 2006 and 2008 (Arizona Department of Environmental Quality - Air Quality Division 2010). While PMc is the dominant fraction of PM$_{10}$ in arid environments and fluctuations in PMc concentrations often drive PM$_{10}$ violations, exceedences of the 24-hour PM$_{2.5}$ NAAQS have also been measured, threatening to put the region in non-attainment of the fine particle standard (Arizona Department of Environmental Quality - Air Quality Division 2010).

This is an ideal location to study coarse particles. A large portion of the 24-hr PM$_{10}$ exceedances were measured at monitors within the Pinal County agricultural basin, where entrainment of crustal-related material is believed to cause elevated PM$_{10}$ concentrations (Arizona Department of Environmental Quality - Air Quality Division 2010). Sources include 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. Being mechanically generated, most of the PM from these sources falls in the PMc (PM$_{10}$-PM$_{2.5}$) size range. Within this region, PMc makes up a large portion of the total PM$_{10}$ concentration. For comparison, PMc in Los Angeles, CA is approximately 49% of the measured PM$_{10}$ while in Pinal County, PMc comprises approximately 71% of the measured PM$_{10}$. As many studies focus on PM$_{10}$ which aggregates PMc and PMf into a single sample - the separate sampling for PMc and PMf can better isolate important sources of mechanically generated aerosols. High PMc concentrations allow for ease in collection and chemical characterization at the 24-hour time resolution (U.S. EPA AirData 2012).
**PM sources in the region require characterization.** There are a number of sources for ambient PM in Pinal County. Of particular interest are the crustal sources (ie. native desert with little stabilizing vegetation, agricultural fields which sometimes lie fallow, dirt road dust, etc.) which can generate fugitive dust. Distinguishing the impact of these sources requires chemical fingerprinting and modeling. Dust control strategies may be improved with a greater understanding of the strength of each type of source. In addition, Pinal County is on the urban fringe of a large metropolitan area leading to a unique, and regulatory relevant juxtaposition of urban and agricultural sources that can be used to investigate the air quality implications of urban growth into agricultural zones.

### 1.4 Research Hypothesis and Objectives

The central hypothesis of this thesis is that the chemical composition of particles can be used to determine the dominant sources and source contributions for both PM$_{2.5}$ and PM$_{10}$, that these sources and source contributions differ by size fraction, and that this information can later be used by regulatory agencies to drive more effective environmental policy at the local level. To test this hypothesis, we have developed specific objectives of this project as follows:

1. Quantify the mass concentration and characterize the chemical composition of PMc and PMf at different locations in Pinal County, AZ;

2. Identify chemical species that are uniquely associated with PMc and PMf and the spatial and temporal variability of these constituents;
3. Determine the sources of coarse particles and fine particles using positive matrix factorization (PMF) and determine the similarities and differences within different particle size fractions.

4. Use data collected at the three different sampling sites to estimate the influence of local sources and regional transport.

5. Characterize the chemical composition of several crustal materials which to contribute to local PM concentrations within the region.

6. Verify PMF source apportionment results using source profiles and the chemical mass balance approach.
Chapter 2: Literature Review

2.1 Particulate Matter

2.1.1 Motivation: Pollution and Health

The London Black Fog of December 1952 is one of most important motivators for regulation and investigation of particulate matter today. At that time, small-scale coal combustion for household heating was common practice, and over a period of four days in early December, a severe inversion developed, trapping emissions close to the ground and causing severe visual impairment that penetrated indoors and even stopped bus service for awhile. As pollution level rose, the daily mortality rate also increased, and the marked increase (approximately 400%) was the first suggestion that human health can be impacted by urban air pollution.
Figure 1: Mortality and Air Pollution during the London Fog of 1952 (Johns Hopkins Bloomberg School of Public Health)

Figure 1 shows how the daily mortality compares with ambient smoke and sulfur dioxide concentrations during that same period. While the concentration of the air pollution (measured as smoke and sulfur dioxide) returned to typical levels once weather conditions changed and ventilated the area, mortality remained elevated for several months following the episode. Although initial reports suggest the deaths were related to influenza (UK Ministry of Health 1954), more recent studies have investigated this possibility and have concluded that this is not a likely explanation (Bell, Davis et al. 2004). Further investigation of the relationship between pollution and mortality and morbidity have found a statistically significant association between the two during this episode (Bell and Davis 2001).
2.1.2 Definitions

In the data presented from the 1952 London Black Fog event, the general term “smoke” encompasses not only gases related to combustion but also the condensed phase which is a complex mixture of fine solids or liquid droplets in the air. To isolate the pollutants responsible for impacting health, clearer separation is required. Particulate matter (PM), typically referring to both suspended solids and liquid droplets, is commonly measured in sizes from nanometers to hundreds of micrometers in diameter. Although we may be able to see PM generated from dust or combustion because these particles absorb light and appear dark, or because as an aggregate they scatter visual radiation and impair visibility, we cannot see the individual particles without aide. Figure 2 illustrates the how the size of PM compares to more familiar objects including fine sand and a human hair (U.S. EPA 2010).

Operationally, PM is generally described in terms of two different size fractions. PM$_{10}$ refers to particles with an aerodynamic diameter (AD) of 10 µm or less. PM$_{2.5}$, PMf or fine particles, refers to particles with an AD of 2.5 µm or less. PMc, coarse particles, represents the difference between these two measurements and is referred to as the PM$_{10-2.5}$ size range. Some references label coarse particles as all entrained particles larger than 2.5 µm but here we are referring to coarse inhalable particles thus the definition of particles with an aerodynamic diameter between 2.5 µm and 10 µm. Figure 2 puts these definitions in perspective as well.
2.1.3 Implications for Human Health

The size of atmospheric particles dictates their atmospheric motion and thus their ultimate fate in the human respiratory system and impacts on human health. Particles in the PM$_{10}$ size range are referred to as inhalable particles because they can enter the human respiratory tract, and the largest of these particles are often trapped within the nose and throat. While some may be absorbed into the body, most are cleared and expelled naturally by the mucus membranes coating the upper respiratory track. Smaller particles with less inertia are able to penetrate further into the lung (Figure 3). Deposition may occur along the airways and when this happens, particles can accumulate there, react
in some way, be cleared by the body, or absorbed. Fine particles can make it all the way into the tiny alveoli of the lung and in these tiny sacks responsible for the gas transfer between the lung and the circulatory system, they are much more difficult to clear, tend to accumulate, and can even pass through the lungs into the bloodstream.

![Deposition of Particles within the Lung](image)

**Figure 3: Deposition of Particles within the Lung (Home Air Purifier Expert).**

Studies have linked PM exposure to a variety of health symptoms, ranging from minor symptoms including irritation of the airways and coughing to more severe symptoms including difficulty breathing, decreased lung function, aggravated asthma, development of chronic bronchitis, heart arrhythmias, heart attacks, cancer, and premature death.
Figure 4: Relative Risk between PM$_{10}$ and Daily Mortality Due to Cardiovascular Disease (Anderson 2009).
Elevations in PM$_{10}$ mass concentrations of just 10 µg/m$^3$ have been associated with an increase daily mortality of 0.5-0.6% (Samet, Dominici et al. 2000; Katsouyanni, Touloumi et al. 2001) and increased hospitalization for asthma and chronic obstructive pulmonary disease or cardiovascular disease of 1-1.5% and 0.5-1.1%, respectively (Zanobetti, Schwartz et al. 2000; Atkinson, Anderson et al. 2001). Figure 4 summarizes major studies that have shown that this impact of elevated PM$_{10}$ concentrations on human health and several cardiovascular mortality measurements has been replicated across the globe (Anderson 2009). Children seem particularly susceptible with a 3% increase in respiratory related hospital emergency room visit as a result of increased PM$_{10}$ concentrations (Krewski and Rainham 2007).

Regarding fine particles, elevated PM$_{2.5}$ concentrations have been linked to increased risk of premature death (Krewski, Burnett et al. 2003) including increased risk of death due to cardiac or respiratory diseases and lung cancer (Pope, Burnett et al. 2002). Dockery and Pope (Dockery and Pope 1994) and Schwartz (Schwartz 1994) have found that the increase mortality is almost linearly correlated with PM$_{2.5}$ concentrations. The effect was quantified by Schwartz whose research found a 10 µg/m$^3$ increase in the 48-hour average PM$_{2.5}$ concentration resulted in a 1.5% increase in the daily mortality (Schwartz, Dockery et al. 1996). Additionally, elevated PM$_{2.5}$ concentrations have been linked to heart arrhythmias in people with heart disease (Peters, Liu et al. 2000) and increased risk of non-fatal heart attack (Krewski and Rainham 2007).

Particle composition has also been found to have a significant effect on human health separate from the link between particle mass and health outcomes. Le Tertre, et. al.
found that hospital admission rates for respiratory symptoms increased 1.1% for each 10 
µg/m³ increase in black smoke (Le Tertre, Medina et al. 2002). Studies conducted to
investigate the toxicity of polycyclic aromatic hydrocarbons (PAH) and transition metals
found that they caused pulmonary inflammation and cellular toxicity in rats suggesting
this can also happen in human tissues (Gerlofs-Nijland, Rummelhard et al. 2009). Happo
et. al. found that dicarboxylic acids, transition metals, and other soil-derived constituents
correlated positively with inflammation in humans but that secondary inorganic ions,
such as sulfate and nitrate, did not (Happo, Hirvonen et al. 2008). That study also found
that PAH concentrations caused an immunosuppressive effect (Happo, Hirvonen et al.
2008). Prahalad, et al. have investigated several dust sources with high metal
concentrations and found that exposure results in the release of reactive oxygen species
within the airway which can cause tissue damage (Prahalad, Soukup et al. 1999). Work
done by Gualtieri et al. found that various chemical properties of PM trigger different
responses such as inflammation, perturbation of cell cycle, and cell death but that the
response was dependent on the cell line used which means that response will not be the
same in all people (Gualtieri, Ovrevik et al. 2010).

2.1.4 National Ambient Air Quality Standards

The link between human health and air pollution was the motivation for the development
of the Clean Air Act of 1970 which gave the U.S. EPA the authority and responsibility of
protecting and improving the nation's air quality. The code required the establishment of
national primary and secondary ambient air quality standards (42 U.S.C. 7409). Primary
standards are mandated to protect the public health including, the health of sensitive
populations including, asthmatics, children, and the elderly. Secondary standards are
mandated to protect the public welfare, including the regulation of air pollution and its impact on visibility and damage to animals, vegetation, and buildings. In response, the U.S. EPA developed National Ambient Air Quality Standards (NAAQS) for six criteria pollutants including, ozone, carbon monoxide, nitrogen oxides, sulfur dioxide, lead, and PM.

The PM NAAQS was initially established in 1971 (36 FR 8186 (1971)) to regulate total suspended particulates (operationally defined by the sampler to include particles with an AD between 4 and 45 μm) and set acceptable PM concentrations as less than a 24-hour averaged concentration of 260 μg/m³ as a primary standard, and 150 μg/m³ as a secondary standard, with the allowance that these levels were not to be exceed more than once per year. A primary annual average concentration limit was also established at 75 μg/m³.

In 1987 (52 FR 24634 (1987)), the original standards were revised to adopt a PM₁₀ standard, with the ultimate goal of regulating only particles small enough to penetrate deep into the respiratory tract. The new standard set equivalent primary and secondary standards with maximum 24-hour average concentrations of 150 μg/m³ not to be exceeded once per year, with an annual average at 50 μg/m³. Exceedances to each standard were averaged over a 3-year period.

In 1997 (62 FR 38652 (1997)), the NAAQS was revised to include both a PM₁₀ standard, as well as an additional fine particle standard. The additional standard was based on research that found evidence of health effects associated with exposure to fine particles in area that were in attainment of the PM₁₀ standard. Again, primary and secondary
standards were set at identical levels and rules were enacted for spatial averaging. The PM$_{2.5}$ standards were set at 65 µg/m$^3$ and 15 µg/m$^3$ for 24-hour and annual averages, respectively. The PM$_{10}$ standards were left unchanged.

The 2006 revisions (71 FR 61144 (2006)) reduced the 24-hour PM$_{2.5}$ standard by about 46% to a level of 35 µg/m$^3$. The annual averaged PM$_{2.5}$ and 24-hour averaged PM$_{10}$ standards remained unchanged while the annual averaged PM$_{10}$ standard was revoked because no evidence was available to support a link between health effects and long-term exposure to PM$_{10}$.

Although data supports the hypothesis that chemical composition is an important factor determining the health impact of atmospheric particles, no provision has been promulgated regulating the specific chemical composition of PM with the NAAQS.

2.1.5 State Implementation Plans

The current NAAQS determines the acceptable ambient PM concentrations but the responsibility for obtaining the necessary emission reductions to comply with the standards lies with individual states. The Clean Air Act (40 CFR 110.51) requires that states submit a State Implementation Plan (SIP) which must include details regarding a monitoring program, and if the area is in non-attainment for a specific NAAQS, it must also include information on the reductions required to reach compliance, modeling results predicting future air quality trends and the effects of emissions reduction strategies, emissions inventories for sources, control strategy studies, measures adopted to ensure reductions will be achieved, and a plan to periodically review the reductions.
Adequate development of the SIP relative to the PM NAAQS involves knowledge about the mass concentration of particles in the area as well as particle sources and the impact of control strategies for particles from those sources.

2.1.6 Sources

PM is generally described as either being, primary or secondary. Primary particles are emitted directly from sources whereas secondary particles are formed in the atmosphere by gas-to-particle conversion processes (Seinfeld and Pandis 1997).

There are numerous sources of ambient PM which are commonly characterized as either natural or anthropogenic. Natural sources may include atmospheric entrainment of soil and dust, primary emissions from trees and plants (including pollen, spores, etc.), sea spray, naturally occurring forest fires, or volcanic eruptions. Natural secondary particles can be formed through reaction of gas phase emissions from trees and plants and forest fires into condensable products. Anthropogenic sources may include primary and secondary emissions from combustion (motor vehicles, biomass burning, etc.), industrial processes (power generation, material handling, etc.), cooking, or anthropogenic activities leading to fugitive dust emissions. Figure 5 shows the emission source categories for Pinal County and the estimated relative strength of each in 2005. In both graphs, the miscellaneous category dominates emissions within the county. Identification of sources grouped within the miscellaneous category motivates additional investigation for adequate planning and regulation.
2.2 Source Apportionment

2.2.1 Modeling Approaches

Source apportionment techniques elucidate source categories, like those listed in Figure 5, based on analysis of ambient air quality and can quantitatively determine the relative contribution of each to ambient concentrations. In this work, the goal of source apportionment is to identify and resolve source categories currently aggregated as miscellaneous emissions.

Two types of receptor-based models were used in this work. Positive matrix factorization (PMF) 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 (Paatero 1997). 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 prior knowledge regarding the sources is needed which makes the technique very useful where source profiles are not readily available, not representative of the area or conditions, or contain significant uncertainty. Although source profiles are not needed, some knowledge regarding the appropriate chemical composition of source emissions is required to accurately identify each source.

The second approach used in this work is chemical mass balance (CMB) analysis (Chow and Watson 2002). This analysis uses known source profile information to determine the optimal contribution of different sources based on minimizing differences between predicted and measured ambient data for the sampling sites. A known number of sources and their chemical profiles, in addition to the ambient data, are needed in this analysis.

2.3.3 Model Robustness and Validation

The application of any source apportionment method results in a certain degree of uncertainty often related to co-linearity between emission sources, difficulty in determining the sources based on resolved profiles, difficulty in finding representative source profiles to use, and difficulty in determining the most appropriate marker species to use for each of the analysis. 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 uncertainties in the model results (Bullock, Duvall et al. 2008).
According to the work of Bullock et al., the selection of species is a key to producing comparable results within and between differing modeling approaches, particularly between a univariate chemical mass balance and a multivariate positive matrix factorization approach (Bullock, Duvall et al. 2008). For modeling purposes, only species with concentrations significantly above the method detection limit can be used. Additionally, model robustness has been evaluated using a subset of the species with significant concentrations (Bullock, Duvall et al. 2008), apportionment to a major variable other than particle mass (Bullock, Duvall et al. 2008), and by bootstrapping the input data set to test the stability of the output results (Dutton, Vedal et al.). Overall, when several of these alternative approaches produce similar source contribution results, the results can be accepted as a robust result.

2.3 Previous Study Results

2.3.1 Source Characterization

In 2003, the Pinal County Air Quality Control District (PCAQCD) and the Desert Research Institute (DRI) conducted sampling of several dust sources within the county and in the vicinity of the sampling sites used in this present work. In particular, samples were collected representing feedlot, agricultural, and road dust in both the PM$_{10}$ and PM$_{2.5}$ size range. Each sample was characterized in terms of three inorganic ions (sulfate, nitrate, and ammonium), select elements (including aluminum, silica, potassium, calcium, and iron), and bulk OC and EC concentrations (Pinal County Air Quality Staff 2005). Results obtained from this field study will be compared with, and augmented by, the results of the current study.
2.3.2 Source Apportionment

In 2003, PCAQCD and DRI conducted CMB source apportionment analysis of a series of samples collected during the winter. Because only a small number of sample days were collected (10 sample days), CMB analysis was used, and seven sources were considered including, soil, feedlot, mobile emissions, vegetative burning, coal-fired power plant emissions, ammonium nitrate, and ammonium sulfate. Modeling results show that at Casa Grande (CG), soil accounts for 62% of the measured PM$_{10}$ concentration, emissions from the feedlot accounts for 20%, and vegetative burning and coal-fired power plants account for 5% of the measured PM$_{10}$ concentrations. Emissions from feedlot operations and atmospheric entrainment of soil accounted for 59% and 32%, respectively at the Cowtown (COW) site while 19% and 67% of measured PM$_{10}$ were attributed to those sources at Pinal County Housing (PCH). The breakdown of source contributions to ambient PM looks a little different in regard to PM$_{2.5}$ concentrations with approximately 40% attributed to soil, 17% to power plants, and 10% to mobile sources and vegetative burning at both the CG and PCH sites. At COW, 50% was attributed to the feedlot, 24% to soil, and 8% to both mobile sources and vegetative burning (Pinal County Air Quality Staff 2005). The current work will allow for corroboration and investigation of differences by using PMF analysis to test the hypothesis if these seven sources, and only these sources, dominate the ambient PM concentrations within the region.
Chapter 3: Measurements – Importance and Context

3.1 Gravimetric Mass

The NAAQS for PM sets permissible ambient mass concentration limits specific to the PM$_{10}$ and PM$_{2.5}$ size ranges. To monitor compliance with these standards, ambient mass measurements are routinely made across sampling networks in local jurisdictions.

Analysis of ambient particle mass is an important part of this study for a number of reasons. First, PM$_{10}$ mass concentrations are being collected at each site studied as part of the current research while PM$_{2.5}$ concentrations are measured at COW and CG. This study will supplement the regulatory-driven data with mass information specifically in the coarse size range (PMc) at all three sites and PM$_{2.5}$ at the PCH site. Second, collection of mass concentration data, when compared to the compliance monitor, serves as an external check on the proper operation of the sampling and analysis techniques used in this study. Third, ambient mass measurements made on the sample of ambient PM to be analyzed for composition aids in the interpretation of data in a timely manner, rather than the delayed release of the compliance monitor data on a quarterly basis. Finally, collection of samples of ambient PM on filters are inherently different from the continuous mass measurement being made for regulatory monitoring at each of the sites using the R&P 1400a TEOM (tapered element oscillating microbalance) monitors. Collection of mass from the filter samples allows for the quantification and investigation of those differences.
3.2 Chemical Composition

As previously mentioned, the complicated 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 routine analytical techniques. Others are present at trace concentrations and require detailed compositional analysis. 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.

3.2.1 Ions

3.2.1.1 Importance

The concentrations of ions present in PM samples are often quantified as they compose a significant fraction of ambient PM mass, some ions govern the formation of acid-rain, 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 typical ambient aerosol ion concentrations are sufficiently above instrument detection limits and a wide range of ions can be determined simultaneously by this method (Derrick and Moyers 1981). A suite of cation and anion species are often quantified, including cations ammonium (NH$_4^+$), potassium (K$^+$), and sodium (Na$^+$) and anions sulfate (SO$_4^{2-}$), nitrate (NO$_3^-$), and chloride (Cl$^-$).
3.2.1.2 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 ammonium (NH₄⁺) or 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 might not 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 improving extraction efficiency.

3.2.1.3 Sources

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⁻ (Lin 2002). The gas-to-particle conversion of gas phase NH₃ can result in particle-bound NH₄⁺ (Glavas and Moschonas 2002). Na⁺ and Cl⁻ commonly arise from atmospheric entrainment of sea salt (Al-Momani, Ya'qoub et al. 2002), while mineral forms of CaCO₃ results in high Ca²⁺ concentrations in airborne particles (Al-Momani, Ataman et al. 1995). Other common constituents of soils include Mg²⁺, Na⁺, and K⁺ (Anatolaki and Tsitouridou 2009). NH₄⁺, SO₄²⁻, NO₃⁻, Cl⁻, and Na⁺ have all been associated with entrainment of agricultural soils (Cao, Chow et al. 2008).
K\textsuperscript+ has been shown to be a good tracer for biomass burning (Andreae, Browell et al. 1988).

### 3.2.2 Elements

#### 3.2.2.1 Importance

The concentrations of trace 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 their presence in the atmosphere can arise from a range of potential sources rather than one individual process.

#### 3.2.2.2 Artifact and Concerns

The method used to quantify elemental composition in this work involves the acid-digestion of Teflon filter samples followed by quantification of soluble 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 corrected for 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. All measurements of metals by ICPMS reported in this thesis were performed by collaborators in the research group of Prof. Herckes in the Chemistry and Biochemistry Department at Arizona State University.

### 3.2.2.3 Sources

Aluminum (Al), calcium (Ca), iron (Fe), potassium (K), magnesium (Mg), silicon (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 (Lough, Schauer et al. 2005). Vanadium (V) has been used as a tracer species for emissions from the shipping industry due to the heavy crude burned for fuel (Martens, Wesolows et al. 1973) while rare earth elements have been shown to result from petroleum refining operations (Kulkarni, Chellam et al. 2007). Based on understanding local emission sources in Pinal County, neither shipping or refining 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 (Pope, Rodermund et al. 2007). At present, Pinal County has one working copper smelter; however, this smelter is in a different air basin. While emissions from this source are not expected impact concentrations observed during this study, measurements are important to monitor for the impact of this potential source.
3.2.3 Bulk OC/EC

3.2.3.1 Importance

Carbon makes up a significant fraction of atmospheric PM and is comprised of many thousands of individual species with variable chemical and physical properties (Seinfeld and Pandis 1997). Elemental carbon is representative of the graphitic form of carbon, while organic carbon constitutes the contribution of many distinct compounds present at ng/m$^3$ concentrations or less. 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, are commonly used in aerosol characterization and source apportionment studies.

3.2.3.2 Artifact and Concerns

OC and EC concentrations vary based on the analytical method used. 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 (Turpin, Cary et al. 1990; Birch and Cary 1996). Analyzers that use a similar, but not equivalent, approach for quantification are available from other vendors. More importantly, the temperature profiles used by various investigators and across
different monitoring networks vary. These complications make data comparison across studies difficult (Birch and Cary 1996; Chow, Watson et al. 2001).

Sample artifacts are of concern with the quantification of organic and elemental carbon because gas phase organic compounds readily absorb to the quartz fiber filter substrate causing positive artifacts and sampling conditions or handling procedures can cause volatile loss of some compounds (Subramanian, Khlystov et al. 2004). 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 oxygen, nitrogen, sulfur or hydrogen associated with the organic compounds 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 (Turpin and Lim 2001) based on measured organic carbon (OC) leading to uncertainty in determining the OM concentration.

**3.2.3.3 Sources**

Characterization of the bulk carbonaceous material provides no information about unique tracers. 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. These OC fractions have been used in source apportionment analysis studies. OC/EC ratios can give some information about the age of an aerosol as secondary organic carbon can be formed through atmospheric reactions over time leading
to larger ratios. Elemental carbon, however, is often associated with combustion processes and has been used as a non-specific tracer for various combustion processes.

### 3.2.4 Organic Speciation

#### 3.2.4.1 Importance

The goal of organic speciation is to identify some of the thousands of individual species that make up the organic carbon portion of ambient PM. These individual compounds are present at trace concentrations making sensitivity of the analytical method of upmost importance. Still, many compounds will never be measured either because concentrations are too low, separation between similar organic isomers is too difficult, or standards are not available for accurate identification and quantification. Currently, available methods routinely identify only 10-20% of the organic mass of the sample (Schauer and Cass 2000). However, the information gathered is often important because it allows for the quantification of compounds that are marker species useful in source apportionment work (Schauer, Rogge et al. 1996; Watson, Chen et al. 2008) and can help elucidate both primary (Simoneit 1999; Hays, Fine et al. 2005) and secondary sources (Hoffmann, Bandur et al. 1998; Kroll and Seinfeld 2008). Knowledge about individual species can also help advance the understanding of the potential toxicity of PM as many organic molecules have been identified as mutagens or potential carcinogens (Zielinska and Samy 2006).

#### 3.2.4.2 Artifact and Concerns

As with bulk OC quantification, sample artifacts are of concern because handling and storage of filter media can cause positive artifacts due to sorption of organic compounds.
(Turpin, Huntzicker et al. 1994; Simoneit 2002). Because the concentration of individual compounds is low, contamination from lab equipment, filter handling, and impure solvents is of concern. Of particular interest in speciation work is contamination from the sorption of organic compounds to the sampling media including impactor greases (Mazurek, Cass et al. 1991) and oils from within the samplers (McDow, Mazurek et al. 2008).

3.2.4.3 Sources

Several organic species have been isolated as potential tracers for sources of ambient PM. Levoglucosan has been isolated as a tracer unique to the thermal breakdown of cellulose in biomass burning (Simoneit 1999; Fraser and Lakshmanan 2000). Cholesterol and oleic acid have been associated with meat cooking (Rogge, Hildemann et al. 1991; Robinson, Subramanian et al. 2006). Hopanes are tracers that are unique to internal combustion emissions and motor vehicle exhaust (Rogge, Hildemann et al. 1993). High molecular weight PAHs may be able to separate the influence of gasoline and diesel engines (Lough, Christensen et al. 2007). Odd numbered n-alkanes in the size range C27-C33 have been associated with plant wax (Simoneit and Mazurek 1982). Several sugars and their derivatives are associated with resuspended soil material (Rogge, Medeiros et al. 2007) and work is ongoing to elucidate species that differentiate between various crustal sources (Jia, Clements et al. 2010).
Chapter 4: Analytical Methods

4.1 Field Sampling Collection Program

4.1.1 Ambient Sampling

Between February 2009 and February 2010, ambient PM samples were collected at three monitoring locations in Pinal County, AZ in and around of the town of Casa Grande, which is located south of Phoenix, AZ and approximately half way between the major metropolitan areas of Phoenix and Tucson. The three sites are within the Pinal County Air Quality District’s (PCAQD) existing network and are shown in Figure 6.

![Sampling Site Locations Within Pinal County, AZ](image)

The Casa Grande (CG) site (401 Marshall St.), denoted by A in Figure 6, 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 potentially impact air quality at this site.

The Cowtown (COW) site (37580 W. Maricopa-Casa Grande Hwy.), denoted by B in Figure 6, 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; the COW 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 COW 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. These localized sources in the immediate vicinity of this sampling site likely contribute to the poor air quality that regularly registers 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 6, 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 storm runoff 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 air quality 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 samples were run concurrently with two collecting particulate samples on Teflon substrates which were used for mass, ion, and elemental composition analysis. The third sampler collected aerosols on quartz fiber substrates which were used for bulk OC and EC concentrations. The quartz filter samples were subsequently composited for organic speciation analysis. The fourth sampler deployed at each site was used periodically for a variety of quality assurance 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 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.

Field sampler operation and filter exchanges were conducted by PCAQD personnel. Samples were stored by PCAQD under freezing conditions until transport to ASU for analysis.

4.1.2 Source Sampling

A number of crustal sources within the region potentially contribute to ambient PM concentrations. 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 feedlot material were 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 additional samples were collected from a cotton field were collected 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.

4.2 Sample Analysis

4.2.1 Crustal Sample Resuspension

4.2.1.1 Analysis

Bulk crustal samples collected during the source characterization program were resuspended to collect size-separated source material using an apparatus assembled in our laboratory. 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 -4°C. 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. This disaggregation was conducted to represent the mechanical forces that lead to dust resuspension through disturbances to the soil surface (i.e. vehicle traffic, agricultural harvesting, etc.)

The loose material was then placed into the resuspension chamber consisting of a 1 L 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 remove particles larger than PM$_{10}$ (URG-2000-30EA operating at a flow rate of 28 lpm) and another used for collection of PM$_{2.5}$ (URG-2000-30EC operating at a flow rate of 42 lpm). Following the cyclone separator, flow was divided into three separate channels, one loaded with a 47 mm 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\textsubscript{10} and PM\textsubscript{2.5} sampling require different flow rates, the flow through the third filter holder will vary from 6.55 lpm for PM\textsubscript{10} sampling to 24.82 lpm for PM\textsubscript{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 10 mg 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.

**4.2.1.2 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 replicate 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.
4.2.2 Mass

4.2.2.1 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 condition 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 quality assurance measurement using a small calibration weight. 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 1 ug level for at least 20 seconds.

4.2.2.2 Sample Validation

The stability of the microbalance between and during filter weighing sessions was verified my repeatedly measuring the zero and a small calibration weight (100 mg) throughout the weighing of filters for quality assurance. Each time a quality assurance weight measurement was taken, the reading was required to be stable and within 0.005 mg of the prescribed weight. If the measured weight fluctuated or was not in the prescribed range, filters containing ambient samples were not weighed until these quality assurance goals were met.
Additionally, 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 previous weighing sessions and differences greater than 0.015 mg were flagged for quality assurance purposes and investigated.

4.2.3 Ions

4.2.3.1 Extraction

For ambient samples, one set of Teflon filters was used for quantification of ionic species. Sampled filters were removed from storage in freezers and defrosted 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. Several blank filters were similarly analyzed.

4.2.3.2 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 (ClO₂⁻), 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 (NH$_4^+$), potassium (K$^+$), magnesium (Mg$^{2+}$), and calcium (Ca$^{2+}$). 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.

4.2.3.3 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 when not being used and were discarded after the expiration date prescribed by the manufacturer. 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 added to 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.

4.2.4 Elements

4.2.4.1 Digestion

For ambient samples and resuspended crustal material samples, elemental analysis was conducted by collaborators working in the research group of Professor Herckes at ASU.
Using off-weighted Teflon filter samples, 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, was 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 were 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.

4.2.4.2 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). ICPMS analysis was conducted by Nabin Upadhyay in Professor Herckes’ research group.
4.2.4.3 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 using 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 digested material from San Joaquin Soil (#2709) and two vials containing digested material from Urban Dust (#1649a). The SRM samples are digested and analyzed in using the same procedures outlines for ambient samples.

4.2.5 Bulk OC/EC

4.2.5.1 Analysis

Bulk elemental and organic carbon concentrations were determined for ambient samples and resuspended source 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 operationally defined as volatilizing in an inert oven. As the evolved carbon flowed through the manganese dioxide oxidizing oven, it was quantitatively converted to CO$_2$ gas. The CO$_2$ gas was swept out of the oxidizing
oven by the helium steam, 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. 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 underwent pyrolysis during the initial inert heating of the sample and was converted during analysis 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 reclassified 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 and continue to rise as native elemental material is oxidized. 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.

4.2.5.2 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), trip 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 briefing 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 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.

4.2.5.3 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 to volatilize the carbonate in the sample, 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 not directly 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 (Chow and Watson 2002), 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 potentially more significant in coarse particles than in fine particles.

4.2.6 OC Speciation

4.2.6.1 Extraction

For ambient samples, a 1.5 cm$^2$ filter punch was first removed for OC/EC analysis and the remaining portion of quartz fiber filter was reserved for analysis by organic extraction and speciation for individual organic compounds. To provide enough organic material for this analysis, a series of 8 filters, representing approximately 1.5 months of ambient sampling, were composited into a single pre-cleaned glass jar. Filters were removed from the freezer and allowed to equilibrate to room temperatures for approximately 30 minutes.

For resuspended soil samples, a single and entire 47 mm quartz fiber filter was extracted and analyzed for individual organic compounds. Filters were removed from the freezer and allowed to equilibrate to room temperature in a manner equivalent to that for ambient samples. Subsequently, each filter was added to its own pre-cleaned glass extraction jar.
Each sample (representing either a composited ambient sample or a single filter resuspended soil sample) was spiked with two recovery standards containing isotopically labeled compounds to monitor extraction efficiencies. An aliquot of 40 µl of the non-polar recovery standard was spiked into each sample. This standard included n-tetracosane-d50, n-triacontane-d62, n-hexatriacontane-d74, chrysene-d12, dibenz[a,h]anthracene-d14, decanoic acid-d19, and tetradecanoic acid-d27 all with a concentration of about 200 µg/L. An aliquot of 40 µl of the polar recovery standard containing 150 µg/L of Beta-d-glucose-1,2,3,4,5,6,6-d7 was also spiked into each sample.

Once dry, 10 ml of methanol (Fisher-Optima) and 20 ml of dichloromethane (Fisher – Optima) were added to each sample and then extracted for 10 min under mild ultrasonic agitation. The solvent was transferred to a 250 ml round bottom flask. The filters were then extracted two additional times using the same suites of solvents and sonication procedure and transferred to the corresponding round bottom flask.

After extraction, samples were concentrated to approximately 8 mL using a rotary evaporator then filtered through a pre-cleaned glass fiber filter and into a 10 mL round bottom flasks. Samples were further concentrated to approximately 2 mL by evaporating the solvent under a gentle steam of ultra-pure nitrogen gas. Samples were then transferred into benzene, a more stable solvent for storage, by adding 2 mL of benzene and further evaporating the solvent until the total volume was approximately 200 µl. The exact volume was determined using a pre-cleaned gas-tight syringe. The sample was measured, transferred into a GC vial with a glass insert, and then stored under freezing conditions until analysis.
4.2.6.2 Derivatization

A portion of each extract was removed and derivatized allowing for the determination of polar compounds within the extract. An aliquot of 50 µL was removed from the underivatized extract vial and transferred to a new GC vial with a glass insert. The sample was then completely dried under a gentle stream of nitrogen. As the targeted compounds for analysis were simple and complex sugars, blowing to dryness was not expected to impact recovery of this class of compounds with glucose used to quantify extraction efficiency and loss during blow-down. Once dry, 150 µL of N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane (TMCS) (Sigma-Aldrich) and 50 µL of pyridine (Pierce) was added to each vial which was then capped and heated to 70°C for 3 hours. The samples were then returned to room temperature and run on the GCMS within 24 hours to minimize hydrolysis of the derivatized sugars.

4.2.6.3 Analysis

Both the original and derivatized samples were analyzed by a Agilent model 6890 gas chromatograph (GC) using a 30 m HP-5MS capillary column coupled to a Agilent model 5973 inert mass selective detector (MSD). Injections were made in splitless mode at 250°C. The GC separation was facilitated using a temperature program consisting of an initial hold at 65°C for 10 minutes followed by a temperature ramp of 10°C per minute to 285°C which was held for 10 minutes. The temperature was ramped at 40°C per minute to a final temperature of 310°C which was held for 5 minutes. The MSD was operated in
electron impact mode at 70 eV and a temperature of 285°C. Mass to charge ratios of 50 to 500 were scanned at 2.94 scans/second.

Each injection used a 2 µl aliquot of sample and 1 µl aliquot of a co-injection standard consisting of 1-phenyldodecane (1-PD) to ensure proper injection. Individual compounds were identified by retention time and comparison of mass spectra with authentic standards, literature and library data, and the interpretation of mass fragmentation patterns. Concentrations were quantified using selected ion peak areas and converted to compound mass using relative response factors from a series of dilutions of authentic standards.

4.2.6.4 Sample Validation

Three different blanks were analyzed along-side ambient and resuspended soil samples. They included solvent blanks (following the entire extraction and analysis procedure without including a filter), laboratory blanks (extraction and analysis of blank filters which never left the lab), and transport blanks (extraction and analysis of blank filters which were transported to and from the field sampling sites). As blanks measured did not contain a measureable amount of the targeted analytes, no blank correction has been made to the data presented.
Chapter 5: Chemical Characterization of Coarse Particulate Matter in the Desert Southwest – Pinal County Arizona, USA

5.1 Abstract

The Desert Southwest Coarse Particulate Matter Study was undertaken as a means of furthering our understanding of ambient concentrations and the composition of fine and coarse particles in rural, arid environments. Sampling was conducted in Pinal County, AZ near the town of Casa Grande between February 2009 and February 2010. The goals of this study were to: 1) chemically characterize the coarse and fine fraction of the ambient particulate matter (PM) in Pinal County in terms of mass, ions, elements, bulk organic and elemental carbon; 2) examine the temporal and spatial variability of particles within the area using a series of three sampling locations and use this information to determine the contribution of local vs. regional sources; 3) collect, re-suspend, and chemically characterize various crustal sources within the area to identify differences which may isolate them (crustal sources) as independent sources, and; 4) use a receptor based modeling approach to identify particle sources and the relative impact of each on ambient PM concentrations in Pinal County. This work reviews the study objectives, design, site descriptions, and measurement techniques relevant to this research effort and presents the general characteristics of PM during the study period. This unique dataset will support efforts to reduce PM$_{10}$ and PM$_{2.5}$ concentrations in the area to below the National Ambient Air Quality Standards (NAAQS) for these pollutants.

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1 This chapter is based on a journal manuscript, lead author Andrea L. Clements, which has been prepared and submitted to US EPA Office of Research and Development for clearance. We intend to submit this manuscript to Atmospheric Environment.
Coarse particle concentrations are, on average, approximately 4-5 times fine particle mass concentrations within the region. Coarse particle concentrations in Pinal County are highest during spring and fall seasons, consistent with the tilling and harvesting seasons while fine particles concentrations are highest during fall. Crustal material is the dominant component of coarse particle composition, representing 50% of the mass on average followed closely by organic material representing 15%. As seen in other studies, a large undefined fraction remains (Cheung, Daher et al. 2011). Fine particles still contain a significant crustal fraction (30%) but organic material dominates at 37% of the particle mass.

5.2 Introduction

In the United States, the National Ambient Air Quality Standards (NAAQS) were promulgated to protect human health, including the health and well-being of susceptible populations (42 U.S.C. 7409). In terms of ambient particles, two standards exist – one for PM$_{10}$ (particles with an aerodynamic diameter [AD] less than or equal to a nominal 10µm) and another for PM$_{2.5}$ (particles with an AD less than or equal to a nominal 2.5µm). The PM$_{10}$ size fraction can be considered to be the sum of fine particulate matter (designated as PM$_{f}$, or PM$_{2.5}$) and coarse particulate matter (PM$_c$, particles in the size range between 2.5 and 10 µm AD).

Rural areas of the desert Southwestern United States experience high concentrations of PM$_c$, and it is often spikes in the PM$_c$ concentrations that drive exceedances of the PM$_{10}$ NAAQS within the region (U.S. EPA AirData 2012). Exceedance of the NAAQS
requires that states formulate plans (State Implementation Plans – SIPs) to reduce the ambient PM concentrations to within acceptable limits. The creation of effective SIPs for achieving this goal relies on knowledge of the current emission sources, the relative impact of each source, and control strategies that might be employed to enact changes in source emissions and ambient concentrations.

Previous research has shown correlations between particular chemical components of ambient PM$_f$ and adverse human health effects (Dockery, Pope et al. 1993; Dockery and Pope 1994; Prahalad, Soukop et al. 1999; Mar, Norris et al. 2000; Pope, Rodermund et al. 2007; Duvall, Norris et al. 2008; Hoppo, Hirvonen et al. 2008; Gerlofs-Nijland, Rummelhard et al. 2009) calling into question whether the NAAQS based on mass concentrations is sufficiently protective of human health. Consequently, extensive measurements of PM$_f$ mass concentrations and chemical composition have been undertaken worldwide with significant effort given to correlating these measurements with human health outcomes (Dockery, Pope et al. 1993; Samet, Dominici et al. 2000; Belleudi, Faustini et al. 2010). However, while recent studies revealed that adverse health effects (e.g., asthma, reduced cardiac variability, etc.) are also associated with coarse particulate matter (PM$_c$) in ambient air (Mar, Norris et al. 2000; Lipsett, Tsai et al. 2006; Hoppo, Hirvonen et al. 2008), the chemical composition of PM$_c$ remains poorly characterized. Although significant PM$_c$ concentrations are generally only found in rural areas, population and urban sprawl has increased public exposure to these high PM$_c$ concentrations, increasing the importance of understanding the resultant health effects. Improved characterization of coarse particles is the critical first step to understanding the health risk they may pose.
The Desert Southwest Coarse Particulate Matter Study was conducted in and around the town of Casa Grande in Pinal County, Arizona. This region has experienced numerous exceedances of the PM$_{10}$ NAAQS and registered the highest PM$_c$ concentrations in the region (U.S. EPA AirData 2012). Previous studies in this region have examined ambient mass concentrations in the PM$_{2.5}$ and PM$_{10}$ size range, characterized some bulk chemical characteristics, and implemented Chemical Mass Balance (CMB) modeling on a limited number of samples (Pinal County Air Quality Staff 2005). This study expands on the previous work by isolating the PM$_c$ and PM$_f$ size fractions, expanding the chemical characterization of the aerosol, creating detailed source profiles for crustal materials within the region, and applying multiple modeling approaches to characterize particle sources and their relative contributions. This paper presents the study objectives, design, measurement locations, analysis methods, and general characteristics of PM during the study period.

5.3 Study Objectives

The Desert Southwest Coarse Particulate Matter Study was designed to achieve several objectives: a) to measure the physical and chemical characteristics of PM$_c$ and PM$_f$ in the desert southwestern United States; b) to determine how the physical and chemical characteristics of PM vary spatially and temporarily; c) to identify chemical species that are uniquely associated with PM$_c$ and PM$_f$; d) to estimate the relative influence of local vs regionally transported PM; e) to measure the chemical characteristics of local sources of crustal PM; f) to determine the sources of ambient PM and the relative contributions of each; g) to determine how source characterization and contribution varies depending on particle size fraction, the modeling approach used, and the chemical constituents used.
5.4 Ambient Sample Collection

Between February 2009 and February 2010, ambient aerosol sampling was conducted at three monitoring locations in Pinal County, AZ in and around the vicinity of the town of Casa Grande. Casa Grande is located to the south of Phoenix, AZ and is approximately half way between the major metropolitan areas of Phoenix and Tucson. Figure 7 shows the geographic location of the monitoring sites within Pinal County and the proximity to the town of Casa Grande, AZ. Also shown in the figure is the general land use in the area including undeveloped native desert, agricultural use, and urban areas.

![Figure 7: Study Region and Ambient Sampling Locations in Pinal County, AZ](image)

The Casa Grande (CG) site (401 Marshall St.), denoted by A in Figure 7, is on the roof of a one-story building located within the town of Casa Grande, AZ, a small city with a population of approximately 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 on which the samplers are situated. Local emissions from railroad traffic, paved roadway traffic, and a few industrial locations likely impact air quality at this site.

The Cowtown (COW) site (37580 W. Maricopa-Casa Grande Hwy.), denoted by B in Figure 7, is located approximately 27 km to the northwest of the city of Casa Grande. It is a rural location, located on a 0.1 km by 0.1 km section of native (unaltered with original vegetation) desert adjacent to a two lane highway connecting Casa Grande with the city of Maricopa. Maricopa is 35 km northwest of Casa Grande. The COW 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 COW site. In the immediate vicinity of the sampling site there are a number of potential sources including fallow cropping fields (within 0.25 km to the west, north, and east), several cattle feedlots (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 at various distances) and paved (adjacent) roads. The regulatory air quality equipment at this site registers numerous 24-hour exceedances of the PM$_{10}$ standard each year (U.S. EPA AirData 2012).

The Pinal County Housing (PCH) site (970 N. Eleven Mile Corner Rd), denoted by C in Figure 7, is located approximately 17 km to the east of the city of Casa Grande. The site is within and immediately surrounded by native desert, is approximately 0.2 km west of the Pinal County Housing Projects and is nearly 0.2 km east-southeast of the wastewater treatment ponds for the complex. Air quality at this site is likely influenced by
agricultural fields, which are located about one km from the site 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 of the site.

At each sampling site, four Sierra-Anderson Model 241 dichotomous samplers were deployed to collect equivalent 24-hr samples on a one-in-six day schedule. These samplers collected PM\textsubscript{f} and PM\textsubscript{c} size fractions simultaneously at a total flow rate of 16.7 Liters per minute (lpm) (approximately 15 lpm and 1.7 lpm to the fine and coarse channels, respectively). Two of the four samplers at each site used Teflon filter media in both channels for analysis of fine and coarse PM mass, ions, and elements. One of the four samplers was equipped with quartz-fiber filters in both channels, which were used for determination of bulk elemental carbon (EC) and organic carbon (OC) content as well as selected organic species using a composite of 6 weeks worth of samples. The remaining sampler was used to collect blanks and other co-located samples for quality assurance/quality control and instrument precision determination.

Filter media was transported between the laboratory and the field seated within the plastic instrument filter holders and sealed inside sterile and cataloged polystyrene Petri dishes (Pall Corporation). Following collection, samples were placed back into their original containers and kept at reduced temperatures (‘blue ice’ during transport and at freezing condition colder than -4°C during storage) until laboratory analysis.

Although not part of the sampling campaign, each sampling site also measured semi-continuous PM\textsubscript{10} mass concentration using a Thermo Scientific Tapered Element
Oscillating Microbalance (TEOM) monitor (Series 1400ab) for compliance monitoring. The unit was operated without a dryer at 50°C. Data was recorded at 5 minute increments and averaged into 24-hour daily concentrations. Meteorological data presented here was measured by independent monitors in Maricopa, AZ (8 km northwest of the COW monitoring site).

5.5 Source Sample Collection

Soil samples were collected from 15 different sites within the sampling region representing a variety of different soil types including agricultural fields, native desert (unaltered desert in close proximity to the site), paved and unpaved road dust, and material representative of a local cattle feedlot. Table 1 details the sampling location, soil types, soil and source category determinations along with information about the nearest ambient monitoring location.

Table 1: Soil Source Sampling Details

<table>
<thead>
<tr>
<th>Site Number</th>
<th>Closest Monitor</th>
<th>Sampling Location</th>
<th>Soil Type</th>
<th>Sample Category</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PCH</td>
<td>20 Meters SW of Monitoring Site</td>
<td>Fine Sandy Loam</td>
<td>Native</td>
<td>NAT</td>
</tr>
<tr>
<td>2</td>
<td>PCH</td>
<td>40 Meters SW of Monitoring Site</td>
<td>Fine Sandy Loam</td>
<td>Native</td>
<td>NAT</td>
</tr>
<tr>
<td>3</td>
<td>COW</td>
<td>20 Meters SW of Monitoring Site</td>
<td>Clay Loam</td>
<td>Native</td>
<td>NAT</td>
</tr>
<tr>
<td>4</td>
<td>COW</td>
<td>Median between Site and Highway</td>
<td>Clay Loam</td>
<td>Native</td>
<td>NAT</td>
</tr>
<tr>
<td>5</td>
<td>COW</td>
<td>East Alfalfa Field</td>
<td>Clay Loam</td>
<td>Agricultural</td>
<td>AGR</td>
</tr>
<tr>
<td>6</td>
<td>COW</td>
<td>West Alfalfa Field</td>
<td>Clay Loam</td>
<td>Agricultural</td>
<td>AGR</td>
</tr>
<tr>
<td>7</td>
<td>PCH</td>
<td>Winter Wheat Field - Edge</td>
<td>Fine Sandy Loam</td>
<td>Agricultural</td>
<td>AGR</td>
</tr>
<tr>
<td>8</td>
<td>PCH</td>
<td>Cotton Field</td>
<td>Fine Sandy Loam</td>
<td>Agricultural</td>
<td>AGR</td>
</tr>
<tr>
<td>9</td>
<td>PCH</td>
<td>Dirt Road Dust - South Edge</td>
<td>Fine Sandy Loam</td>
<td>Dirt Road-Ag</td>
<td>DRA</td>
</tr>
<tr>
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<td>Dirt Road Dust - North Edge</td>
<td>Fine Sandy Loam</td>
<td>Dirt Road-Ag</td>
<td>DRA</td>
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<tr>
<td>11</td>
<td>CG</td>
<td>Paved Road - Edge Composite</td>
<td>Fine Sandy Loam</td>
<td>Paved Road</td>
<td>PRD</td>
</tr>
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<td>Dirt Road Dust - Near Feedlot</td>
<td>Clay Loam</td>
<td>Dirt Road-Feed</td>
<td>DRF</td>
</tr>
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<td>13</td>
<td>COW</td>
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<td>Clay Loam</td>
<td>Feed Lot</td>
<td>FDL</td>
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<td>14</td>
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<td>Empty Feedlot Material</td>
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<td>Empty Feed Lot</td>
<td>FDL</td>
</tr>
<tr>
<td>15</td>
<td>COW</td>
<td>Old Feedlot Surface Material</td>
<td>Clay Loam</td>
<td>Empty Feed Lot</td>
<td>FDL</td>
</tr>
</tbody>
</table>

PCH - Pinal County Housing, COW - Cowtown, CG - Casa Grande
NAT - native soil, AGR - agricultural soil, PRD - paved road dust, DRA - unpaved road dust from an agricultural area, DRF - unpaved road dust from a cattle feedlot area (UPF), and FDL - soil from a cattle feedlot
Most sites were sampled during three different seasons including spring, fall, and winter but a few (i.e. cotton field) were sampled during unique events (i.e., cotton defoliation). In total, 35 soil samples were collected. All samples were obtained from the top 15 mm of the surface using a trowel, or by broom on the paved surface, and placed into a pre-baked glass jar for storage and transport (Hagen 2004).

5.6 Sample Analysis

5.6.1 Mass

Mass was obtained gravimetrically on all Teflon filters by difference (post-collection weight minus pre-collection weight). Filters were removed from frozen storage and then equilibrated for 24 hours and weighed under controlled temperature (22°C < T < 24°C) and humidity conditions (45% < RH < 55%) to achieve reproducible and stable mass measurement readings. These conditions attempt to follow the filter mass analysis outlined in the NAAQS (U.S. EPA 2006) as closely as possible but were adjusted slightly upward to minimize the error on the microbalance measurement. Elevated relative humidity conditions can cause water retention by particles during equilibration causing mass measurements to be slightly biased high. Every 10th filter was reweighed and if weights were outside quality control limits of 5 µg, all 10 filters were re-weighed. A National Institute of Standards and Technology (NIST) traceable 100 mg metal weight standard was used for calibration of the microbalance. The average of the two co-located filter mass measurements is presented here unless one sample was invalidated due to user, instrument operation, or experimental error.
5.6.2 Ions

After gravimetric analysis, ions were determined on one set of the Teflon filters by ion chromatography (IC) with a Dionex IC20 system. Filters were wet with 200 µl of ethanol (Fisher HPLC Grade) (Derrick and Moyers 1981) and extracted by sonication in 7.5 ml ultrapure water for 15 minutes at room temperature (22°C < T < 24°C). Extracts were filtered using a syringe filter (Millex GP 0.22 µm pore size PES membrane filter) and then transferred to a 10 mL Dionex polyvial for analysis. Cations, including lithium, sodium, potassium, ammonium, calcium, and magnesium were quantified using a CG12A analytical column and 11 mM methylsulfonic acid eluent running at 1.00 mL/min.

Anions, including chloride, nitrite, nitrate, phosphate, and sulfate were quantified using an AS12A analytical column and 2.7 mM sodium carbonate/0.3 mM sodium bicarbonate eluent running at 1.5 mL/min. The instrument was calibrated using a series of standard dilutions from a certified calibration standard for each suite of compounds (Dionex P/N 056933 and 046070), laboratory and field blanks were periodically analyzed, and every 7th filter was reanalyzed for method precision determination.

5.6.3 Elements

Following gravimetric analysis, the second set of Teflon filters were analyzed for 63 trace elements (including, but not limited to, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, Sb, Se, Sn, Ti, U, V, Zn) using high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS, herein referred to as ICP-MS) by Nabin Upadhyay in Professor Herckes’ research group. Samples were microwave-digested in 30 mL Teflon vials using an acid mixture of 4 mL nitric acid, 0.9 mL hydrochloric acid,
and 0.1 mL hydrofluoric acid (Fisher) (Upadhyay, Majestic et al. 2009). The temperature profile included a 6 minute temperature ramp to 140°C, holding for 2 minutes, followed by a 5 minute temperature ramp to 165°C, holding for 6 minutes. The temperature was further increased to 180°C and held for 15 minutes. The digestion solution was diluted to 25 mL using ultrapure water, from which a 1.25 mL aliquot was transferred to a 15 mL centrifuge vial and diluted to 5 mL using ultrapure water. This final solution was analyzed for elements by ICP-MS (Thermo Finnigan ELEMENT 2) using an internal indium standard. The instrument was calibrated using a multi-element standard (SPEX Certiprep Inc., USA). Quality control included analysis of laboratory and field blanks, replicate analyses, and analysis of two NIST standard reference materials (San Joaquin Soil, SRM 2709 and Urban Dust, SRM 1649) using the same analytical procedure.

5.6.4 Bulk Carbon

A 1 cm x 1.5 cm punch was removed from each quartz-fiber filter and analyzed for bulk OC and EC using a thermal—optical EC/OC analyzer (Sunset Laboratory Inc., Tigard OG) (Birch and Cary 1996). The filters were analyzed according to a slightly modified Sunset Labs’ thermal-optical transmittance (TOT) method with variable time steps lasting between 60 and 200 seconds during OC evolution at temperature plateaus of 310, 475, 615, and 870°C. The temperature profile during EC evolution included 45 second holds at 550, 625, 700, 775, and 850°C with a final hold at 870°C for 120 seconds. Quality control included analysis of laboratory and field blanks, replicate analyses, and analysis of a sucrose standard prepared by Sunset Labs.
5.6.5 Soils

Prior to laboratory resuspension, soil samples were dried in an oven at 110°C for 24 hours. Samples were then lightly ground using a mortar and pestle to gently break up large aggregates within the sample using less physical force than what might be exerted by a simple foot step so as to minimally impact the size of particles in the desired size range. Soil samples were resuspended by passing HEPA-filtered air over the sample in a resuspension chamber and then through a size-selective cyclone (URG Corporation). The operating flow rates were determined based on the cyclone design – 28 Lpm for PM$_{10}$ sampling and 42 Lpm for PM$_{2.5}$ sampling. Size-selected particle samples were then collected at separate times onto three parallel Teflon and quartz-fiber filters. Filters were stored in the same manner as field samples until chemical analysis. Teflon filters were analyzed for mass and elements. Punches from the quartz-fiber filter were analyzed for water-soluble ions (3 cm$^2$) and for bulk OC and EC (1.5 cm$^2$) concentrations. All samples were analyzed for mass, bulk OC and EC, and elements in a manner analogous to the analysis of ambient filters collected from the field sampling campaign. Quartz-fiber filter punches for ion determination were not wetted with ethanol prior to extraction as was done with the Teflon filter samples. Extraction by sonication and subsequent sample preparation and analysis was performed in a manner similar to the field samples.

5.7 Results and Discussion

Prior to the start of the field sampling campaign, all twelve dichotomous samplers were set up in one location and a series of co-located samples were collected for the purposes of precision determination and quality assurance. A total of 13 samples from the 12 co-
Located samplers were collected for purposes of quality assurance prior to the field sampling campaign. The use of simultaneous determination of aerosol mass and composition allowed determination of not only the variability in measurements due to variability in sampling, but the variability arising from response of the analytical measurements.

A total of 10 sets of 12 co-located samples were collected on Teflon substrates and all filters were analyzed to determine ambient mass concentrations. The dynamic range of the coarse mass concentration was significantly smaller (20 µg/m³) than the mass concentration measured during the actual study period (180 µg/m³). All individual and independent mass measurements were well correlated (r² > 0.95) to the mean of the 12 samples deployed and no systematic bias was noted among any on the individual samplers. Using two times the standard deviation of the measurements, 95% certainty was achieved within approximately 15% of mean for PMc and within about 25% of the mean for PMf samples. Similar analysis was done on the chemical measurements made on this set of samples. The first 5 sets of co-located Teflon samples were analyzed for important water soluble ion species, including nitrate, sulfate, and ammonium. Again, using two standard deviations of the measurements, 95% certainty was achieved at approximately 25% for anion species and at approximately 15% for cation species, the difference can mainly be attributed to column sensitivity. Three sets of co-located quartz fiber samples were also collected and those samples were analyzed for bulk OC/EC concentrations. Significant outliers were observed for measurements made on one sampling date (12/29/08) but the root cause for this anomaly is uncertain. However, as other sampling on both quartz and Teflon filters do not show similar bias, the issue is
believed to be isolated and not endemic with the sampling or analytical equipment and thus, that sampling date was excluded. A certainty level of 95% was achieved at approximately 25% of the carbon concentration.

Throughout the field sampling campaign, two samplers at each site collected on Teflon substrates and samples from both of these instruments were used for duplicate mass concentration measurements and the results were continuously compared for quality assurance evaluation of the sampler operation. Samples were invalidated from the data set for a number of reasons including instrument error based on log sheet notations (loss of power, improperly set timer, failed equipment, etc.), handling error (filters that were accidentally mishandled during transportation or weighing), or measurement error (inconsistency in the determined mass measurement). The latter was the most difficult to justify but was evoked if: (a) the recorded pre-sampling weight of the filter was more than 10% different from the pre-sampling weight of other filters from the same batch, (b) if the resulting mass was more than 50% different from the mass measurement made on the co-located filter, or (c) if the resulting ambient concentration was more than 50% different from the ambient mass concentration measured by the co-located filter or TEOM measurement. Of the six samplers operated in the field that were used for Teflon filters to collect particle mass measurements, five samplers required invalidation of 5% or less of the collected filters. The remaining sampler required invalidation of 10% of the collected filters strictly due to instrument errors at the end of the sampling campaign.

Figure 8 shows the agreement in the mass measurements made at each site. Agreement is very good between coarse particle measurements made at each site and the universal trend line shown falls within the 95% confidence interval for each of the individual sites.
The agreement between each of these samples is within 3% for coarse particles. Measurement of fine particles mass shows greater deviation partly due to analytical uncertainty that arises in measuring smaller mass augmentations on Teflon filters originating from the lower ambient fine particle concentration. The agreement between fine particle mass measured on two separate samplers at CG, PCH, and COW is within 20%. Bias may also originate from the need to precisely balance flows to achieve size selective cut-points which are routinely adjusted pre-sampling, measured pre- and post-sampling, and change over the course of the sampling period due to filter loading. Regardless, data collected during the year-long study period displays tighter agreement within the mass measurement than pre-study samples do, indicating the confidence intervals illustrated in Figure 8 are conservative estimates.

![Figure 8: Comparison of Mass Concentration Measured by Co-Located Dichot Samplers](image)

Each of the ambient monitoring sites was equipped with an R&P 1400a Tapered Element Oscillating Microbalance (TEOM), operated by the Pinal County Air Quality Control
District, which is used for compliance monitoring or determining the ambient mass concentration of particles in the PM$_{10}$ size range. Although reported in 5-min intervals, this data was averaged into daily mass concentration values and compared to the reconstructed PM$_{10}$ daily mass concentration, measured as the sum of filter based PM$_{f}$ and PM$_{c}$ measurements. Figure 9 shows the agreement between the filter measurements at the Casa Grande site, made as part of this sampling campaign, and the co-located TEOM measurements at the site was well correlated (at 95% confidence, slope = 0.74 ± 0.07, intercept = 5±4, R$^2$=0.96). The 18% error estimate for the TEOM PM$_{10}$ mass measured was estimated based on the work of Wanjura (Wanjura, Shaw et al. 2008).

![Figure 9: PM$_{10}$ Mass Measurement Comparison](image)

Filter based measurements are approximately 25% lower than the TEOM-based measurements, which may be an artifact of variations in the sampler inlet design or
analytical differences. Additionally, filter based mass measurements were made in a controlled laboratory environment in which humidity conditions were closely monitored and controlled. During some seasons, this resulted in the removal of particle-bound water from the sample and in other seasons particles were humidified, causing both positive and negative artifacts. The extent to which particles lose or absorb water is dependent on particle composition and cannot be estimated based on the experimental setup deployed in this study.

Table 2 details the average, maximum, and minimum coarse and fine particle mass concentration and chemical composition at all three of the ambient monitoring sites. Negative values imply an over-characterization of aerosol mass. On average, the coarse particle mass concentration (47.6 µg/m³) is on the order of 5 times higher than the fine particle mass concentrations (9.4 µg/m³) within the region; the comparison was observed to be within the range of 2 to 9 times the fine particle concentration at times. Coarse particles have a much larger concentration range and more variability (5.55 - 177.60 µg/m³) than fine particle mass concentrations (2.50 - 20.35 µg/m³), suggesting an influence from one or more significant local sources of coarse particles.
Table 2: Average Chemical Composition of Ambient Particles

<table>
<thead>
<tr>
<th>Coarse Particle Fraction</th>
<th>Casa Grande</th>
<th>Cowtown</th>
<th>Pinal County Housing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
<td>Maximum</td>
<td>Minimum</td>
</tr>
<tr>
<td>Ambient Mass Concentration</td>
<td>30.60</td>
<td>78.00</td>
<td>5.75</td>
</tr>
<tr>
<td>Crustal</td>
<td>16.37</td>
<td>30.52</td>
<td>2.22</td>
</tr>
<tr>
<td>Organic Material</td>
<td>3.77</td>
<td>8.06</td>
<td>1.05</td>
</tr>
<tr>
<td>Nitrate</td>
<td>0.72</td>
<td>0.46</td>
<td>0.21</td>
</tr>
<tr>
<td>Sulfate</td>
<td>0.29</td>
<td>0.35</td>
<td>0.22</td>
</tr>
<tr>
<td>Ammonium</td>
<td>0.06</td>
<td>0.07</td>
<td>bdl</td>
</tr>
<tr>
<td>Other Measured Species</td>
<td>1.99</td>
<td>2.90</td>
<td>1.91</td>
</tr>
<tr>
<td>Unidentified</td>
<td>7.41</td>
<td>55.64</td>
<td>0.14</td>
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</table>

<table>
<thead>
<tr>
<th>Fine Particle Fraction</th>
<th>Casa Grande</th>
<th>Cowtown</th>
<th>Pinal County Housing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
<td>Maximum</td>
<td>Minimum</td>
</tr>
<tr>
<td>Ambient Mass Concentration</td>
<td>7.68</td>
<td>14.85</td>
<td>3.25</td>
</tr>
<tr>
<td>Crustal</td>
<td>1.86</td>
<td>3.44</td>
<td>0.44</td>
</tr>
<tr>
<td>Organic Material</td>
<td>3.83</td>
<td>6.91</td>
<td>1.61</td>
</tr>
<tr>
<td>Nitrate</td>
<td>0.68</td>
<td>2.21</td>
<td>0.00</td>
</tr>
<tr>
<td>Sulfate</td>
<td>1.00</td>
<td>1.69</td>
<td>0.16</td>
</tr>
<tr>
<td>Ammonium</td>
<td>0.37</td>
<td>0.62</td>
<td>0.07</td>
</tr>
<tr>
<td>Other Measured Species</td>
<td>0.57</td>
<td>0.74</td>
<td>0.11</td>
</tr>
<tr>
<td>Unidentified</td>
<td>-0.62</td>
<td>-0.76</td>
<td>0.85</td>
</tr>
</tbody>
</table>

*concentrations expressed in µg/m³

In general, particle concentrations were lowest at the CG monitoring location. This is consistent with the more urban nature of this site, having fewer large particle sources and more paved surfaces which limit the amount of particle resuspension. Particle concentrations were significantly higher at the PCH and COW sites, which are much more rural in nature and are in closer proximity to sources of large particles. Generally, the concentrations at the COW site were the highest mass concentrations measured. This is consistent with historical data which show numerous NAAQS exceedances at this monitoring location (U.S. EPA AirData). This observation suggests that the local cattle feedlot and/or grain processing plant may be significant particle sources impacting this monitoring site.

Figure 10 illustrates the chemical composition of coarse particles at each of the ambient monitoring locations. Organic matter was reconstructed by multiplying the bulk OC measurement by a factor of 2, a common assumption for organic PM found in rural
environment (Turpin and Lim 2001). The contribution of fugitive dust was estimated based on the common metal oxides present in crustal material based on the measured concentrations elements Al, Ca, Fe, and Ti. As Si was not measured by ICP-MS, the Si contribution was estimated as 3.5 x [Al] (Taylor and McLennan 1995; Watson and Chow 2001; Chow, Watson et al. 2004), and the total crustal component was calculated as 1.89[Al] + 1.4[Ca] + 1.87[Fe] + 1.67[Ti] + 2.14[Si] (Marcazzan, Vaccaro et al. 2001). All other ions and trace metal species are included in the form in which they were measured and no assumptions were made about the unmeasured ‘counter’ ions or oxide forms of these species. The unidentified fraction is calculated as the difference between the measured mass concentration and the mass associated with the components previously mentioned.

On average, crustal material is the largest chemical component of coarse particles within the region, representing close to 50% on the ambient particle mass at each of the sampling sites. This crustal fraction is very significant when compared to many urban areas, but when compared to other sites in the desert southwest, this fraction is comparable to the range (41-62%) measured at other locations (Cheung, Daher et al. 2011). Organic material makes up another significant fraction of the coarse particle mass. On average, organics make up approximately 15% of the particle mass but the fraction is the largest (26%) at the COW site. Organic matter in the feedlot material was thought to be a significant source for the organic fraction of the coarse particle mass and source soil samples confirmed the observation (see discussion below). A significant fraction (24%) of the coarse particle concentration remains uncharacterized and could include particle bound water which was not measured but is most likely a result of biases
caused by sample extraction, the choice of analytical techniques, and estimations that were made to account of species that could not be measured.

![Chemical Composition of Particles Collected at Each of the Ambient Sampling Sites](image)

**Figure 10: Chemical Composition of Particles Collected at Each of the Ambient Sampling Sites**

The chemical composition of fine particles is also illustrated in Figure 10. Fine particles within the region also contain a significant, although smaller, crustal component (30%). This fraction is much larger than that found in most urban areas (<10 percent) where combustion sources are more significant. The substantial influence of crustal material on fine particles suggests that reducing emissions from crustal sources may reduce both PM$_{10}$ and the upward trending PM$_{2.5}$ particle mass concentrations. Instead, organic material dominates fine particle mass at all sites representing 37% on average. The organic material fraction is highest in the CG area, where overall concentrations are
lowest but where vehicle traffic is highest. Water-soluble ion species (sulfate and nitrate especially) make up a large fraction of the fine particle mass concentration. Mass closure within the fine particle size fraction is significantly tighter (within 8%) than it was for coarse particles indicating that the measurements, assumptions about scaling, and crustal component reconstruction reflect an accurate characterization of ambient fine particles.

The seasonal differences in particle mass and chemical composition are shown in Figure 11. In terms of both coarse and fine particle mass concentrations, the highest concentrations are observed during the months of March and October/November and are driven by changes in the crustal component. This observation is most pronounced at the rural sites, especially in fine particles at the PCH site, and is consistent with the tilling, crop planting, and harvesting activities indicating that agricultural crustal material is a significant source of PM in the region. Another significant peak in mass concentration is noted in coarse particle concentrations in August at each of the two rural sites and the increase is again dominated by changes in the crustal component. This increase is consistent with the onset of the Arizona monsoon season, noted for increases in the number and intensity of dust storm events and the proximity of dust sources.
Surprisingly, total coarse particle concentrations are not elevated during September when wind gusts were highest, but the increased entrainment may have been tempered by precipitation that was also observed (Table 3). Precipitation also tempered coarse particle mass at the rural sites in July and the marked decrease in coarse particle
concentrations in winter months (December, January, and February) is facilitated by an
increased relative humidity.

Table 3: Summary of Monthly Averaged Meteorological Conditions

<table>
<thead>
<tr>
<th>Month</th>
<th>Average Temperature (°F)</th>
<th>Average Relative Humidity (%)</th>
<th>Average Wind Speed (mph)</th>
<th>Maximum Wind Speed (mph)</th>
<th>Total Precipitation (in)</th>
</tr>
</thead>
<tbody>
<tr>
<td>February</td>
<td>55.0</td>
<td>49.2</td>
<td>4.1</td>
<td>33.6</td>
<td>0.52</td>
</tr>
<tr>
<td>March</td>
<td>62.8</td>
<td>27.6</td>
<td>4.9</td>
<td>36.5</td>
<td>0.00</td>
</tr>
<tr>
<td>April</td>
<td>68.1</td>
<td>25.6</td>
<td>5.8</td>
<td>31.5</td>
<td>0.08</td>
</tr>
<tr>
<td>May</td>
<td>83.2</td>
<td>23.2</td>
<td>5.1</td>
<td>30.0</td>
<td>0.15</td>
</tr>
<tr>
<td>June</td>
<td>84.7</td>
<td>23.3</td>
<td>5.4</td>
<td>24.4</td>
<td>0.00</td>
</tr>
<tr>
<td>July</td>
<td>93.6</td>
<td>32.4</td>
<td>5.2</td>
<td>49.7</td>
<td>1.70</td>
</tr>
<tr>
<td>August</td>
<td>90.8</td>
<td>28.9</td>
<td>4.6</td>
<td>32.9</td>
<td>0.43</td>
</tr>
<tr>
<td>September</td>
<td>84.0</td>
<td>34.4</td>
<td>4.0</td>
<td>55.3</td>
<td>0.39</td>
</tr>
<tr>
<td>October</td>
<td>68.8</td>
<td>31.4</td>
<td>4.2</td>
<td>29.8</td>
<td>0.00</td>
</tr>
<tr>
<td>November</td>
<td>59.3</td>
<td>38.9</td>
<td>2.8</td>
<td>23.7</td>
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<tr>
<td>December</td>
<td>47.5</td>
<td>52.4</td>
<td>3.5</td>
<td>40.3</td>
<td>0.39</td>
</tr>
<tr>
<td>January</td>
<td>51.2</td>
<td>56.5</td>
<td>4.0</td>
<td>43.6</td>
<td>2.64</td>
</tr>
<tr>
<td>February</td>
<td>54.1</td>
<td>62.3</td>
<td>3.8</td>
<td>35.1</td>
<td>0.56</td>
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</tbody>
</table>

In terms of chemical composition, the crustal component within both the coarse and fine
particles shows the greatest fluctuations month-to-month, indicating that changes in this
component are responsible for the majority of total mass concentrations and exceedances
of the federal standard. With respect to the coarse particle fraction, only the COW site
demonstrates significant organic material concentrations and fluctuations within this
component often mirror changes in the crustal component. This observation not only
suggests a strong influence from the nearby cattle feedlot, but it suggests that the
influence of the feedlot can be seen in a number of components – namely in higher
organic material and crustal concentrations, but also in other chemical species including
phosphate (not shown). Further confirmation is provided by the severe decrease in
overall particle mass concentrations during the last month of the study when cattle were being transferred out of a nearby feedlot. With respect to the fine particle fraction, nitrate becomes a significant component during the winter months (December, January, and February) when temperatures are the lowest and relative humidity is highest allowing nitrate to be found in the particle phase rather than the gas phase.

**Figure 12: Comparison of Fine and Coarse Particle Mass Concentrations**

Figure 12 illustrates the relationship between fine and coarse particle mass concentrations, and displays a correlation between the measured concentrations, which is consistent among the sampling sites. Using the pooled dataset (all sites combined), the orthogonal regression line (at 95% confidence, \( \text{PM}_f \) mass concentration = (0.10±0.01) \( \times \) \( \text{PM}_c \) mass concentration + (4.9±0.5)) shows a positive correlation between the fine and coarse particle concentrations. Because coarse particles do not have a long atmospheric residence time and are believed to be local in nature, the y-intercept from this regression,
interpreted as the fine particle mass concentrations when coarse particle concentrations are at a minimum, may indicate the average fine particle concentration regional background which may include PM$_{f}$ transported into the local air shed.

**Figure 13: Crustal Versus Total Coarse Particle Mass**

Figure 13 examines the relationship between the coarse particle crustal component mass concentrations versus the coarse particle mass concentration. A strong linear relationship is observed within the data collected at each of the monitoring locations. This relationship reinforces the observation that resuspension of crustal material is a major contributor to local PM$_{c}$ levels at all times. In this case, the linear relationships observed at CG and PCH are remarkably similar (slopes and intercepts of the orthogonal regressions are within the 95% confidence interval), but the slope of the regression line on the data collected at COW is statistically different and significantly lower. This is
consistent with the observation that resuspended dust from the cattle feedlot contains a significant amount of organic material which would accompany the traditionally categorized crustal material when resuspended. Feedlot material contains approximately 25% organic material. If this percentage was added to the crustal component, the slope of the regression line for COW becomes statistically similar to relationships observed at both the CG and PCH sites.

Several species (including Na, Mg, K, Ca, and P) were measured in their water soluble form (by IC) and in their elemental form (by ICP-MS). Figure 14 shows the comparison between these two measurements on a seasonal basis. Total phosphorous concentrations measured at the CG and PCH were often below detection limits or measured at extremely low concentrations. Phosphorous concentrations at the COW site were routinely measurable (exceeding 2 µg/m³) in the coarse particle size fraction and almost all present in the soluble phosphate form. Detection of phosphate in ambient samples is not widely reported in the literature. Measurements have been made in rural areas near Sierra Nevada, CA (Vicars, Sickman et al. 2010) and Lake Tahoe, NV (Zhang, Carroll et al. 2002), which have found coarse particle phosphate concentrations as high as 90 ng/m³, but measurements near cattle feedlots have shown elevated concentrations (Razote, Maghirang et al. 2006; McGinn, Flesch et al. 2010) consistent with our measurements at COW.

Approximately 60% of the total sodium and calcium mass, 15% of the potassium mass, and 10% of the magnesium mass is found in the soluble forms at the CG and PCH sites. The COW site appears to be different, as only about 20% of the calcium mass and 25% of the potassium mass, and 20% of the magnesium mass is found in the soluble ion form.
This information indicates the presence of a unique source impacting the COW that may be traceable with the use of the solubility ratio of these key elements.

Figure 14: Coarse Particle Solubility of Several Chemical Species
5.8 Summary and Conclusions

This year long aerosol characterization study, undertaken in Pinal County, AZ – an area experiencing high PM$_c$ concentrations due to crustal sources common to rural, arid environments, has further developed the understanding of particulate matter within the region by allowing for chemical characterization and investigation of temporal and spatial variability.

Coarse particle concentrations are, on average, approximately 5 times higher than the fine particle mass concentrations within the region and highest concentrations were observed during spring and fall seasons, consistent with the tilling and harvesting seasons, and also increase during the late summer monsoon season. Coarse particles are comprised mainly (50%) of crustal material which drives the fluctuation in total coarse particle mass. Organic material is also a significant factor representing approximately 15% of the coarse particle mass. The strong correlation between the coarse particle crustal component and the coarse particle mass verifies the significance of the crustal source of these particles.

Fine particle concentrations within the region are within NAAQS for PM$_{2.5}$. Mass concentrations vary seasonally, with highest concentrations observed during spring and fall seasons, consistent with the tilling and harvesting seasons. Overall variation within the total fine particle mass is much less than that found in the coarse particle mass measurement. Fine particles are comprised mainly (37%) of organic material with a similar influence (30%) from crustal material. Approximately 5 µg/m$^3$ can be attributed to regional background of local and transported fine particulate matter.
Spatially, rural sites experienced much higher mass concentrations than the urban site. This is consistent with the proximity and abundance of coarse particle sources located near the sampling locations and the shorter residence time of larger particles. Second, the chemical composition varies by sampling location. Higher concentrations of organic matter and water-soluble ions are measured at COW consistent with the close proximity of the cattle feedlot. The solubility ratios for calcium, potassium, and magnesium in feedlot material make them potential marker species for differentiation from other forms of crustal material.

Coarse PM is likely responsible for a number of violations of the PM$_{10}$ and PM$_{2.5}$ NAAQS in the Desert Southwest and especially in areas of growing population located in more rural areas. This unique data set described here will provide a better understanding of the source impacts of coarse particles in the area, giving guidance to policy makers as to the best approaches for reducing levels of PM$_{10}$ and PM$_{2.5}$ to below their ambient air quality standards, and therefore, protect public health.
Chapter 6: Summertime Characterization of Fine and Coarse Particulate Matter in the Desert Southwest – Arizona, USA

6.1 Abstract

A year-long study was conducted in Pinal County, AZ to characterize fine and coarse particulate matter (PMf and PMc, respectively) as a means of furthering our understanding of ambient concentrations and composition in rural, arid environments. Detailed measurements of ambient fine and coarse mass, ions, elements, and carbon concentrations at one-in-six day resolution were conducted at three sites within the region. Data collected between May and September 2009, representing the summer season and local monsoon period, is presented here.

The monsoon for this region began in early July with several substantial rain and/or high wind events. The rain events served to clean the atmosphere, resulting in a decrease in ambient coarse mass, and resulted in a period where local coarse PM concentrations measured at all sites became more uniform. The monsoon period is also characterized by high wind events that may or may not be associated with rain. Elevated wind speeds resulted in increased ambient coarse PM mass concentrations, possibly due to increased local wind erosion or transport.

Observations suggest a strong impact from local dust sources, with concentrations measured at the Cowtown site commonly exceeding measurements at the other two monitoring sites located at Pinal County Housing and in the town of Casa Grande. To

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2 This chapter is based on a journal manuscript, lead author Andrea L. Clements, which has been reviewed and approved for publication by the US EPA Office of Research and Development. We have submitted this manuscript to the Journal of the Air and Waste Management Association.
confirm the influence of dust entrainment on local coarse PM levels, a series of soil samples representing native soil, agricultural soil, road dust, and material representative of a local feedlot was collected, resuspended in the laboratory, and analyzed for a similar set of measurements as the ambient samples. This work produced source profiles for each soil type, served to confirm the influence of dust sources on ambient particle concentrations, and yielded insights into unique source signatures observed in the ambient coarse PM data including elevated phosphate at the Cowtown monitoring location.

6.2 Introduction

Much of the desert southwest is designated as being in non-attainment for the Federal 24-hour National Ambient Air Quality Standard (NAAQS) for PM$_{10}$ (particles with an aerodynamic diameter [AD] less than or equal to a nominal 10 µm) including both urban and rural areas in central Arizona (U.S. EPA 2008). In particular, Pinal County, located just south of the Phoenix metropolitan area, registered the second highest 24-hour averaged PM$_{10}$ concentration, the highest number of 24-hour average PM$_{10}$ concentration exceedances, and the highest annual averaged PM$_{10}$ concentration in the nation in 2007 (U.S. EPA AirData 2012). For the period 2006-2008, six monitoring locations within the county were in violation of the PM$_{10}$ NAAQS (US Environmental Protection Agency - Region 9 2010). Pinal County Air Quality Control District (PCAQCD), through the Arizona Department of Environmental Quality (ADEQ), has asked that several exceedances be excluded from the attainment calculations citing "exceptional" weather events, such as high winds, often associated with frontal passages and monsoon storms,
which cause particulate matter concentrations to soar and visibility to be reduced (US Environmental Protection Agency - Region 9 2010).

Between 2006 and 2008, measured exceedances of the 24-hr PM$_{10}$ NAAQS occurred at six different monitors all located within the Pinal County agricultural basin, where high wind conditions can increase re-entrainment of exposed crustal-related material and cause elevated PM$_{10}$ and PMc (PM$_{10-2.5}$; particles in the size range between 2.5 µm and 10 µm AD) concentrations in the region (Arizona Department of Environmental Quality - Air Quality Division 2010). Results from a 2003 source apportionment study (Pinal County Air Quality Staff 2005), described below, indicate that much of the PMc is comprised of crustal-related material, which has many possible sources within the basin including dust from paved highways and roads, unpaved roads, agricultural fields, arid desert land, earth moving, plowing or harvesting activities, and mining as well as concentrated animal feeding operations and bulk material handling operations like cotton gins and grain processing.

Most violations of the PM$_{10}$ NAAQS however, were measured at Cowtown (COW), located northwest of Casa Grande, and only a small number of these exceedances can be excluded due to high wind events (US Environmental Protection Agency - Region 9 2010). Fine particle or PM$_{2.5}$ (particles with an AD less than or equal to a nominal 2.5 µm) concentrations measured at COW are also of concern because of a number of PM$_{2.5}$ NAAQS exceedances at the site. Fine and coarse particles typically come from different source categories and for that reason are composed of different chemical species, and thus, a separate determination of the fine and coarse fractions of PM$_{10}$ is needed to better
understand the impact of sources on ambient PM concentrations (Arizona Department of Environmental Quality - Air Quality Division 2010).

In the fall of 2003, PCAQCD conducted a one month PM$_{2.5}$ and PM$_{10}$ source apportionment study using an Airmetrics MiniVol™ Portable Air instrument running on a 1-in-3 day schedule. These ambient samples were collected using Teflon and quartz-fiber filters and analyzed for mass, ions, OC, EC, CO$_3^{2-}$, and elements (by XRF). Agricultural soils, road dust, and cattle feedlot material were collected for chemical fingerprinting for the same components as the ambient filters. Based on the 2003 source apportionment (CMB version 8) results, approximately 60% of the ambient PM$_{10}$ at Cowtown and 20% at both Pinal County Housing and Casa Grande was apportioned to cattle feedlot material, while 50%, 8%, and 0% was apportioned to this source in the PM$_{2.5}$ fraction (Pinal County Air Quality Staff 2005). These results indicate that the feedlots adjacent to COW may contribute to the high number of exceedances at this site.

Results presented here expand on the 2003 study. Ambient samples were collected for a full year on a 1-in-6 day schedule and analyzed for additional ions and elements. Soil samples were collected and chemically analyzed using the same analysis methods to more accurately identify the various dust sources in this region. Determination of the additional chemical species allows for differentiation between agricultural soils and road dust. The full year of sampling allows for the investigation of seasonal differences, and in particular, the effect of the monsoon season and the influence of wind and rain on the observed ambient concentrations. Lastly, this study uses dichotomous samplers to collect the fine and coarse particle fractions of PM$_{10}$ separately, thus making it possible to more accurately identify unique sources of elevated concentrations of coarse particles within
this region. In particular, an estimate of the influence of local crustal-related material is presented.

6.3 Methods

6.3.1 Sample Collection

Between February 2009 and February 2010, ambient aerosol sampling was conducted at three monitoring locations in Pinal County, AZ in and around the vicinity of the town of Casa Grande. Casa Grande is located to the south of Phoenix, AZ and approximately halfway between the major metropolitan areas of Phoenix and Tucson. Figure 15 shows the geographic location of the monitoring sites within Pinal County and in proximity to the town of Casa Grande, AZ. Also shown is a satellite image showing the typical land use in the area including undeveloped native desert, agricultural use, and urban areas.

Figure 15: Map of Ambient Monitoring Locations
The Casa Grande (CG) site (401 Marshall St.), denoted by A in Figure 15, is on the roof of a one-story building located within the town of Casa Grande, AZ, a small city with a population of approximately 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 industrial locations likely impact air quality at this site.

The Cowtown (COW) site (37580 W. Maricopa-Casa Grande Hwy.), denoted by B in Figure 15, is located approximately 27 km to the northwest of the city of Casa Grande. It is a rural location, located on a 0.1 km by 0.1 km section of native (unaltered with original vegetation) desert adjacent to a two lane highway connecting Casa Grande with the city of Maricopa. Maricopa is 35 km northwest of Casa Grande. The COW 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 COW site. In the immediate vicinity of the sampling site there are a number of potential sources including fallow cropping fields (within 0.25 km to the west, north, and east), several cattle feedlots (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 regulatory air quality equipment at this site registers numerous 24-hour exceedances of the PM$_{10}$ standard each year (U.S. EPA AirData 2012).

The Pinal County Housing (PCH) site (970 N. Eleven Mile Corner Rd), denoted by C in Figure 15, is located approximately 17 km to the east of the city of Casa Grande. The site
is within and immediately surrounded by native desert, about 0.2 km west of the Pinal County Housing Projects and about 0.2 km east-southeast of the wastewater treatment ponds for the complex. Air quality at this site is likely influenced by agricultural fields, which are located about one km from the site 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 of the site.

At each sampling site, four Sierra-Anderson Model 241 dichotomous samplers were deployed to collect equivalent 24-hr samples on a one-in-six day schedule. These samplers collected PMf and PMc size fractions simultaneously at a total flow rate of 16.7 Lpm (approximately 15 Lpm and 1.7 Lpm to the fine and coarse channels, respectively). Two of the four samplers at each site used Teflon filter media in both channels for analysis of fine and coarse PM mass, ions, and elements. One of the four samplers was equipped with quartz-fiber filters in both channels, which were used for determination of bulk elemental carbon (EC) and organic carbon (OC) content. The remaining sampler was used to collect blanks and other co-located samples for quality assurance/quality control and instrument precision determination.

Filter media was transported between the laboratory and the field seated within the plastic instrument filter holders sealed inside sterile and cataloged polystyrene petri dishes (Pall Corporation). Following collection, samples were placed back into their original containers and kept at reduced temperatures (blue ice during transport and \(< -4^\circ\text{C}\) during storage) until laboratory analysis.
Although not part of our sampling campaign, each sampling site also measured semi-continuous PM$_{10}$ mass concentration using a Thermo Scientific Tapered Element Oscillating Microbalance (TEOM) monitor (Series 1400ab) for compliance monitoring. The unit was operated without a dryer at $50^\circ$C. Data was recorded at 5 minute increments and averaged into 24-hour daily concentrations.

6.3.2 Sample Analysis

6.3.2.1 Mass

Mass was obtained gravimetrically on all Teflon filters by difference (post-collection weight minus pre-collection weight). Filters were removed from frozen storage and then equilibrated for 24 hours and weighed under controlled temperature ($22^\circ$C $< T < 24^\circ$C) and humidity conditions ($45\% < RH < 55\%$) to achieve reproducible and stable mass measurement readings (40 CFR 50 (2006)). Every 10$^{th}$ filter was reweighed and if weights were outside quality control limits all 10 filters were re-weighed. Traceable metal standards were used for calibration. The average of the two mass measurements collected each day is presented here unless one sample was invalidated due to user, instrument operation, or experimental error.

6.3.2.2 Ions

After gravimetric analysis, ions were determined on one set of the Teflon filters by ion chromatography (IC) with a Dionex IC20 system. Filters were wet with 200 µl of ethanol (Fisher HPLC Grade) (Derrick and Moyers 1981) and extracted by sonication in 7.5 ml ultrapure water for 15 minutes at room temperature ($22^\circ$C $< T < 24^\circ$C). Extracts
were filtered using a syringe filter (Millex GP 0.22µm pore size PES membrane filter) and then transferred to a 10 mL Dionex polyvial for analysis. Cations, including lithium, sodium, potassium, ammonium, calcium, and magnesium were quantified using a CG12A analytical column and 11 mM methylsulfonic acid eluent running at 1.00 mL/min. Anions, including chloride, nitrite, nitrate, phosphate, and sulfate were quantified using an AS12A analytical column and 2.7 mM sodium carbonate/0.3 mM sodium bicarbonate eluent running at 1.5 mL/min. The instrument was calibrated using a series of standard dilutions from a certified calibration standard for each suite of compounds (Dionex P/N 056933 and 046070), laboratory and field blanks were periodically analyzed, and every 7th filter was reanalyzed for method precision determination.

6.3.2.3 Elements

Following gravimetric analysis, the second set of Teflon filters were analyzed for 63 trace elements (including, but not limited to, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, Sb, Se, Sn, Ti, U, V, Zn) using high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS, herein referred to as ICP-MS) by Nabin Upadhyay in Professor Herckes’ research group. Samples were microwave-digested in 30 mL Teflon vials using an acid mixture of 4 mL nitric acid, 0.9 mL hydrochloric acid, and 0.1 mL hydrofluoric acid (Fisher) (Upadhyay, Majestic et al. 2009). The temperature profile included a 6 minute temperature ramp to 140ºC, holding for 2 minutes, followed by a 5 minute temperature ramp to 165ºC, holding for 6 minutes. The temperature was further increased to 180ºC and held for 15 minutes. The digestion solution was diluted to 25 mL using ultrapure water, from which a 1.25 mL aliquot was transferred to a 15 mL centrifuge vial and diluted to 5 mL using ultrapure water. This final solution was
analyzed for elements by ICP-MS (ThermoFinnigan ELEMENT 2) using an internal indium standard. High-resolution was used to quantify sodium and potassium. The instrument was calibrated using a multi-element standard (SPEX Certiprep Inc., USA). Quality control included analysis of laboratory and field blanks, replicate analyses, and analysis of two National Institute of Standards and Technology (NIST) standard reference materials (San Joaquin Soil, SRM 2709 and Urban Dust, SRM 1649) using the same analytical procedure.

**6.3.2.4 Bulk Carbon**

A 1 cm x 1.5 cm punch was removed from each quartz-fiber filter and analyzed for bulk OC and EC using a thermal—optical EC/OC analyzer (Sunset Laboratory Inc., Tigard OG) (Birch and Cary 1996). The filters were analyzed according to a slightly modified Sunset Labs’ thermal-optical transmittance (TOT) method with variable time steps lasting between 60 and 200 seconds during OC evolution at temperature plateaus of 310, 475, 615, and 870°C. The temperature profile during EC evolution included 45 second holds at 550, 625, 700, 775, and 850°C with a final hold at 870°C for 120 seconds. Quality control included analysis of laboratory and field blanks, replicate analyses, and analysis of a sucrose standard prepared by Sunset Labs.

**6.3.2.5 Soils**

Soil samples were collected in the vicinity of each sampling site representing a variety of different soil types including agricultural fields, native desert (unaltered desert in close proximity to the site), paved and unpaved road dust, and the cattle feedlot. Most sites were sampled during three different seasons including spring, fall, and winter with
additional samples being collected during unique events such as cotton defoliation season. In total, 35 soil samples were collected. All samples were obtained from the top 15 mm of the surface using a trowel, or by broom on the paved surface, and placed into a pre-baked glass jar for storage and transport (Hagen 2004, Domingo 2008). Samples are labeled with a location ID number (1-15), season in which it was collected (s-spring, w-winter, f-fall) and the closest ambient sampling location (PCH, CG, or COW). Samples 1-4 were collected in the native desert areas in close proximity to the sampling sites (at 15 m and 30 m away). Samples 5 and 6 were collected in the fallow agricultural fields near COW while samples 7 and 8 were collected from active agricultural fields near PCH. Samples 9 and 10 represent dirt roads in close proximity to agricultural fields, sample 11 is a road dust sample from a paved road, and sample 12 was collected from a dirt road adjacent to a cattle feedlots. Samples 13-15 represent various conditions near cattle.

Prior to laboratory resuspension, soil samples were dried in an oven at 110°C for 24 hours. Samples were then lightly ground using a mortar and pestle to gently break up large aggregates within the sample using less physical force than what might be exerted by a simple foot step so as to minimally impact the size of particles in the desired size range. Soil samples were resuspended by passing HEPA-filtered air over the sample in a resuspension chamber and then through a size-selective cyclone (URG Corporation). The operating flow rates were determined based on the cyclone design – 28 Lpm for PM$_{10}$ sampling and 42 Lpm for PM$_{2.5}$ sampling. Size-selected particle samples were then collected at separate times onto three parallel Teflon and quartz-fiber filters. Filters were stored in the same manner as field samples until chemical analysis. Teflon filters were
analyzed for mass and elements. Punches from the quartz-fiber filter were analyzed for water-soluble ions (3 cm$^2$) and for bulk OC and EC (1.5 cm$^2$) concentrations. All samples were analyzed for mass, bulk OC and EC, and elements in a manner analogous to the analysis of ambient filters collected from the field sampling campaign. Quartz-fiber filter punches for ion determination were not wetted with ethanol prior to extraction as was done with the Teflon filter samples. Extraction by sonication and subsequent sample preparation and analysis was performed in a manner similar to the field samples.

6.4 Results and Discussion

6.4.1 Mass and Meteorology

The summer period was subjectively determined to include months with any days with maximum air temperatures over 37.8°C, and included May, June, July, August, and September. Within the summertime period, the Arizona monsoon season, where tropical moisture from the south leads to localized thunderstorms, has traditionally been defined as beginning after the third consecutive day of dew point temperatures above 12.8°C (Maricopa County Cooperative Extension Home Horticulture 1997). Using the dew point temperature criteria and the meteorology data collected in Maricopa, AZ (8 km northwest of COW), the 2009 monsoon season started on July 1$^{st}$ and ended in mid-September when dew point temperatures fell below this criteria. Five significant monsoon events, defined here as rain and high wind speeds at the Maricopa meteorological site were observed during this period, including episodes on July 3$^{rd}$, 15$^{th}$, and 22$^{nd}$, as well as August 22$^{nd}$ and September 3$^{rd}$. Rainfall data was not collected local to the three sampling sites and thus the significance of rainfall events at each site cannot be verified.
Filter-based measurements of PMc concentrations during this period varied between 14 and 150 µg/m³ (Figure 16a). Concentrations measured at CG are less influenced by direct agricultural emissions and are often the lowest measured. Concentrations observed at CG and PCH commonly trended together but the concentrations observed at PCH were on average approximately 10µg/m³ (approximately 35%) higher than those measured at
CG, most likely indicating the influence of nearby crustal sources, which are indicated above. PMc concentrations at COW are 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 (Zhuang, Chan et al. 1999). The localized effect of substantial emissions in the vicinity of the COW site resulted in elevated PMc concentrations of 5 and 90 µg/m$^3$ over levels at the other two sites, as well as different temporal variations relative to GC and PCH.

During this same period, filter-based fine particle concentrations ranged between 4 to 18 µg/m$^3$ (Figure 16b). When compared, fine particle concentrations were 10-30% of the coarse particle concentrations at any one time. Figure 17 examines the relationship between fine and coarse particle concentrations and found that there is a relationship within the measured concentrations that is consistent among the sampling sites. The orthogonal regression shows that PMf concentrations are approximately 10% of PMc concentrations. The statistically significant non-zero intercept suggests a regionally transported PMf source measuring approximately 5 µg/m$^3$. 
Figure 17: Comparison of Fine and Coarse Particle Mass Concentrations

The orthogonal regression between the time-integrated filter-based mass measurements and the co-located semi-continuous TEOM measurements on a PM$_{10}$ basis (shown in Figure 18) was quite good (slope 0.74 ± 0.07, R$^2$=0.96). However, filter based measurements are approximately 25% lower than the TEOM based measurements and is likely due to differences in instrument design, collection efficiency, analytical methods, and instrument bias.
The influence of the monsoon weather pattern on the mass concentrations can be seen in the daily PM$_{10}$ TEOM data presented in Figure 19. Monsoon events (impact of wind and/or rain) are denoted by vertical dashed lines and after each event; there was a decrease in the PM$_c$ concentrations consistent with wet deposition of particles. During the last event, meteorological data from Maricopa showed high winds preceding the rain event. PM$_c$ levels at all three sites also showed less spatial variability within a day or two after rain events. Beyond the effect of increased particle deposition, summer monsoon storms are often associated with strong wind gusts that can lead to severe dust storms. Some, but not all of the monsoon events are associated with increased wind speeds and conversely, some high wind events are not associated with rain. The former situation was observed during September 3$^{rd}$ when the monsoon event was accompanied...
by wind gusts and increased PM concentration likely followed by rain that significantly reduced PM$_{10}$ concentrations. The latter situation was observed on July 17$^{th}$, shortly after the 2$^{nd}$ monsoon event, when wind speed rose nearly 10 m/s (as reported at the Maricopa meteorological station) resulting in increased particle entrainment or transport and a very large increase in ambient PM concentrations.

![Figure 19](image.png)

**Figure 19:** Daily Averaged PM$_{10}$ Mass Concentration Measured by TEOM and the Local Rain Events

The coarse and fine PM mass concentrations measured at PCH on August 5$^{th}$ are much higher than at any other time and are higher than concentrations at the COW site (Figure 19 shows this in terms of PM$_{10}$). Earth moving activities for construction of a lift station for the nearby PCH housing facility occurred around this date within a 0.2 km of this site suggesting a possible reason for this unusual event.
6.4.2 Coarse Particle Composition

The measured concentration of several elements is compared to total coarse particle mass concentration in Figure 20. The metals selected are major components of soils and can be used to estimate the impact of fugitive dust emissions on atmospheric particle concentrations. The strong linear correlation relationship observed at each site, between elemental concentration and total PMc mass reinforces the observation that resuspension of crustal material is a major contributor to local PMc levels at all times. In addition, the ratio of these metals between one-another and to total PMc can be an important signature for the impact of soil within this region. The data presented in Figure 20 illustrates K/Al, Ca/Al, and Fe/Al ratios of 0.53, 0.96, and 0.63, respectively. Potassium, aluminum, and iron ratios are similar to those measured for resuspended PM$_{10}$ soil samples collected in the US-Mexico border region (Watson and Chow 2001; Chow, Watson et al. 2004) and near Owens (Dry) Lake, CA (Rojo, Gill et al. 2008) suggesting the ratios are regional in nature.
Significant levels of phosphate were observed in PMc at the COW site. Detection of phosphate in ambient samples is rare and not widely reported in the literature. Measurements have been made in rural areas near Sierra Nevada, CA (Vicars, Sickman et al. 2010) and Lake Tahoe, NV (Zhang, Carroll et al. 2002), which have found coarse particle phosphate concentrations as high as 90 ng/m$^3$, much lower than the PMc phosphate levels observed at COW, which routinely exceeded 2 µg/m$^3$. Comparison of PMc phosphate (measured by IC) and phosphorous (measured by ICP-MS) at the COW site, as shown in Figure 21, strongly suggests that most measured P is present as
phosphate. PMf phosphate concentrations, as well as PMc phosphate concentrations at the other sampling sites, were below detection limit of this method.

Figure 21: Comparison of Phosphorous Concentrations Measured in Elemental Form and Ion Form

Concentrations of EC in PMf and PMc were low and often non-detectable. Figure 22 shows the coarse OC concentrations for each location. All sites follow a similar temporal pattern as PMc mass. Concentrations of PMc OC at the PCH and CG sites were similar, despite the apparent differences in localized sources, suggesting agricultural operations in the vicinity of PCH do not always contribute significantly to the observed ambient OC concentrations. Concentrations of PMc OC were up to 15 µg/m³ higher at the COW site than at the other two sites, reinforcing the unique influence of the cattle feedlot adjacent to the COW site. Fine OC concentrations at CG and PCH were low ranging from 0.8 to
4.3 µg/m³ and often followed a similar temporal pattern to PMf mass, suggesting similar source impacts and/or meteorological influence.

![Graph showing coarse organic carbon concentrations measured during the Arizona Monsoon Season.](image)

**Figure 22:** Coarse Organic Carbon Concentrations Measured During the Arizona Monsoon Season

### 6.4.3 Resuspended Dust

Based on the 2003 source apportionment study, crustal related material contributed substantially to the ambient PM$_{2.5}$ and PM$_{10}$ mass concentrations (Pinal County Air Quality Staff 2005). To better understand the impact of the soil contribution to fine and coarse PM, 35 soil samples from local fields and roads were obtained during three different seasons. These samples were resuspended and PM$_{2.5}$ and PM$_{10}$ fractions were collected on filters as described earlier. Although not directly comparable to the ambient PM$_c$ fraction, the PM$_{10}$ soil results are presented here.
Figure 23 presents the PM$_{10}$ OC soil results by site and season. Each data point is labeled with the soil sampling location (numbered 1-15), season (S, W, F for spring, winter, and fall, respectively), the closest ambient sampling site, and are further grouped by the representative type of source sampled (native soils, agricultural soils, road dust, and cattle feedlot).

![Figure 23: Organic Carbon Concentrations Measured in Resuspended Soil Samples Collected from 15 Sites](image)

Both increasing and decreasing seasonal variations are observed within the soil samples. Within native soil samples, a seasonal difference between 10 and 30% is observed. A 30-60% difference was observed when comparing native soil collected near PCH and COW with concentrations ranging from 6 to 16 mg OC/g soil. OC concentrations at PCH were higher than those found at COW, which may be attributed to the closer proximity of active agricultural fields.
Variations within the agricultural soils were larger with concentrations ranging from 6-50 mg OC/g soil. Data indicates a 30% difference in the OC content of soils collected from fallow fields (sampled near COW) and active fields (sampled near PCH) with greater concentrations (~30 mg of carbon/g of soil) in actively farmed fields. Within each sub-fraction, a season difference between 40 and 60% is observed.

Samples numbered 13 through 15 were collected from the vicinity of local cattle feedlots and are expected to be representative of material resuspended from this source. Samples numbered 13(w), 14(w), and 15(w) were collected during the winter, but at various proximities to cattle. Concentrations of PM$_{10}$ OC within these samples varied by over a factor of 2, indicating the large spatial variability of material from such sources.

The chemical composition of similar soil sources (i.e. native soils, agricultural soils, unpaved road dusts, etc.) were averaged to further examine the impact of local crustal material on air quality. The aggregated PM$_{10}$ characteristics of the local crustal sources are summarized in Figure 24, for phosphate, sulfate, potassium, calcium, lead, and iron. The differences between native and agricultural soils were minimal on an absolute basis. Lead concentrations were highest in the paved road dust sample collected near CG, suggesting the influence of motor vehicle traffic and brake wear in this relatively small urbanized area. Sulfate and calcium concentrations were elevated in the sample from a local dirt road located adjacent to the cattle feedlot, and to a lesser extent, in soil representative of the feedlot itself. Both compounds are reportedly found in liquid cattle feed (Toledo and Kuznesof 2008) or as an emulsifying agent in cattle feed. High concentrations on the dirt road are likely the result of spillage or transport by vehicles.
Relatively lower concentrations of these ions were found in the feedlot samples, which is likely simply a result of dilution by high organic carbon concentrations.

**Figure 24: Chemical Composition of Six Different Soil Types**

The chemical composition of the sampled feedlot soil was more varied than the other soil sources. Samples were enriched in organic carbon, phosphate, potassium, and calcium. Previous studies have shown that up to 90% of the PM emitted from a feedlot is organic in nature (McGinn, Flesch et al. 2010). Studies have also documented that many cattle housed in concentrated feeding operations are fed diets containing a liquid finisher and oil (McGinn, Flesch et al. 2010). The composition of liquid finishers are propriety in nature but many of the available brands are reported to contain the trace elements Ca and
P (Sievering, Boatman et al. 1991). Thus, these compounds can be reasonably expected to be found in feedlot material and the associated PM that contains a significant amount of manure (McGinn, Flesch et al. 2010). Measurement of elevated concentrations of these unique compounds in ambient PMc samples at the COW monitoring location confirmed the influence of resuspended feedlot material.

6.5 Conclusions

Pinal County, AZ represents a confluence of small urban and agricultural land uses. The current study was undertaken to better understand the chemical characteristics of ambient coarse and fine particle concentrations within this region to and identify major sources impacting the monitoring sites.

PMc mass was highly variable ranging between 14 and 150 μg/m³ while PMf mass ranged between 4 and 18 μg/m³. Analysis showed that PMf concentrations are approximately 10% of PMc concentrations. Monsoon events served to reduce observed PM concentrations by wet deposition of particles and suppression of dust entrainment. Two high wind events occurred during the monsoon period during which the daily averaged wind speed increased by 10 m/s. These events served to dramatically increase PM concentrations.

PMc phosphate and organic carbon concentrations were higher at the COW site than the other two sites due to local emissions from a cattle feedlot. Emissions in the vicinity of the COW site also impacted PMf concentrations on occasion resulting in PMf mass concentrations 50% higher than those measured at the other sites. Based on these marker
species, fugitive dust emissions representative of material from local feedlots were quite significant, at times dominating the observed PMc concentrations at COW.

The dominant PMc source in this region is atmospheric entrainment of crustal material and analysis of soil composition for species such as bulk carbon and elements confirms this observation. Source profiles for a series of different crustal materials were created, and typical crustal components including Al, Ca, K, Ti, and Fe dominated all collected samples. Paved road dust collected in CG had elevated lead concentrations possibly from non-exhaust motor vehicle emissions. Dirt road samples in the vicinity of the cattle feedlot had high calcium and sulfate concentrations, which are likely associated with cattle feed supplements. Of particular interest, soil representative of material resuspended from the local cattle feedlot proved to have a unique signature not previously reported in the literature featuring high concentrations of organic carbon, phosphate, and potassium, resulting in the mass fraction of other typical crustal components to be relatively lower than typically found in soils.
Chapter 7: Size-Differentiated Chemical Composition of Re-
Suspended Soil Dust from the Desert Southwest United States³

7.1 Abstract

As part of the Desert Southwest Coarse Particulate Matter Study, source samples were collected from several different soil types in Pinal County, AZ. These samples were collected for chemical characterization analysis in support of local source apportionment efforts. Soil types included native desert dust (NAT), agricultural soils (crop farming, AGR), dirt-road dust adjacent to agricultural areas (DRA), paved road dust (PAV), dirt road dust from within and adjacent to a cattle feedlot (DRF), and material from an active cattle feedlot (FDL). Following resuspension of the soil in the laboratory, size-segregated PM$_{2.5}$ and PM$_{10}$ fractions for each soil type were collected on filters and characterized for mass, ions, organic carbon (OC), elemental carbon (EC), trace elements, and a range of organic species. The unique chemical composition of soils in this region (e.g., high As and Sb) shows the importance of using local soil profiles (e.g., native soils) as compared to Upper Continental Crust (UCC) or soil profiles from other regions in receptor modeling studies. Soil composition also indicates the impact of local sources modifying the soil composition from NAT. For example, high OC and phosphate associated with the cattle feedlot and Cu, Sb, and Zn associated with paved roads.

³ This chapter is based on a journal manuscript led by author Nabin Upadhyay but contributed to significantly by Andrea L. Clements. The portions included here are those related to the work of Andrea L. Clements. The full manuscript has been prepared and submitted to US EPA Office of Research and Development for clearance. We intend to submit this manuscript to Aerosol and Air Quality Research.
7.2. Introduction

Entrainment of crustal material is a major source of ambient particulate matter (PM) pollution. On a local scale, large fugitive dust sources can contribute to high pollution events of both fine (PM$_{2.5}$, particles with aerodynamic diameter (AD) < 2.5 µm) and coarse (PM$_{c}$ or PM$_{10-2.5}$, particles in the size range between 2.5 and 10 µm AD) particles. Both size ranges have been associated with adverse health effects (Prahalad, Soukup et al. 1999; Ramanathan, Crutzen et al. 2001; Harrison, Smith et al. 2004; Solomon, Costantini et al. 2011).

Identifying and quantifying the sources of PM is an essential step in developing emissions control strategies designed to reduce levels of air pollutants to below those specified in the National Ambient Air Quality Standards (NAAQSs) (40 CFR 50 2006). This is often achieved through observational studies linking emission sources to measured ambient concentrations using receptor models or other statistical tools (Hopke 1991; Hopke 2003; Solomon and Hopke 2008; Watson, Chen et al. 2008). In most cases, a detailed knowledge of source composition is needed. Still, many studies only characterized either the organic or inorganic components of fugitive dust sources, not both simultaneously. Studies that characterize crustal material are often limited to a few source samples. Frequently, the average composition of upper continental crust (UCC) is substituted as a source profile for crustal material without consideration of how representative it is of local or regional dust sources.

To assess the contribution of crustal material to ambient PM concentrations using source attribution approaches, it is essential to understand the chemical composition of the
source material. On a local scale, the extent of crustal material entrainment strongly depends on soil type, land-use pattern, and wind speed (Holcombe, Ley et al. 1997; Macpherson, Nickling et al. 2008). The influence of various dust sources can be discriminated only by specific chemical markers. Most source attribution studies rely on chemical profiles for soil samples obtained outside the study area, which can result in large uncertainties due to the representativeness of source materials, leading to a possible under or overestimate of the dust contribution to PM concentrations in the study area.

Information on local soil composition is particularly important in areas with substantial dust contributions to PM. One such region is the arid desert of the southwestern United States (US), including Arizona. A recent study estimated that resuspended dust accounts for as much as 20% of PM$_{2.5}$ and 90% of PM$_c$ in the southwestern US (Malm, Pitchford et al. 2007). Pinal County, in central Arizona, is an area that frequently exceeds the PM$_{10}$ NAAQS (U.S. EPA AirData 2012). Many of these exceedances are attributed to resuspended dust from agricultural activities, unpaved and paved roads, construction, and desert lands. In addition, agricultural activities, like soil preparation, cattle farming, and movement of cattle in feedlots might contribute substantially to local high PM events. However, lack of comprehensive chemical characterization of various soil types in different particle size ranges within the study area limits the understanding of potential sources and the relative impact of each on the PM concentrations on a local scale.

This study presents the detailed chemical composition and variability of soils local to central Arizona. Source profiles are developed for several soil types including soils that are potentially representative of the southwestern US. The specific objectives of the study are: i) to characterize the chemical composition of soils associated with possible
sources that contribute to ambient PM$_{2.5}$ and PM$_{10}$ concentrations; and ii) to determine if there are specific chemical markers to differentiate among various soil types.

Size-segregated soil samples (PM$_{2.5}$ and PM$_{10}$) collected from twelve different locations in Pinal County were analyzed for detailed chemical composition allowing source profiles to be developed and compared to the composition of UCC and to local unfertilized and undisturbed native desert soils.

### 7.3 Experimental

#### 7.3.1 Soil Sampling

A summary of the sampling locations and soil types and classifications used in this study is provided in Table 4. All soil samples were collected in Pinal County, AZ (USA) in the vicinity of three different air quality monitoring sites, including Pinal County Housing (PCH), Casa Grande (CG), and Cowtown (COW). A detailed description of the monitoring sites and local PM composition can be found in Clements et al. (Clements, Fraser et al. 2012). A brief summary of the sites is given here. PCH is a rural site located in a native (unfertilized) desert area with agricultural fields within a mile in all directions. Soil samples near PCH were collected from native desert soils in the immediate vicinity of the air quality monitoring site (less than 40 meters distant), from the edge and within the cropping area of a winter wheat field to the north of the monitoring site, and from the edge of a dirt road used to access the agricultural fields in the area. The CG site is located in the small urban area of Casa Grande, south of Phoenix, AZ. Soil samples in the vicinity of CG were collected at the edge of a local roadway representing paved road dust samples. COW is a rural monitoring location with
unique local emission sources, which include a grain processing plant to the southwest and a confined cattle feedlot to the south. Samples near this location included soils from the native desert in the immediate vicinity of the monitoring site (less than 40 meters distant), within the active and fallowed alfalfa fields to the east, north, and west of the site, the median between the monitoring site and a local two-lane highway, and the edge of the dirt roads near the cattle feedlot. Material representative of the soil found within the cattle feedlots was also collected.

Table 4: Soil Sampling Locations and Soil Type Information

<table>
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<tr>
<th>Site Number</th>
<th>Season</th>
<th>Closest Monitor</th>
<th>Sampling Location</th>
<th>Soil Type</th>
<th>Sample Category</th>
<th>Classification</th>
</tr>
</thead>
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<td>Spring</td>
<td>PCH</td>
<td>20 Meters SW of Monitoring Site</td>
<td>Fine Sandy Loam</td>
<td>Native</td>
<td>NAT</td>
</tr>
<tr>
<td>1</td>
<td>Fall</td>
<td>PCH</td>
<td>20 Meters SW of Monitoring Site</td>
<td>Fine Sandy Loam</td>
<td>Native</td>
<td>NAT</td>
</tr>
<tr>
<td>1</td>
<td>Winter</td>
<td>PCH</td>
<td>20 Meters SW of Monitoring Site</td>
<td>Fine Sandy Loam</td>
<td>Native</td>
<td>NAT</td>
</tr>
<tr>
<td>2</td>
<td>Spring</td>
<td>PCH</td>
<td>40 Meters SW of Monitoring Site</td>
<td>Fine Sandy Loam</td>
<td>Native</td>
<td>NAT</td>
</tr>
<tr>
<td>2</td>
<td>Fall</td>
<td>PCH</td>
<td>40 Meters SW of Monitoring Site</td>
<td>Fine Sandy Loam</td>
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<td>NAT</td>
</tr>
<tr>
<td>3</td>
<td>Spring</td>
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<td>20 Meters SW of Monitoring Site</td>
<td>Clay Loam</td>
<td>Native</td>
<td>NAT</td>
</tr>
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<td>3</td>
<td>Fall</td>
<td>COW</td>
<td>20 Meters SW of Monitoring Site</td>
<td>Clay Loam</td>
<td>Native</td>
<td>NAT</td>
</tr>
<tr>
<td>3</td>
<td>Winter</td>
<td>COW</td>
<td>20 Meters SW of Monitoring Site</td>
<td>Clay Loam</td>
<td>Native</td>
<td>NAT</td>
</tr>
<tr>
<td>4</td>
<td>Winter</td>
<td>COW</td>
<td>Median between Site and Highway</td>
<td>Clay Loam</td>
<td>Native</td>
<td>NAT</td>
</tr>
<tr>
<td>5</td>
<td>Spring</td>
<td>COW</td>
<td>East Alfalfa Field</td>
<td>Clay Loam</td>
<td>Agricultural</td>
<td>AGR</td>
</tr>
<tr>
<td>5</td>
<td>Fall</td>
<td>COW</td>
<td>East Alfalfa Field</td>
<td>Clay Loam</td>
<td>Agricultural</td>
<td>AGR</td>
</tr>
<tr>
<td>5</td>
<td>Winter</td>
<td>COW</td>
<td>East Alfalfa Field</td>
<td>Clay Loam</td>
<td>Agricultural</td>
<td>AGR</td>
</tr>
<tr>
<td>6</td>
<td>Spring</td>
<td>COW</td>
<td>West Alfalfa Field</td>
<td>Clay Loam</td>
<td>Agricultural</td>
<td>AGR</td>
</tr>
<tr>
<td>7</td>
<td>Spring</td>
<td>PCH</td>
<td>Winter Wheat Field - Edge</td>
<td>Fine Sandy Loam</td>
<td>Agricultural</td>
<td>AGR</td>
</tr>
<tr>
<td>7</td>
<td>Spring</td>
<td>PCH</td>
<td>Winter Wheat Field - Center</td>
<td>Fine Sandy Loam</td>
<td>Agricultural</td>
<td>AGR</td>
</tr>
<tr>
<td>7</td>
<td>Fall</td>
<td>PCH</td>
<td>Winter Wheat Field - Center - Cut</td>
<td>Fine Sandy Loam</td>
<td>Agricultural</td>
<td>AGR</td>
</tr>
<tr>
<td>8</td>
<td>Fall</td>
<td>PCH</td>
<td>Defoliated Cotton Field</td>
<td>Fine Sandy Loam</td>
<td>Agricultural</td>
<td>AGR</td>
</tr>
<tr>
<td>8</td>
<td>Winter</td>
<td>PCH</td>
<td>Fallow Cotton Field</td>
<td>Fine Sandy Loam</td>
<td>Agricultural</td>
<td>AGR</td>
</tr>
<tr>
<td>9</td>
<td>Spring</td>
<td>PCH</td>
<td>Dirt Road Dust - South Edge</td>
<td>Fine Sandy Loam</td>
<td>Dirt Road-Ag</td>
<td>DRA</td>
</tr>
<tr>
<td>9</td>
<td>Fall</td>
<td>PCH</td>
<td>Dirt Road Dust - South Edge</td>
<td>Fine Sandy Loam</td>
<td>Dirt Road-Ag</td>
<td>DRA</td>
</tr>
<tr>
<td>9</td>
<td>Winter</td>
<td>PCH</td>
<td>Dirt Road Dust - South Edge</td>
<td>Fine Sandy Loam</td>
<td>Dirt Road-Ag</td>
<td>DRA</td>
</tr>
<tr>
<td>10</td>
<td>Spring</td>
<td>PCH</td>
<td>Dirt Road Dust - North Edge</td>
<td>Fine Sandy Loam</td>
<td>Dirt Road-Ag</td>
<td>DRA</td>
</tr>
<tr>
<td>10</td>
<td>Fall</td>
<td>PCH</td>
<td>Dirt Road Dust - North Edge</td>
<td>Fine Sandy Loam</td>
<td>Dirt Road-Ag</td>
<td>DRA</td>
</tr>
<tr>
<td>11</td>
<td>Winter</td>
<td>PCH</td>
<td>Winter Wheat Field - Edge Composite</td>
<td>Fine Sandy Loam</td>
<td>Paved Road</td>
<td>PAV</td>
</tr>
<tr>
<td>12</td>
<td>Spring</td>
<td>COW</td>
<td>Dirt Road Dust - Near Feedlot</td>
<td>Clay Loam</td>
<td>Dirt Road-Feed</td>
<td>DFR</td>
</tr>
<tr>
<td>12</td>
<td>Fall</td>
<td>COW</td>
<td>Dirt Road Dust - Near Feedlot</td>
<td>Clay Loam</td>
<td>Dirt Road-Feed</td>
<td>DFR</td>
</tr>
<tr>
<td>13</td>
<td>Spring</td>
<td>COW</td>
<td>Feedlot Material</td>
<td>Clay Loam</td>
<td>Feed Lot</td>
<td>FDL</td>
</tr>
<tr>
<td>13</td>
<td>Fall</td>
<td>COW</td>
<td>Feedlot Material</td>
<td>Clay Loam</td>
<td>Feed Lot</td>
<td>FDL</td>
</tr>
<tr>
<td>13</td>
<td>Fall</td>
<td>COW</td>
<td>Feedlot Material</td>
<td>Clay Loam</td>
<td>Feed Lot</td>
<td>FDL</td>
</tr>
<tr>
<td>13</td>
<td>Winter</td>
<td>COW</td>
<td>Feedlot Material</td>
<td>Clay Loam</td>
<td>Feed Lot</td>
<td>FDL</td>
</tr>
<tr>
<td>14</td>
<td>Winter</td>
<td>COW</td>
<td>Empty Feedlot Material</td>
<td>Clay Loam</td>
<td>Empty Feed Lot</td>
<td>FDL</td>
</tr>
<tr>
<td>15</td>
<td>Winter</td>
<td>COW</td>
<td>Old Feedlot Surface Material</td>
<td>Clay Loam</td>
<td>Empty Feed Lot</td>
<td>FDL</td>
</tr>
</tbody>
</table>

PCH - Pinal County Housing, COW - Cowtown, CG - Casa Grande
NAT - native soil, AGR - agricultural soil, PAV - paved road dust, DRA - dirt (unpaved) road dust from an agricultural area, DFR - dirt (unpaved) road dust from a cattle feedlot area (UPF), and FDL - soil from a cattle feedlot
Using this set of 11 fixed sampling sites, soil samples were collected during spring, fall, and winter with additional samples collected during unique events (e.g., a cotton field during cotton defoliation). In total, 35 soil samples were collected. All samples were obtained from the top 15 mm of the surface using a trowel, or by a hand broom from the paved surface, and placed into pre-baked glass jars for storage and transport (Hagen 2004).

7.3.2 Soil Resuspension

All soil samples were resuspended in the laboratory to simulate the process of windblown dust entrainment within the region and to obtain PM\(_{2.5}\) and PM\(_{10}\) size fractionated samples for subsequent chemical analysis.

Soil source samples were prepared for resuspension by baking at 110 °C for 24 hr and gently compressed to break up large aggregates but were not ground so as to avoid mechanical abrasion of small particles. Once prepared, samples were introduced into a clean flask and HEPA-filtered air was passed over the sample to resuspend small particles. The resuspended particles were passed through a size-selective cyclone (URG Corporation) and onto downstream filter media for collection. The operating flow rates were determined based on the cyclone design – 28 L/min for PM\(_{10}\) sampling and 42 L/min for PM\(_{2.5}\) sampling. Three filters, including one Teflon and two quartz-fiber filters were collected in parallel for each reentrainment experiment.
7.3.3 Soil Chemical Analysis

Re-suspended soil samples were analyzed chemically in a manner similar to the ambient PM samples (Clements, Fraser et al. 2012). Detailed information about quality control measures are also reported therein.

Gravimetric mass was determined by the difference between the pre- and post-collection weights of the Teflon filter. Sample weights were measured under controlled temperature (22 °C < T < 24 °C) and humidity conditions (45% < RH < 55%) to minimize water-uptake (U.S. EPA 2006). A minimum target of ~8 mg of resuspended material was established and sampling continued until this target was achieved or exceeded.

Following gravimetric analysis, the Teflon filter was microwave-digested using an acid mixture according to the method of Upadhyay, et. al 2011 (Upadhyay, Majestic et al. 2009; Clements, Fraser et al. 2012). The extract was then analyzed for 63 elements by high-resolution inductively coupled plasma mass spectrometry (ICP-MS) (ThermoFinnigan ELEMENT 2) using an internal indium standard. Elements quantified included, but were not limited to, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, Sb, Se, Sn, Ti, U, V, Zn. The instrument was calibrated using a multi-element standard (SPEX Certiprep Inc., USA) and two National Institute of Standards and Technology standard reference materials (San Joaquin Soil, SRM 2709 and Urban Dust, SRM 1649) were also measured for quality control.

Water-soluble ions were measured from a set of two 1.5-cm² punches that were removed from the quartz-fiber filter and extracted in 7.5 mL ultrapure water for 15 minutes in an
ultrasonic bath at room temperature. Extracts were filtered using a syringe filter (Millex GP 0.22 µm pore size PES membrane filter) and then analyzed for cations (sodium, potassium, ammonium, calcium, and magnesium) and anions (chloride, nitrate, phosphate, and sulfate) by ion chromatograph (Dionex IC20, Dionex Corporation) equipped with CG12A and AS12A analytical columns.

Bulk organic (OC), elemental (EC), and total carbon (TC) concentrations were analyzed by thermal-optical transmittance (TOT) (Birch and Cary 1996) using a slightly modified thermal protocol as described in Clements et al. 2012 (Clements, Fraser et al. 2012).

7.4 Results and Discussion

7.4.1 Chemical composition

Tables 5 and 6 present the average chemically speciated source profiles for PM$_{2.5}$ and PM$_{10}$ for each soil type, respectively. Standard deviations (SD) represent the pooled average of the soil samples for each soil type. Method detection limits (MDLs) for chemical species were calculated based on 3 x SD of filter blanks and the notation BDL refers to concentrations below the MDL. The chemical profiles of PM$_{2.5}$ and PM$_{10}$ are similar within the range of the variability (SD) among the samples taken within a given soil type for most chemical species. Al, Ca, Fe, K, and Mg are the most abundant elemental species observed (weight percent ≥ 1%) for all soil types, which is consistent with the known bulk composition of crustal material. OC is also a substantial component (>1% of PM mass) for all soil types in both size fractions.
The relative abundance of OC is between 2 and 17 times higher for FDL compared to the other soil types. Sulfate and phosphate are both found in the greatest abundance in FDL samples. The elevated abundance of these particular species is consistent with the cattle feeding operations and more specifically with the cattle feed itself.

Table 5: Average (±SD) of source profile chemical compositions (weight percent by mass) of resuspended PM$_{2.5}$ soils

<table>
<thead>
<tr>
<th>Species</th>
<th>Site</th>
<th>NAT</th>
<th>AGR</th>
<th>DRA</th>
<th>PAV</th>
<th>DRF</th>
<th>FDL</th>
</tr>
</thead>
<tbody>
<tr>
<td>OC</td>
<td>1.2 ± 0.7</td>
<td>3 ± 2</td>
<td>1.7 ± 0.5</td>
<td>7</td>
<td>2.8 ± 0.9</td>
<td>20 ± 6</td>
<td></td>
</tr>
<tr>
<td>EC</td>
<td>1.2 ± 0.7</td>
<td>3 ± 2</td>
<td>1.7 ± 0.5</td>
<td>7</td>
<td>2.8 ± 0.9</td>
<td>20 ± 6</td>
<td></td>
</tr>
<tr>
<td>TC</td>
<td>0.02 ± 0.03</td>
<td>0.04 ± 0.03</td>
<td>0.2 ± 0.2</td>
<td>0.08</td>
<td>0.5 ± 0.0</td>
<td>0.8 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>0.05 ± 0.09</td>
<td>0.03 ± 0.02</td>
<td>0.2 ± 0.2</td>
<td>0.05</td>
<td>0.8 ± 0.9</td>
<td>0.04 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>PO$_4^{3-}$</td>
<td>0.06 ± 0.03</td>
<td>0.09 ± 0.06</td>
<td>0.02 ± 0.02</td>
<td>0.15</td>
<td>0.10 ± 0.08</td>
<td>3 ± 1</td>
<td></td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>0.03 ± 0.04</td>
<td>0.1 ± 0.2</td>
<td>0.6 ± 0.2</td>
<td>0.2</td>
<td>17 ± 15</td>
<td>4 ± 4</td>
<td></td>
</tr>
<tr>
<td>Na$^+$</td>
<td>0.09 ± 0.05</td>
<td>0.20 ± 0.08</td>
<td>0.8 ± 0.2</td>
<td>0.2</td>
<td>0.46 ± 0.02</td>
<td>0.9 ± 0.3</td>
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</tr>
<tr>
<td>NH$_4^+$</td>
<td>0.06 ± 0.05</td>
<td>0.12 ± 0.10</td>
<td>0.5 ± 0.5</td>
<td>0.02</td>
<td>0.2 ± 0.3</td>
<td>0.2 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>K$^+$</td>
<td>0.11 ± 0.03</td>
<td>0.14 ± 0.07</td>
<td>0.07 ± 0.02</td>
<td>0.07</td>
<td>0.369 ± 0.005</td>
<td>3 ± 1</td>
<td></td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>0.02 ± 0.01</td>
<td>0.04 ± 0.02</td>
<td>0.02 ± 0.01</td>
<td>0.02</td>
<td>0.09 ± 0.06</td>
<td>0.5 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>0.4 ± 0.2</td>
<td>0.7 ± 0.5</td>
<td>0.5 ± 0.2</td>
<td>0.6</td>
<td>6 ± 6</td>
<td>1.1 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>8 ± 1</td>
<td>7 ± 3</td>
<td>7 ± 1</td>
<td>7</td>
<td>5 ± 1</td>
<td>4 ± 2</td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>0.0012 ± 0.0003</td>
<td>0.0014 ± 0.0003</td>
<td>0.0014 ± 0.0002</td>
<td>0.002 ± 0.001</td>
<td>0.0007 ± 0.0003</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba</td>
<td>0.054 ± 0.004</td>
<td>0.05 ± 0.02</td>
<td>0.05 ± 0.01</td>
<td>0.06</td>
<td>0.04 ± 0.01</td>
<td>0.03 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>2.2 ± 0.3</td>
<td>4 ± 2</td>
<td>6 ± 1</td>
<td>3</td>
<td>10 ± 5</td>
<td>7 ± 3</td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>0.002 ± 0.002</td>
<td>0.002 ± 0.001</td>
<td>0.0016 ± 0.0002</td>
<td>0.002 ± 0.001</td>
<td>0.0007 ± 0.0002</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>0.005 ± 0.001</td>
<td>0.004 ± 0.001</td>
<td>0.005 ± 0.000</td>
<td>0.007</td>
<td>0.003 ± 0.001</td>
<td>0.003 ± 0.001</td>
<td></td>
</tr>
<tr>
<td>Cs</td>
<td>0.0016 ± 0.0003</td>
<td>0.002 ± 0.001</td>
<td>0.0011 ± 0.0002</td>
<td>0.001</td>
<td>0.0011 ± 0.0003</td>
<td>0.0008 ± 0.0004</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.008 ± 0.002</td>
<td>0.10 ± 0.005</td>
<td>0.0049 ± 0.0004</td>
<td>0.03</td>
<td>0.007 ± 0.001</td>
<td>0.009 ± 0.002</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>4.0 ± 0.2</td>
<td>3.7 ± 1.0</td>
<td>3.7 ± 0.4</td>
<td>4</td>
<td>2.5 ± 0.6</td>
<td>1.8 ± 0.8</td>
<td></td>
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<tr>
<td>Ga</td>
<td>0.0022 ± 0.0002</td>
<td>0.002 ± 0.001</td>
<td>0.0017 ± 0.0002</td>
<td>0.002 ± 0.0015</td>
<td>0.0004 ± 0.0009</td>
<td>0.0004 ± 0.00004</td>
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<tr>
<td>K</td>
<td>3.6 ± 0.7</td>
<td>3.0 ± 0.5</td>
<td>3.2 ± 0.9</td>
<td>2</td>
<td>2.8 ± 0.5</td>
<td>6 ± 5</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>1.9 ± 0.4</td>
<td>1.6 ± 0.5</td>
<td>2.1 ± 0.5</td>
<td>2</td>
<td>1.2 ± 0.3</td>
<td>2.1 ± 1.0</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.15 ± 0.01</td>
<td>0.13 ± 0.04</td>
<td>0.12 ± 0.02</td>
<td>0.09</td>
<td>0.08 ± 0.01</td>
<td>0.06 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>0.31 ± 0.03</td>
<td>0.4 ± 0.1</td>
<td>1.2 ± 0.2</td>
<td>0.6</td>
<td>0.56 ± 0.07</td>
<td>1.0 ± 0.6</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>0.004 ± 0.001</td>
<td>0.004 ± 0.001</td>
<td>0.003 ± 0</td>
<td>0.005</td>
<td>0.002 ± 0</td>
<td>0.004 ± 0.001</td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>0.12 ± 0.01</td>
<td>0.13 ± 0.04</td>
<td>0.11 ± 0.01</td>
<td>0.2</td>
<td>0.26 ± 0.05</td>
<td>1.9 ± 1.0</td>
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</tr>
<tr>
<td>Pb</td>
<td>0.007 ± 0.002</td>
<td>0.006 ± 0.002</td>
<td>0.003 ± 0</td>
<td>0.02</td>
<td>0.004 ± 0.001</td>
<td>0.003 ± 0.001</td>
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</tr>
<tr>
<td>Rb</td>
<td>0.013 ± 0.002</td>
<td>0.011 ± 0.004</td>
<td>0.012 ± 0.002</td>
<td>0.01</td>
<td>0.008 ± 0.001</td>
<td>0.010 ± 0.003</td>
<td></td>
</tr>
<tr>
<td>Sb</td>
<td>0.0002 ± 0.0001</td>
<td>0.0002 ± 0.0001</td>
<td>0.00015 ± 0.00001</td>
<td>0.001</td>
<td>0.0002 ± 0.0000</td>
<td>0.0002 ± 0.0001</td>
<td></td>
</tr>
<tr>
<td>Sr</td>
<td>0.019 ± 0.002</td>
<td>0.03 ± 0.01</td>
<td>0.045 ± 0.005</td>
<td>0.02</td>
<td>0.041 ± 0.001</td>
<td>0.04 ± 0.04</td>
<td></td>
</tr>
<tr>
<td>Th</td>
<td>0.0017 ± 0.0003</td>
<td>0.002 ± 0.001</td>
<td>0.0015 ± 0.0003</td>
<td>0.002</td>
<td>0.0014 ± 0.0002</td>
<td>0.0009 ± 0.0004</td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>0.30 ± 0.04</td>
<td>0.27 ± 0.09</td>
<td>0.27 ± 0.05</td>
<td>0.3</td>
<td>0.17 ± 0.03</td>
<td>0.12 ± 0.05</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>0.0081 ± 0.0003</td>
<td>0.008 ± 0.002</td>
<td>0.007 ± 0.001</td>
<td>0.008</td>
<td>0.006 ± 0.001</td>
<td>0.003 ± 0.001</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>0.020 ± 0.002</td>
<td>0.020 ± 0.007</td>
<td>0.014 ± 0.001</td>
<td>0.1</td>
<td>0.018 ± 0.008</td>
<td>0.09 ± 0.05</td>
<td></td>
</tr>
</tbody>
</table>

SD was calculated from the average of the aggregated samples from each site BDL is defined as below detection limit

The relative abundance of OC in PAV is about 2-6 times higher than in the other soil types (excluding FDL). The relative abundance of EC is at least an order of magnitude
higher than in samples from other sites, including NAT, DRA, and AGR, where the EC values are below their MDL. Several anthropogenic elements including copper, lead, and zinc are higher by factors of 3-10 over other soil types as well. The presence and abundance of these elements suggest impacts from traffic. These results are consistent with high concentrations of these elements in ambient PM$_{2.5}$ collected from a parking garage in Tempe, Arizona (Majestic, Anbar et al. 2009). Lough et al (Lough, Schauer et al. 2005) suggest that the dominance of Ba, Cu, Pb, and Zn are associated with both tailpipe emissions and mechanical abrasion of vehicle breaks and lead weights used to balance tires.
The relative abundance of the chemical components measured in NAT, AGR, and DRA soil types are in general similar even though the land use patterns are different.

Exceptions include sulfate and sodium ion, which are about 4 – 10 times higher in DRA than in NAT and AGR samples. Although there is considerable variability among the soil types, ammonium, nitrate, and chloride ions also show a pattern of being an order or magnitude higher in DRA than the other two sites. These species are components of agricultural wastes and fertilizers and have been reported as markers for active...
agricultural farms (Cao, Chow et al. 2008). Elevated relative abundances of these ions found in DRA samples, rather than AGR samples, are likely due to overspray of fertilizers, the active mixing of soil by moving vehicles, deposition of windblown dust onto the road from the adjacent agricultural fields, runoff from fields, and/or the lack of regular irrigation that occurs on AGR during growing season. Depressed abundances of these ions in the NAT and AGR samples may be the result of uptake by plants.

The relative abundances of calcium, nitrate, and sulfate were higher in DRF than the other soil types and were of similar magnitude in both the PM$_{2.5}$ and PM$_{10}$ size fractions. Calcium and sulfate species may be a result of the application of calcium lignosulfonate, a by-product of wood processes, being used as a dust suppressant (Ouyang, Qiu et al. 2006) as well as an animal feed binder (Kaliyan and Vance Morey 2009). Concentrations of these species, in excess of that found in the natural soils, may be distinct fingerprints for the use calcium lignosulfonate as a soil or animal feed binder.

As previously noted, the relative abundances of Al, Ca, Fe, K, and Mg are high in all soil types in both the PM$_{2.5}$ and PM$_{10}$ size fractions. However, the lowest relative abundance of Al and Fe are found in feedlot samples due to the higher fraction of organic material associated with the feedlot (Tables 2 and 3). Of particular interest in the FDL samples are the concentrations of PO$_4^{3-}$ and P, which have similar relative abundances in both size fractions and are considerably higher than observed in the other soil types. PO$_4^{3-}$ and P abundances were 2.8% and 1.4% in PM$_{2.5}$ and 3.9% and 1.3% in PM$_{10}$, respectively. Similar abundances of PO$_4^{3-}$ in feedlot profiles (5.7 ± 2.4%) were observed in Fresno and (4.0 ± 1.0%) in Kern County as reported by (Chow, Watson et al. 2003). Higher concentrations of nutrient-related species (e.g., K, K$^+$, Na$^+$, Mg$^{2+}$, Cl$^-$, Ca$^{2+}$, Ca, and
SO$_4^{2-}$) are also found in FDL samples. These results indicate that PO$_4^{3-}$ and K$^+$ may be distinct marker species for the FDL samples, although soluble K (K$^+$) also is a marker for wood combustion (Calloway, Li et al. 1989; Khalil and Rasmussen 2003). These results are consistent with feedlot profiles reported in a previous study (Chow, Watson et al. 2003). The Cl$^-$ content in FDL is fairly well-correlated with Na$^+$, K$^+$, and NH$_4^+$ ($R^2 \geq 0.82$) and Mg$^{2+}$ and PO$_4^{3-}$ and K$^+$ and SO$_4^{2-}$ pairs are also well-correlated ($R^2 \geq 0.90$) indicating that these correlated components may be associated salts.

7.4.2 Total versus soluble fractions of elements

Samples were extracted in water to determine the water-soluble ionic fraction of the sample relative to the total element content determined by acid digestion. The water-soluble fraction of selected elements in PM$_{2.5}$ and PM$_{10}$ is shown in Figure 25 for each soil type. The mole fraction of P in PO$_4^{3-}$ (soluble P) was used to calculate the water-soluble fraction of phosphorus since PO$_4^{3-}$ is the measured species. Results show distinct solubility patterns for Mg, K, and P in FDL samples and Ca in DRF relative to the other soil types. Over half the Na is in the form of soluble salts in both size fractions for DRA, DRF, and FDL and in PM$_{10}$ at AGR. With the exception of Ca for DRF and K and P for FDL the other components were less than 50% soluble in water. For FDL, all components appeared to be more soluble in PM$_{10}$ than PM$_{2.5}$ by about 30-40%. The fraction of soluble Mg and K was higher (> 5%) for DRF and FDL which may be attributed to the proximity to the cattle feedlot. The higher solubility of the selected elements in PM$_{10}$ rather than in PM$_{2.5}$ suggests that the “fertile” soils, characterized by the soluble forms of these elements, are associated more with the coarse particle fraction.
Figure 25: Solubility of Five Chemical Species in Local Resuspended Soil Samples

DRF is distinct in terms of soluble Ca with about 70% and 80% solubility in PM$_{2.5}$ and PM$_{10}$, respectively. In other soil types, soluble Ca ranged between 10% to 20% in both size fractions. Higher solubility of Ca in conjunction with high SO$_4^{2-}$ content at DRF supports the application of calcium salts. Overall, results suggest that the soils impacted by feedlot activities are chemically different and the markers species, especially K$^+$ and
PO$_4^{3-}$, can be used to discriminate this soil type from the natural soil sources, although care must be taken as soluble K (K$^+$) is also a marker for wood combustion (Calloway, Li et al. 1989).

### 7.4.3 Reconstructed Mass Balance

A mass balance is estimated to verify that major components have been accounted for by the measured species, thus providing a quality assurance check on the measured components and mass. The mass balance summary and major components are shown in Figure 26. The organic matter (OM) component was determined as 1.4 x OC. The crustal component was based on the reconstructed soil mass determined by the IMPROVE (Interagency Monitoring of Protected Visual Environment) approach.

\[
\text{Crustal} = 2.20* \text{Al} + 2.49* \text{Si} + 1.63* \text{Ca} + 2.42* \text{Fe} + 1.94* \text{Ti}
\]  

(1)

The carbonate and water components often included in the crustal calculation were not included as they were not directly measured in this study. Since Si was not analyzed by ICP-MS, its mass in the sample was estimated based on the average ratio of Si/Al = 3.5. This value was estimated based on the average Si/Al ratios of 3.8, 3.0, and 3.5 observed in the average composition of UCC (Taylor and McLennan 1995); road dust or agricultural soil in the Imperial Valley, California, USA (Watson and Chow 2001); and road dust in an urban area of Texas, USA (Chow, Watson et al. 2004), respectively. The phosphate and sulfate components are pure components containing just the ionic species themselves. The non-soil K component was determined by difference between the measured K and the calculated soil K where soil K was determined as 0.6 x Fe. The trace element component was determined as the sum of all other trace metals not included in
the soil equation with no correction factors applied and ionic species not accounted for as pure components. The reconstructed mass balance showed that these components, on average, account for $102 \pm 8\%$ of resuspended soil mass across all sites, with crustal as the single dominant component of PM$_{2.5}$ and PM$_{10}$.

Crustal material is the dominant contributor to all soil types in both size fractions (Figure 26). It accounts for 63% and 81% of FDL and DRF, respectively and from 94-100% across the other soil types in the PM$_{2.5}$ size range and for 44% of FDL and between 78-91% of the other soil types in the PM$_{10}$ size range. These results are consistent with findings that report soil elements are the major components of fine and coarse PM in Phoenix (Katrinak, Anderson et al. 1995; Tolocka, Solomon et al. 2001; Lewis, Norris et al. 2003). OM in PM$_{2.5}$ ranged from less than 5% in NAT, AGR, and DRA to 10% in PAV, to a maximum of 27% in FDL. SO$_4^{2-}$ was only high in DRF accounting for approximately 21% of the PM$_{10}$ mass. The smaller crustal fraction in FDL was due to the higher fraction of OM, SO$_4^{2-}$, and non-soil K, accounting for 49% PM$_{10}$ mass consistent with modification by cattle farm activities appearing to greatly modify the chemical characteristics of soils as observed in the OM and SO$_4^{2-}$ content of both DRF and FDL.

Overall, the mass closure agrees to within 20%, which is typical for mass balance estimates given the assumptions associated with estimating compounds based on the measured elements and species. These results indicate that human activities, such as motor vehicle traffic and cattle farming activities, can greatly modify the chemical characteristics of soils impacted by these sources.
Figure 26: Bulk Chemical Composition of Local Resuspended Soil Samples
7.5 Conclusions

Samples collected from different soil types in Pinal County, AZ were resuspended in the laboratory. Soil types included native (NAT), agricultural (crop farming, AGR), dirt roads adjacent to agricultural areas (DRA), paved road (PAV), dirt road within and adjacent to a cattle feedlot (DRF), and a cattle feedlot (FDL). Following resuspension of the soil in the laboratory, size-segregated PM$_{2.5}$ and PM$_{10}$ fractions for each soil type were collected on filters and characterized for mass, ions, OC, EC, trace elements, and a range of organic species. Results showed that the chemical abundances for the majority of species are similar in PM$_{2.5}$ and PM$_{10}$ samples. Crustal related elements (Al, Ca, Fe, and Mg), K, and OC are abundant in all soil types (mass percent by weight $\geq 1\%$), Ca and Ca$^{2+}$, and SO$_{4}^{2-}$ are most abundant in DRF, and OC and PO$_4^{2-}$ are most abundant in FDL. Phosphate is a possible unique marker for cattle feedlots. Calcium and sulfate may be related to calcium lignosulfonate used as a dust suppressant and animal feed binder.

Vehicular movement and wind likely help mix agricultural soil with dirt roads in the vicinity of agricultural fields (DRA). This mixing and overspray of fertilizers likely results in an increase in the relative abundance of NH$_4^+$, SO$_4^{2-}$, NO$_3^-$, Cl$^-$, and Na$^+$, which are an order of magnitude more abundant in DRA than in NAT and AGR samples. Decreased abundances of these elements in the fallow and crop lands are suggestive of removal by plant uptake. Fugitive dust emissions from the undisturbed agricultural soil may therefore contain lower concentrations of these species than the dust released during the land preparation.
The abundance of Cu, Pb, and Zn are an order of magnitude higher in PAV, consistent with motor vehicle sources. Mass balance analysis showed that the crustal component comprises most of the particle mass in both PM$_{2.5}$ and PM$_{10}$. This is consistent with previous aerosol studies in Phoenix, Arizona.

This work delineates the variation in chemical composition of various soil types impacting the study region. The chemical composition of native soils within the region shed some light on the regional composition of soils in the desert southwest. In total, the results from this study can be used to assess the contribution of local dust emission sources to atmospheric PM pollution.
Chapter 8: Source Identification of Coarse Particles in the Desert Southwest, USA using Positive Matrix Factorization

8.1 Abstract

The Desert Southwest Coarse Particulate Matter Study was undertaken to further our understanding of particulate matter (PM) in rural, arid, desert environments. Sampling was conducted between February 2009 and February 2010 in Pinal County, AZ near the town of Casa Grande where particulate matter (PM) concentrations routinely exceed the National Ambient Air Quality Standards (NAAQS) for both PM$_{10}$ and PM$_{2.5}$. In this desert region, exceedances of the PM$_{10}$ NAAQS are dominated by high coarse particle concentrations, a common issue in the desert southwest. This work expends on previously published measurement and chemical characterization work by examining the sources of fine and coarse particles and the relative contribution of each to ambient PM mass concentrations using the positive matrix factorization receptor model.

Coarse particles within the region were apportioned to nine sources including primary biological aerosol particles (PBAPs - 25%), crustal material (20%), re-entrained road dust (11%), feedlot (11% at the COW site), secondary particles (10%), boron-rich crustal material (9%), transported soil (6%), ammonium nitrate (4%), and salt (2%). Fine particles within the region were apportioned to six sources including motor vehicles (37%), road dust (29%), lead-rich (10%), break wear (5%), crustal (4%), and salt (3%).

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4 This chapter is based on a journal manuscript, led author Andrea L. Clements, which has been prepared and submitted to US EPA Office of Research and Development for clearance. We intend to submit this manuscript to Atmospheric Pollution Research.
About 8% of coarse particle mass and 12% of fine particle mass remained un-apportioned.

8.2 Introduction

The National Ambient Air Quality Standards (NAAQSs) were established as a means of protecting human health from the damaging effects of air pollution (42 U.S.C. 7409). Numerous studies have demonstrated a link between ambient particulate matter (PM) and adverse human health effects (Mar, Norris et al. 2000; Peters, Liu et al. 2000; Samet, Dominici et al. 2000; Krewski and Rainham 2007; Anderson 2009). These findings have lead to the establishment of two Federal NAAQS for particles, one for PM$_{10}$ (particles with an aerodynamic diameter [AD] less than or equal to a nominal 10$\mu$m) and another for PM$_{2.5}$ (particles with an AD less than or equal to a nominal 2.5$\mu$m) (http://www.epa.gov/air/criteria.html). The PM$_{10}$ is the sum of the fine fraction (PM$_f$), also known as PM$_{2.5}$, and the coarse fraction (PM$_c$; particles with AD in the size range between 2.5 and 10 $\mu$m AD). Many counties in the Southwest United States (SW US) have measured ambient concentrations of these particles in excess of the Federal standards (U.S. EPA 2008). Previous monitoring work in the region has shown that exceedances of the PM$_{10}$ NAAQS in the SW US are often the result of spikes in the PM$_c$ mass concentration because coarse particles dominate the overall mass concentrations within the region (U.S. EPA AirData ; Cheung, Daher et al. 2011). When a region is out of compliance with the NAAQS, the law requires the State containing that region to develop State Implementation Plans (SIPs) designed to reduce PM concentrations to levels below the NAAQS (40 CFR 110.51). The development of SIPs requires
knowledge of emission sources, emission strength, spatial and temporal variation in ambient particle concentrations, and source impacts.

In rural areas like the desert Southwest, elevated coarse particle concentrations are often attributed to the landscape or desert concluding that little can be done to manage high concentrations. Previous studies have indeed found links between the entrainment of soil dust and weather conditions (Brazel and Nickling 1986), wind conditions (Holcombe, Ley et al. 1997; Hagen 2004), soil type (Macpherson, Nickling et al. 2008), as well as with soil moisture conditions (Ellis, Brommer et al. 2006). Several studies have found that crustal sources are major contributors to coarse particle mass concentrations desert Southwest (Gertler, Lowenthal et al. 1995; Watson and Chow 2001; Lewis, Norris et al. 2003; Pinal County Air Quality Staff 2005; Cheung, Daher et al. 2011). Recent work to address exceedances of the PM$_{2.5}$ NAAQS have found that local dust sources responsible for PM$_{10}$ NAAQS violations are also contributing to elevated fine particle concentrations (ADEQ 2010).

A few studies have been conducted to distinguish between several similar soil types – for example, road dust and agricultural soils (Paode, Shahin et al. 1999; Hwang, Hopke et al. 2008), while still others have measured the composition of soil source materials to identify chemical species unique to that source or source type (marker species), which can help to further distinguish soil types (Rogge, Hildemann et al. 1993; Rogge, Medeiros et al. 2007). Still, more work is needed to understand the magnitude of the crustal source and to understand what sources, crustal and otherwise, can be regulated to reduce PM levels below NAAQS. A few studies have been conducted within this region to better understand the range of source impacts, beyond crustal material, and their
relative contribution to ambient particle concentrations (Gertler, Lowenthal et al. 1995; Watson and Chow 2001; Pinal County Air Quality Staff 2005).

The Desert Southwest Coarse Particulate Matter Study was conducted in and around the town of Casa Grande in Pinal County, Arizona which experiences the highest PM$_c$ concentrations in the region (U.S. EPA AirData). Previous studies have lacked the scope, in terms of length (number of samples and seasons studied) and chemical characterization available from this study. This large data set also allows application of the positive matrix factorization (PMF) source-receptor model, rather than the chemical mass balance (CMB) model used when the number of chemically resolved samples is limited. This paper expands on the work already presented from this study (Clements, Fraser et al. 2012) by detailing the PMF modeling results for PM$_c$ and PM$_f$ within the region including source profiles, source identification, and spatially resolved yearly averaged and seasonal contributions to PM mass within the region.

8.3 Methods

8.3.1 Ambient Sampling and Chemical Characterization

The PMF modeling approach was used on the 1-in-6 day data set derived from filter-based ambient aerosol samples collected between February 2009 and February 2010 at three monitoring locations in Pinal County, AZ in and around the vicinity of the town of Casa Grande, population of roughly 50,000, located south of Phoenix, AZ. Detailed information about the ambient sampling locations can be found in Clements et al. 2012a (Clements, Fraser et al. 2012). Briefly, samples were collected at three ambient monitoring locations including the town of Casa Grande (CG), a small urban location
located in a business district more distantly surrounded by residential neighborhoods with trees; Cowtown (COW), a rural site located approximately 27 km to the northwest of the city of Casa Grande locally impacted by a cattle feedlot, a grain processing operation, and railroad and vehicle traffic; and Pinal County Housing (PCH), another rural site more closely impacted by active agricultural fields.

Each sampling site was equipped with Sierra-Anderson Model 241 dichotomous samplers which collected three sets of equivalent 24-hr samples ambient particular matter samples on a one-in-six day schedule. Each sampler collected two filters representing PM$_{t}$ and PM$_{c}$ size fractions, respectively. Two of the three filters sets were collected on Teflon media and were used to determine ambient PM mass, ion, and element concentrations. The remaining filter set was collected on quartz-fiber filter media and was used to determine ambient bulk elemental carbon (EC) and organic carbon (OC) concentrations.

Ambient mass concentrations were determined gravimetrically from each of the Teflon filters and the average of the two colocated filters was used unless one measurement was invalidated. After gravimetric measurement, one set of Teflon filters was wetted with 150 µl of ethanol (Fisher HPLC grade) and then extracted into 10 ml of ultrapure water and analyzed for five anion and five cation species by ion chromatography (Dionex IC20 system with CG12A and AS12A analytical columns). The second set of Teflon filters was microwave digested into a nitric, hydrochloric, and hydrofluoric acid mixture and then analyzed for 63 trace elements by high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS, herein referred to as ICP-MS, ThermoFinnigan ELEMENT 2) by Nabin Upadhyay in professor Herckes’ research group. Ambient bulk OC and EC concentrations were determined by thermal-optical analysis of a 1 cm x 1.5 cm punch
from the quartz-fiber filters using the Sunset Labs EC/OC analyzer (Tigard OG) (Birch and Cary 1996).

8.3.2 Positive Matrix Factorization Framework

PMF modeling was conducted on the 1-in-6 day measurements using the EPA PMF model version 3.0 (U.S. EPA 2011). This approach looks for statistical correlations within the chemical components to isolate factors based on observed co-variation within the chemical species. These data from the three ambient sampling locations were combined into two datasets (one for PMc and one for PMf) and modeled as a group to isolate a number of sources that were similar across this sampling region. This allowed for consistency in the factor, and therefore, in the estimated source profiles. These data were combined by assigning the data set from each ambient site with a fake sampling year. The sampling month and day were not altered leaving the chronological order intact for each site. Treating the data in this manner allowed for the resolution of one consistent set of source profiles, while still allowing for the influence of each to be investigated based on sampling location. Initially, two distinct factors were isolated. Additional factors were added in successive PMF modeling runs as long as three criteria were met.

1. The resulting factor profiles either became more consistent with expected source profiles or a new distinct source was isolated;
2. The model estimation of the variation in factor profiles between multiple model runs was further minimized; and
3. The reconstructed mass concentration showed better agreement with the measured data.

The modeling results were considered optimized when additional factors failed to meet these criteria.

The modeling results were also optimized based on other criteria. Analysis was initially performed on the entire 1-in-6 day dataset using the available concentrations and a detection limit substitution for all species which were not detected under these circumstances. Next, a set of species was removed from consideration during the analysis based on the dynamic range of the data. If the dynamic range of a species’ concentration was small and just a few distinct concentrations were observed, the species was excluded from consideration during the analysis because variation is essential to source factor separation. Next, several species with low and consistent concentrations were designated as weak, thereby increasing the uncertainty and loosening the constraints on the model fitting of these species’ concentrations. At this point, the optimal number of factors was determined. The results were refined by eliminating just a few sampling dates, which appeared to have significant outliers (greater than three standard deviations of the mean) in the concentration of one or more species being modeled. This resulted in the removal of four sampling dates across the entire data set. Next, the uncertainty for species that were not well modeled was increased by designating them weak variables. If the model performance was enhanced, this designation remained. Lastly, some species were eliminated if successive modeling runs resulted in large variation in the apportionment of species to source factor profiles.
Once optimized, the factor composition was used to identify prominent sources of PMc and PMf particles within the region. Factors were either named for their prominent species or named based on a familiar compositional signature as described below.

### 8.4 Results and Discussion

#### 8.4.1 Fine and Coarse Particle Mass Balance

Table 7 details the study average chemical composition of fine and coarse particles collected at each of the ambient monitoring locations. Additional details about the PMc and PMf composition and seasonality can be found in Clements et al. (Clements, Fraser et al. 2012).

**Table 7: Average Particle Mass and Composition**

<table>
<thead>
<tr>
<th></th>
<th>Casa Grande</th>
<th>Cowtown</th>
<th>Pinal County Housing</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Coarse Particle Mass</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mass</td>
<td>31 µg/m³</td>
<td>67 µg/m³</td>
<td>46 µg/m³</td>
</tr>
<tr>
<td>Crustal</td>
<td>54%</td>
<td>47%</td>
<td>52%</td>
</tr>
<tr>
<td>Organic</td>
<td>12%</td>
<td>26%</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>0.1%</td>
<td>0.1%</td>
<td>0.1%</td>
</tr>
<tr>
<td>Other Measured Species</td>
<td>7%</td>
<td>8%</td>
<td>6%</td>
</tr>
<tr>
<td>Unidentified</td>
<td>24%</td>
<td>17%</td>
<td>30%</td>
</tr>
<tr>
<td><strong>Fine Particle Mass</strong></td>
<td>8 µg/m³</td>
<td>11 µg/m³</td>
<td>9 µg/m³</td>
</tr>
<tr>
<td>Crustal</td>
<td>22%</td>
<td>24%</td>
<td>46%</td>
</tr>
<tr>
<td>Organic</td>
<td>46%</td>
<td>38%</td>
<td>27%</td>
</tr>
<tr>
<td>Nitrate</td>
<td>8%</td>
<td>13%</td>
<td>6%</td>
</tr>
<tr>
<td>Sulfate</td>
<td>12%</td>
<td>9%</td>
<td>10%</td>
</tr>
<tr>
<td>Ammonium</td>
<td>0.1%</td>
<td>0.1%</td>
<td>0.1%</td>
</tr>
<tr>
<td>Other Measured Species</td>
<td>7%</td>
<td>6%</td>
<td>7%</td>
</tr>
<tr>
<td>Unidentified</td>
<td>5%</td>
<td>10%</td>
<td>4%</td>
</tr>
</tbody>
</table>
Organic matter was estimated by multiplying the bulk OC measurement by a factor of 2 and the crustal material component was estimated based on assuming the common oxide form of 5 abundant trace elements found in soils as detailed by Marcazzan et. al (Marcazzan, Vaccaro et al. 2001). The unidentified component was determined by the difference between the gravimetric mass and the sum of the chemical components.

On average, coarse particles measured at all sites are: crustal material (~50% of the particle mass), organic material (10%), nitrate and sulfate (2%), and other measurable ions and elemental species (8%). Approximately 24% of PMc was unidentified based on the chemical analyses performed and may include particle bound water, which was not measured and other metal oxides not identified as major soil related species. The organic material fraction varied the most among the three sites as shown in Table 7.

On average, fine particles measured at all sites are: organic material (~37% of the particle mass), crustal material (30%), nitrate and sulfate (19%), and other measurable ions and elemental species (7%). Approximately 8% of PMf was unidentified based on the chemical analyses performed. For PMf, the organic material fraction was highest at CG where motor vehicles (MV) emissions are assumed to be more dense due to the residential nature of the community. Vehicle traffic count on a residential road within one block of the CG monitor site and the paved highway a similar distance from the COW monitor show nearly twice as much traffic in the vicinity of the CG site further supporting this assumption.
8.4.2 Model Performance Evaluation

Figure 27 shows the agreement between measured and model estimated mass for both PMc and PMf mass concentrations at each of the sampling sites, one criterion for good model performance. For PMc, the correlation is excellent, yielding modeled concentrations within 30 percent of the measured mass concentrations. Based on the regression slope, model performance appears best at the COW sampling site where modeled concentrations are roughly within 5% of the measured mass. Although agreement is still within 30% at the CG site, the variation in the data is greater reflected by an $r^2$ of 0.74. For PMf the agreement is within 30 percent, similar to PMc; however, the data are not as well correlated.

![Figure 27: PMF Model Mass Performance Evaluation](image)

8.4.3 PMc Source Profiles

Nine PMc source factor profiles were isolated by PMF as shown in Figure 28 and identified based on the sources they were believed to represent. Four factors were
identified based on their dominant constituents - ammonium nitrate, salt, secondary, and boron-rich. The likely sources of the first two of these factors appears straightforward. Fertilizer is likely responsible for the ammonium nitrate source. Salt may result from the desert playa dust and marine particles which are blown into the area during the monsoon season.

The secondary source factor was so named based on the dominance of sulfate and nitrate in this factor. Although not paired with a counter-ion like ammonium as expected when considering fine particles, the sulfate and nitrate was assumed to have been formed by the atmospheric oxidation of gaseous precursors and/or reaction of nitric and sulfuric acids with basic crustal material. The boron-rich source has not been definitively identified. Half of the measured boron was attributed to this factor, which also appears to contain a small fraction of some of the crustal elements which is consistent with an observation that boron may have an agricultural source.
Figure 28: Coarse Particle Source Profiles for the 9 Factor Solution
Three factors, crustal material, road dust, and transported soil, have similar profiles containing a number of trace elements representing a soil-like particle. The differentiation between crustal factors has been made based on the ion species within each profile. The crustal source factor lacks ion species, but contains approximately half of the measured aluminum, iron, and calcium known to be dominant elements in almost all crustal materials. The road dust factor included similar elements but also contained approximately 40% of the measured lead and 30% each of the measured copper and zinc. These elements are hypothesized to be most closely associated with tire and brake wear from motor vehicles and thus also from re-suspended road dust. However, past and present smelting operations may also be responsible for Pb, Cu, and Zn emissions. There are no currently operating smelters within the same air shed as these monitoring locations, but historical operations may have contaminated surface soils. The transported soil factor included a significant amount of organic carbon and sulfate. Again, the sulfate is assumed to be a result of atmospheric oxidation of SO$_2$ gas which occurred in an aqueous coating on the soil-like aerosol particles.

One factor was isolated that impacts COW more than the other two sampling sites. This factor was labeled feedlot in reference to the local source impacting this site. This factor contains high concentrations of organic carbon as well significant amounts of the measured magnesium, potassium, and phosphate. The last two components had measurable concentrations only at the COW site and have also been found in source soil samples collected near and within cattle feedlots (Upadhyay, Clements et al. 2012).

Primary biological aerosol particles (PBAPs), the most abundant factor, were identified based on the OC component as well as the large portion of cation species and sulfate.
These two observations suggested the factor may be biological in nature (Elbert, Taylor et al. 2007). Seasonal analysis revealed additional information, which lent weight to the assignment and is discussed below. A previous study within the region has shown a positive correlation with some allergens and coarse particles (Boreson, Dillner et al. 2004).

8.4.4 PMc Source Apportionment by Site

Figure 29 shows the relative source contribution, as a percent of the apportioned PMc mass, for each source factor identified at each site averaged over the course of the study. The apportioned PBAP factor contributes about 25% to the apportioned mass on average. This contribution is highest at COW, which is impacted by the grain processing plant, feedlot, and other agricultural activities in close proximity. On average, the crustal component contributes approximately 20% to the apportioned mass. The contribution is highest at PCH, which is impacted by agricultural activities near the site. Apportioned contributions of crustal material, road dust, and transported soil, all associated with crustal material, comprise about 35-40% of the apportioned mass, similar to the estimated crustal fraction based on the measured chemistry (Table 7). The large contribution of road dust at the urban CG location maybe due to its location in the center of Casa Grande and proximity to a large number of mobile sources within the area. The feedlot factor is only important at COW, which is adjacent to this unique source. The overall contribution of feedlot material to PMc mass concentrations measured at COW may be greater than what has been modeled. The feedlot source factor profile only includes the unique soluble ion species and not the significant crustal component found in the chemical
profile of feedlot material (Upadhyay, Clements et al. 2012). Overall approximately 10% of the particle mass remains unattributed to any of the resolved sources.

![Graph showing PMF Source Apportionment of Coarse Particles](image)

**Figure 29: PMF Source Apportionment of Coarse Particles**

8.4.5 **Apportionment of PMc by Season**

Figure 30 shows the monthly averaged PMc mass apportioned at each site. The influence of the PBAPs factor is most important and also most variable at the COW site driven by the feedlot and associated agricultural sources. Concentrations are highest during the spring (March and April) and fall (October) months, consistent with the planting, harvesting, and blooming, within the region. The crustal source is most important and most variable at PCH. Elevated apportioned PMc mass concentrations measured during March, August, October, November, and December are driven by variations in this factor likely due to the farming activities in the area and wind storms.

The contribution from the road dust source is fairly low but tends to peak during the planting and harvesting seasons and results from more dust on local roadways as well and vehicle traffic to accomplish these tasks. The highest apportioned concentrations found
at the urban CG site, suggesting the influence of a motor vehicle source. At CG, the apportioned mass from this factor was slightly elevated during the cooler winter months (October through March) consistent with the increase in the number of winter residents in the area (Arizona Office of Tourism). The feedlot factor is only important at COW and appears to be one of three main sources influencing peak PMc months, such as October. Apportioned concentrations from the feedlot are highest during spring (April, May, June) and again in August and October. A large decline in the feedlot contribution at the end of the sampling period (February) is likely due to removal of cattle from the adjacent fields to other feedlots within the region. The PMc mass contribution from the remaining sources is relatively small. The contributions from secondary sources are lowest during the spring months (February through April). The contribution from transported soil is elevated during the fall and winter months. The ammonium nitrate source exhibits the strongest seasonal differences contributing least during the summer months when fertilizer use is at a minimum and temperatures are highest, promoting volatilization into the gas phase. Lastly, the salt factor contributes most during the planting and harvesting month when the desert playa soil is disturbed but also shows an increased contribution during the summer (June and July) months when the winds shift during summer monsoons bringing air masses from the Gulf of Mexico region.
Figure 30: Seasonal Variation of PMF Apportioned Coarse Particle Mass
8.4.6 PMf Source Profiles

The optimal PMf solution resulted in six source factors for PMf as shown in Figure 31. Fewer PMf species, relative to PMc, resulted in the optimum source apportionment. Several species were eliminated from the profiles because model fit was better with the exclusion or because these individual species were poorly modeled and thus, the apportionment to the factors were not trusted. Within this size fraction, three factors were identified based on dominant chemical species. A lead-rich (also labeled Pb-rich) factor was isolated based on a profile which included nearly 70% of the measured lead concentration. A salt factor, which contains approximately 85% of the measured chloride, was identified but this factor does not contain sodium as it did in the PMc results because this species was eliminated due to poor fit. When observed on a seasonal basis, this factor contributes less than 1 µg/m³ at all times. Finally, the brake wear factor was identified based on the dominant copper and zinc species. The influence of this factor peaks in March, August, and again in the winter (November through January) months. This suggests influence from vehicles needed for planting and harvesting operations as well as from seasonal residents and lower winter time mixing heights. It may also suggest an influence from agricultural crustal material. This PMf brake wear factor is different from the PMc road dust factor which contained these same chemical constituents. Specifically, it lacks the lead found in the PMc factor. This difference likely helps to separate the influence of motor vehicles and re-entrained road dust on fine particles which was not possible for coarse particles.

For PMf, brake wear and motor vehicles were isolated as separate sources. The motor vehicle factor was identified based on the strong influence from both organic and
elemental carbon found in its source profile. Elemental carbon was not often measured in PMc particles making isolation of a similar profile impossible. During this study, elemental carbon concentrations were highest at the CG site consistent with greater traffic and motor vehicles density.

Figure 31: Fine Particle Source Profile for the Six Factor Solution

Two factors contained signatures with multiple elementals giving them a crustal particle-like chemical profile. These two factors were identified as road dust and crustal based on the organic carbon concentration found in each. The road dust factor was so named due
to the high organic carbon concentration consistent with motor vehicle emissions. The crustal factor contained less organic carbon consistent with source samples collected in the area (Upadhyay, Clements et al. 2012).

### 8.4.7 PMf Source Apportionment by Site

Figure 32 shows the relative source contribution of each of the six source factors at each site averaged over the study period. The motor vehicle source represents between 25-45% of the apportioned mass. This contribution is highest at the urban CG site, which experiences a higher traffic volume. The contribution at COW comparable to that at CG and larger than the contribution at PCH likely because it is situated closer to the roadways connecting Maricopa and Casa Grande and servicing the cattle feedlots and grain processing plant.

The road dust component is the second largest individual contributor to PMf mass making up approximately 30% of the PMf mass. This fraction is fairly uniform among the sampling locations, which is consistent with a de-coupling of the motor vehicle, brake
wear, and road dust components unlike the combined road dust component found for coarse particles. The uniformity may result from a balancing of two influences: traffic which can re-entrain dust (influence greatest near the urban center) and nearby crustal sources which can lead to dust on and near the roadways (influence greatest at more rural sites). The lead-rich factor accounts for 10% of the PMf mass at each of the sampling sites and may be representative of surface soils in the region, which may have an elevated lead concentration caused by deposits of tailing materials from copper mines previously operated within the region. The crustal factor represents between 2-7% of the PMf mass within the region. Overall approximately 10% of the particle mass remains unattributed to any of the resolved sources.

**8.4.8 PMf Source Apportionment by Season**

On average, the motor vehicle source is the main contributor to fine particle mass concentrations within the region. Monthly average MV contributions at GC and COW are similar. At CG, the lowest contributions are observed during the summer months with higher contributions during the winter (November through February) consistent with an increase in the local population and driven miles during this time period. The brake wear contribution behaves similarly during the winter months but also appears to be influenced by the planting and harvesting seasons which may suggest that this factor also contains an influence from agricultural crustal material. At COW, the mass contribution from the MV source is of a similar magnitude as the contribution at CG however, smaller fluctuations are observed. This may be a result of steady operations from nearby sources including the railroad, grain processing equipment, and vehicles servicing the feedlots and grain processing plant.
Figure 33: Seasonal Variation of PMF Apportioned Fine Particle Mass
The road dust factor has a monthly contribution profile that is fairly consistent among the sampling sites. In general, concentrations are lowest during the winter and much higher during the rest of the year. Failure to strictly follow the seasonal profile of the MV source and an observation that peaks in the contribution from the crustal factor correlate well with peaks in the road dust contribution suggest that this source may not be a pure road dust factor but may be both road dust and other crustal material.

The crustal source contributes most during the tilling (March) and harvesting (October) seasons. The lead-rich source contributes least during the summer (June-August) time period. Measurements of rainfall measured at the Maricopa meteorological station showed several monsoon rain events during this same time period suggesting that this source is suppressed by wet deposition and decreased erosion from wetted surfaces. The salt source factor contributes less than 0.5 $\mu$g/m$^3$ and does not have a consistent monthly contribution profile across each of the sampling sites. This suggests that the contribution is fairly low without much variability.

**8.5 Summary and Conclusions**

This study has improved our understanding of the sources impacting ambient particle concentrations in Pinal County, AZ – a rural area with a growing population that experiences some of the highest PM$_c$ concentrations in the US. Detailed chemical composition was obtained for one year at three sites providing new insights into the spatial and temporal resolution of fine and coarse particle sources in the area the impacts of which were quantified by applying the PMF receptor model. Several unique PM
sources were identified including agricultural fields, cattle feeding operations, grain processing, and motor vehicles.

Coarse particles within the region were apportioned to nine sources including primary biological aerosol particles, crustal, road dust, feedlot, secondary, boron-rich, transported soil, ammonium nitrate, and salt. About 8% of coarse particles remain un-apportioned. In terms of mass, PBAPs contribute most significantly at the rural COW site, which is influenced by agriculture and grain processing. The crustal source contributes most significantly at the rural PCH site, which is influenced most by agricultural activities. Road dust contributes most at the urban CG site. The amount of mass remaining un-apportioned is largest when particle mass concentrations spike indicating an important local source may be missing.

Fine particles within the region were apportioned to six sources including motor vehicles, road dust, lead-rich, brake wear, crustal, and salt. The motor vehicle source shows a behavior common in this desert southwest with highest concentrations observed during the winter months. The reasons for this are two-fold. First, mixing heights are often lower during this time of year and second, temperatures are much milder contributing to an influx of seasonal residents and more traffic. Spring and fall seasons have increased particle mass concentrations often influenced by the crustal and lead-rich source indicating these may result from agricultural planting and harvesting operations. Motor vehicles and road dust are the highest contributors to PMf.
Chapter 9: Chemical Mass Balance Source Apportionment of PM$_{2.5}$ and PM$_{10}$ Particulate Matter in the Desert Southwest, USA$^5$

9.1 Abstract

The Desert Southwest Coarse Particulate Matter Study was undertaken in Pinal County, Arizona, to better understand the sources and the relative impacts of those sources to fine and coarse particulate matter (PM) concentrations in rural, arid regions of the desert Southwest. The desert Southwest experiences some of the highest PM$_{10}$ mass concentrations in the country. Previously reported characterization and positive matrix factorization modeling source apportionment results relied on the 1-in-6 day fine and coarse particles data. Previous daily averaged results were averaged to match 6-week aggregated organic species data that included alkanes, polycyclic aromatic hydrocarbons, organic acids, and saccharides. Chemical mass balance (CMB) modeling was then conducted on the 6-week averaged data set. A set of re-suspended soil samples were analyzed for the same chemical components and these profiles, as well as previously collected plant and fungal spore profiles, were combined with published source profiles for several other sources and used in the CMB analysis. The six new source profiles (four soils, desert plants, and fungal spores) were developed as part of this work and include not only a range of inorganic species but organic species as well.

$^5$ This chapter is based on a journal manuscript, led author Andrea L. Clements, which has been prepared and submitted to US EPA Office of Research and Development for clearance. We intend to submit this manuscript to Journal of the Air and Waste Management Association.
Results indicate that up to half of PM$_{2.5}$ was apportioned to motor vehicles with the highest contributions found in the small urban center of Casa Grande. Apportioned crustal material accounted for up to 50% of PM$_{2.5}$ mass with the highest contributions observed at the sites closest to active agricultural fields. Apportioned secondary PM, biomass burning, and road dust typically contributed less than about 35% to the apportioned mass. Crustal material was the primary component apportioned to PM$_{10}$ accounting for between 50-90% of the apportioned mass. Of the other apportioned sources, motor vehicles and road dust showed relatively large contributions at the urban and one of the rural sites, whereas road dust and meat cooking operations showed relatively large contributions at the other rural site.

**9.2 Introduction**

Pinal County, Arizona, an arid, desert and agricultural region located south of the Phoenix metropolitan area routinely exceed the PM$_{10}$ National Ambient Air Quality Standards (NAAQS) and fine particle mass concentrations also are approaching the NAAQS for PM$_{2.5}$ (ADEQ 2010). Because PM$_{10}$ concentrations exceed the federal standard, government agencies, in conjunction with local stakeholders, have the responsibility of developing and enacting policies to reduce PM concentrations to below the NAAQS levels (40 CFR 110.51).

In October 2003, a short-term source apportionment study was conducted to identify emission sources that contribute to elevated particulate matter (PM) concentrations in the region (Pinal County Air Quality Staff 2005). The chemical mass balance (CMB) source apportionment analysis conducted during the fall season indicated that crustal material
was the main contributor to elevated PM$_{10}$ concentrations within the region.

Resuspension of material from feedlot operations also was an important contributor to PM$_{10}$, even at monitoring locations well removed from these sources.

Since that study, the region, as well as other parts of the desert southwest, have continued to struggle with elevated PM concentrations and have retained the non-attainment designation (ADEQ. 2010). Urban growth, spilling over from the nearby Phoenix and Tucson metropolitan regions, has altered the demographics and emissions in Pinal County. While extreme weather conditions, such as late summer monsoons are believed to occasionally contribute to elevated PM levels (Clements, Fraser et al. 2012), a considerable number of NAAQS exceedances also occur at other times of the year (U.S. EPA AirData 2012). A fresh look at the PM sources in this area and the relative impact of each can provide policy makers with critical information needed to reduce levels of PM in the area, and thereby improve air quality and reduce health risks from air pollution.

The Desert Southwest Coarse Particulate Matter Study was undertaken in Pinal County, Arizona to better understand the sources and their relative impacts to fine (particles less than 2.5 µm aerodynamic diameter [AD]) and coarse (particles in the range between 2.5 and 10 µm AD) particles concentrations. Clements et al. (Clements, Fraser et al. 2012; Clements, Fraser et al. 2012) reported results of the 1-in-6 day sampling, which examined the spatial and temporal chemical characteristics of fine and coarse particles and apportioned both size fractions using positive matrix factorization. Results presented here detail 6-week time-averaged data that align with the organic speciation analysis obtained during the study. Chemical mass balance (CMB) modeling was conducted
using the full inorganic and organic speciated data set to apportion ambient PM observed at the three receptor sites to identify and quantify source impacts. New source profiles for four local soil types, plants, and fungal spores in the area also are presented and used in the CMB modeling.

9.3 Methods

9.3.1 Ambient Sampling and Chemical Characterization

Filter-based ambient PM samples were collected on a 1-in-6 day schedule between February 2009 and February 2010 at three monitoring locations in Pinal County, AZ. Detailed information about the ambient sampling program, sampling locations, and chemical analysis of the collected samples can be found in Clements et al. (Clements, Fraser et al. 2012). Briefly, samples were collected at Casa Grande (CG), an urban location located in a small urban business district more distantly surrounded by residential neighborhoods; Cowtown (COW), a rural site located approximately 27 km to the northwest of Casa Grande and in the immediate vicinity of a cattle feedlot, a grain processing operation, and railroad and vehicle traffic; and Pinal County Housing (PCH), a rural site surrounded by native desert and active agricultural fields.

Three Sierra-Anderson Model 241 dichotomous samplers were operated at each site, each collecting one fine and one coarse particle sample during each 24-hr sampling period, which ran from mid-night to mid-night in accordance with the PCAQCD schedule. Two of the three samplers employed Teflon filters which were used for subsequent determination of PM mass, ion, and elemental concentrations. The other sampler employed quartz-fiber filters which were used for determination of bulk
elemental carbon (EC) and organic carbon (OC) concentrations. Remaining portions of the quartz-fiber filters were used for determination of a series of organic species as described later.

9.3.2 Source Sampling

A series of local soil samples were also collected as part of the field campaign to characterize the composition of potential sources of resuspended crustal material (Upadhyay, Clements et al. 2012). Samples were collected from 15 different sites within the sampling area representing the soil from different types of land use including agricultural cropping, native desert (unaltered desert in close proximity to the site), paved and unpaved roads, and material representative of the local cattle feedlot. All samples were obtained from the top 15 mm of the surface using a trowel, or by broom on the paved surface, and placed into a pre-baked glass jar for storage and transport. These samples were resuspended in the laboratory to provide PM$_{2.5}$ and PM$_{10}$ size fractions from each soil type. More information about the re-suspension procedure can be found in Clements, et al. (Clements, Fraser et al. 2012; Upadhyay, Clements et al. 2012). Samples were collected on one Teflon and two quartz fiber filters for each sample and PM size fraction. At least 5 mg of resuspended soil was collected on each filter. The Teflon filter sample was analyzed for mass and elements. One quartz-fiber filter was analyzed for bulk organic and elemental carbon as well as water soluble ions, and the second quartz fiber filter was extracted for GCMS analysis of organic species in a manner similar to that used for the ambient filters. For this work, chemical species data were averaged to provide an average source signature for agricultural soils, native desert dust, paved-road dust, and feedlot material.
9.3.3. Chemical Analysis

Ambient PM and resuspended soil samples were analyzed for a variety of chemical components as indicated in Clements et al. (Clements, Fraser et al. 2012; Upadhyay, Clements et al. 2012). Ambient PM mass concentrations and total soil mass collected during re-suspension were determined gravimetrically from the Teflon filters. After gravimetric analysis, one set of Teflon filters was microwave digested in a nitric, hydrochloric, and hydrofluoric acid mixture and analyzed for 63 trace elements by high-resolution inductively coupled plasma mass spectrometry (ICP-MS, Thermo Finnigan ELEMENT 2) (Upadhyay, Majestic et al. 2009). The second set of Teflon filters (for ambient samples) was wetted with ethanol (Fisher HPLC grade) and then extracted into ultrapure water. For soil samples, 3 cm$^2$ from one of quartz fiber filter samples was removed and then extracted into ultrapure water. The extracts from both ambient and resuspended soils were then analyzed for five anion and five cation species by ion chromatography (Dionex IC20 system with CG12A and AS12A analytical columns) (Derrick and Moyers 1981). Ambient bulk OC and EC concentrations were determined by thermal-optical transmission (Sunset Laboratories, Tigard, OR) using a 1 cm x 1.5 cm punch from a quartz-fiber filter (Birch and Cary 1996).

This study expands previously reported results (Clements, Fraser et al. 2012; Clements, Fraser et al. 2012; Clements, Fraser et al. 2012; Upadhyay, Clements et al. 2012) by quantifying key organic molecular markers. Due to the relatively low amount of sample collected by the low volume samplers, eight samples were combined to produce sufficient organic material for gas chromatography mass spectrometry (GCMS) analysis.
To obtain a uniform database for all species, the 1-in-6 day data were combined into 6-week averages.

For GCMS analysis, compiled filters were placed in a clean glass extraction vessel and spiked with 40 µl of two different internal calibration standards to monitor the extraction efficiency and compound loss during concentration. The non-polar standard included n-tetracosane-D50, n-triacontane-D62, n-hexatriacontane-D74, chrysene-D12, dibenz[a,h]anthracene-D14, decanoic acid-D19, and tetradecanoic acid-D27 at a concentration of 200 mg/L each. The polar standard included 100 mg/L of β-D-glucose-1,2,3,4,5,6,6-D7. Once dry, filters were extracted by adding 20 mL of dichloromethane and 10 mL of methanol to the glass extraction vessel to a depth that covered the filters. The sealed vessels were then placed in an ultrasonic bath for 10 minutes. After sonication, the liquid was decanted from the extraction vessel into a clean 250 ml round bottom flask. Two more sequential, equivalent extractions were performed and the supernate from each was poured off into the flask and combined.

The extract was concentrated using a Buchi rotary evaporator to reduce the total volume from 90 mL to 10 mL. The system was operated at ambient pressure with a water bath at 70 degrees Celsius. The sample was removed from the rotary evaporator, filtered through a pre-baked glass-fiber filter, and transferred to a clean 15 mL round bottom flask. The sample was then evaporated to a volume of 200 µL under ultrapure nitrogen. The exact sample volume was measured using a glass syringe and the sample was transferred to a new GC vial with a glass insert. An aliquot from this total extract was analyzed by GCMS to measure non-polar compounds.
A 50 µL aliquot from the 200 µL extract was silylated to derive the trimethylsilyl derivatives of carboxylic acids, alcohols, and sugars to improve GCMS instrument response to these polar compounds (Medeiros and Simoneit 2007). The 50 µL aliquot for derivitization was placed in a new GC vial with a glass insert and reduced to dryness under ultrapure nitrogen. Once dry, the sample was reconstituted with 150 µL of N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane (TMCS) and 50 µL pyridine. The vial was capped, inverted to mix, and then heated to 70 degrees Celsius for 3 hours. An aliquot from this sample was analyzed by GCMS to identify and quantify polar compounds.

For each GCMS analysis, 2 µL aliquots of the original or derivatized extracts were manually injected into the GC, along with a 1µL aliquot of 30 mg/L 1-phenyldodecane (1-PD), in splitless mode at 250 degrees Celsius. The GC oven was programmed to hold a temperature of 65 degrees Celsius for 10 minutes followed by a ramp to 310 degrees Celsius at a rate of 5 degrees per minute to a final isothermal hold 2 minutes. The mass selective detector was operated in electron impact mode at 70 eV at 230 degrees Celsius in ion scan mode, which scanned mass to charge ratios of 50 to 500 at 2.94 scans/second. The 1-phenyldodecane co-injection was used to monitor proper injection, while internal denuterated standards were used to monitor extraction efficiency. Authentic calibration standards, which were derivitized and analyzed with equivalent methods, were used to determine instrument response and to confirm elution time. Compounds were identified by retention time and mass fragmentation patterns and were quantified using the selected ion peak area and converted to compound mass using the relative response factor method.
9.3.4 Chemical Mass Balance Analysis

CMB modeling was employed on the organic molecular marker concentrations as well as 6-week aggregated PM mass, ion, and element concentrations.

The chemical mass balance (CMB) model (EPA-CMBv8.2) uses known source profiles to determine the optimal contribution of different sources to best fit the ambient data measured at the receptor sites. All sources modeled in the 2003 study were initially included in the CMB modeling, including mobile sources, vegetative burning, coal-fired power plants, and secondary sources (Pinal County Air Quality Staff 2005). Factors for secondary aerosol formation included only ammonium nitrate and ammonium sulfate while other associated salts of nitrate and sulfate were not considered. Source profiles for three additional factors including meat cooking, gasoline powered motor vehicles, and diesel engines were obtained from published literature (Chow, Watson et al. 2004).

Previously developed plant and fungal profiles obtained from Central Arizona also were included (Jia and Fraser 2011) along with the four soil source profiles generated in this study. The latter included agricultural/native soil, dirt-road dust, paved-road dust, and cattle feedlot material. These six source profiles, not previously reported in the literature, are included in Table 8.

Data from the three ambient sampling locations were modeled independently as were the two size fractions. Initially, all source profiles were considered and modeled but, sources were eliminated when excessive co-variation prevented model convergence. Sources providing the best improvement to model metrics were retained. Metric improvements included an adjustment of $R^2$ toward 1 and the percentage of mass apportioned toward
Once co-linear source profiles were eliminated, sources were investigated one by one to determine if inclusion or exclusion improved the model performance. Once the best possible fit was achieved, the list of chemical species used for the apportionment was reviewed. Species that were not well modeled were investigated to determine if model performance was greatly enhanced by the exclusion of one or more species. Once optimized, excluded sources were tested one more time to determine if the elimination of a chemical species affected the model performance enough to warrant re-inclusion of one of the previously excluded sources.
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**Table 8: Source Profiles for Desert Plant, Spore, and Crustal Sources**
9.4 Results and Discussion

9.4.1 Measured Particle Composition

Figure 34 details the average particle chemical composition for the six-week averaged data collected during the study. Information about coarse particles (PM$_{10-2.5}$) and more time-resolved chemical composition data can be found in Clements et al. (Clements, Fraser et al. 2012).

The chemical composition was described in terms of eight components, which included crustal material, other elements, secondary ions, other measured ions, sum of organic species, uncharacterized organic carbon, EC, and unidentified mass. The crustal material component was calculated by assuming that the major trace elements found in soil were present in their most common oxide forms using the equation of $1.89[Al] + 1.4[Ca] + 1.87[Fe] + 1.67[Ti] + 2.14[Si]$ (Marcazzan, Vaccaro et al. 2001). Silicon was not determined by ICP-MS, so it was estimated based on the ratio of Si to Al in upper continental crust (Taylor and McLennan 1995) and road and dust samples from California and Texas (Watson and Chow 2001; Chow, Watson et al. 2004). The other elements component included the sum of the other elements determined by ICP-MS. The secondary ions component included the sum of sulfate, nitrate, and ammonium whereas other ions, as measured by IC, were included as the other measured ions component. The concentrations of all organic chemical species itemized by GCMS analysis were summed and included in the organic species component. Uncharacterized organic carbon was determined by the difference between twice the measured organic carbon concentration and the organic species measured by GCMS analysis. The EC component was measured
directly and the *unidentified mass* component represents the difference between measured mass and the sum of the other components.

Six-week PM$_{10}$ mass concentrations were approximately 2 to 8 times higher than PM$_{2.5}$ with mean PM$_{10}$ and PM$_{2.5}$ mass concentrations of roughly 57 and 9 µg/m$^3$, respectively. Overall, the highest mass concentrations (both size fractions) were found at COW, which is consistent with compliance monitoring data within the county (U.S. EPA AirData 2012). Measurements at show several periods of elevated PM mass in February-March, July-August, and November-December. The higher levels in July-August were consistent with the monsoon season and were likely associated with wind-blown dust events (Clements, Fraser et al. 2012). Elevated PM$_{10}$ and PM$_{2.5}$ concentrations are elevated during periods of tilling and harvesting (March and late October/early November) when these activities resulted in dust entrainment into the atmosphere (Clements, Fraser et al. 2012).

On average, crustal material was the largest component of PM$_{10}$, comprising approximately 50% of the PM$_{10}$ mass. COW had an elevated organic carbon component representing approximately 10% of the PM$_{10}$ mass concentration and this was not observed at other monitoring sites. Closer analysis of COW PM$_{10}$ data showed elevated concentrations of sulfate and measureable amounts of soluble potassium that were not observed at the other sites. These observations were consistent with the chemical composition of feedlot material (Table 8) and represent a departure from previous work that found feedlot material to be a significant PM source at all monitoring locations whereas chemical information from this study suggests that it is only a major source at the COW site (Pinal County Air Quality Staff 2005).
The regional composition of PM$_{2.5}$ was more varied; however, crustal material is still a major component comprising 14-51% of the mass. Elevated fine particle mass
concentrations at PCH were accompanied by higher levels of crustal material showing that dust entrainment can drive elevated PM$_{2.5}$ mass concentrations. The organic carbon (sum or organic species and uncharacterized organic portions) and secondary ion components each comprise approximately 20% of the fine particle mass at all sites. The organic carbon and secondary ion components show a fairly consistent contribution month to month for each sampling location. There are occasional exceptions which can measure a factor or 2 to 3 but these variations do not correlate well with the local crustal variations, suggesting a regional rather than local impact of these sources during most months. A large change in the impact of secondary ions was observed during the last months of the study at the rural sampling locations, which may be caused by the application of fertilizers; however, this cannot be verified based on this study.

9.4.2 Measured Source Profiles

Table 8 gives a detailed characterization of the chemical composition of the novel source types characterized as part of this study, and lists the chemical compounds used for CMB modeling. The source profiles given in Table 8 were developed with two goals. First, detailed chemical composition was used to differentiate between measured and model contributions of several different crustal source types. Second, it was believed that the use of source profiles representative of sources in the region would reduce uncertainty in the CMB analysis since previous work showed differences between local soils and the more generic upper continental crust profiles (Upadhyay, Clements et al. 2012).

Plant and spore source profiles were derived from abraded samples of plant leaves and branches and spores collected from the local ecosystem. While the samples used in this
study were characterized prior to this work, they remain the most representative characterization available. These samples were analyzed only for carbon and organic saccaride species. As seen in Table 8, mannitol appears to be an effective chemical marker species for the desert plants characterized since it was below the minimum detection limit in the other source samples. Sucrose was found to be a good chemical marker species for plant material as its concentration was 2 to 3 orders of magnitude higher in this source than the others. Fungal spores were easily distinguished by the high trehelose concentration which was almost 2 orders of magnitude higher in the fungal source when compared to all other source profiles used in this study. These observations are consistent with other studies which have found mannitol, sucrose, and trehelose associated with primary biological aerosol particles (Jia, Clements et al. 2010).

Differences in the chemical composition of the soil types characterized in this study were more subtle. Elemental carbon was found in road and feedlot samples, with the highest concentrations in the former, consistent with proximity to motor vehicle traffic. The measureable amount of elemental carbon found in the feedlot samples may be a result of nearby railroad or truck traffic serving the feedlot. The feedlot samples were further distinguished by cholesterol in their soil profiles. Furthermore, the concentration of sulfate was 4 times greater within feedlot samples when compared to the other soil types.

**9.4.3 Model Performance Evaluation**

Figure 35 shows the agreement between measured (horizontal axis) and model (vertical axis) PM$_{10}$ and PM$_{2.5}$ mass, which is one metric used to determine model performance. Error bars represent 20% uncertainty in the aerosol mass measurement. As shown, for
most PM$_{10}$ samples, the agreement between the measured and modeled mass is within 20%. Mass concentrations for COW were among the highest measured and the model mass was under-predicted for a number of these samples suggesting that an important source impacting this site may be missing from the model source profiles. The linear nature of the predicted vs. measured mass for PM$_{2.5}$ suggests that the sources impacting fine particles were appropriately accounted for within the model. Agreement between mass concentrations falls within approximately 30% with a slight over apportionment of mass, with the exception of COW which showed an underestimation at high mass concentrations.

![Figure 35: CMB Model Mass Performance Evaluation](image)

### 9.4.4 Average Source Apportionment Results

Figure 36 shows the modeled source apportionment results for PM$_{10}$ for the three monitoring locations. Results confirm the chemical characterization (Clements et al.
that indicated PM$_{10}$, measured as part of this study was largely crustal in nature. This result was also consistent with the 2003 study (Pinal County Air Quality Staff 2005) and the PMF results from the current study (Clements, Fraser et al. 2012). CMB modeling was unable to reliably separate the influence of agricultural/native dust, dirt-road dust, and feedlot material, whereas the separation was achieved with PMF. This lack of separation of these different soil related sources was likely due to co-linearity or random assignment as a result of the source profiles having similar chemical characteristics. Thus, the attribution of the measured PM mass to each of the three soil types was combined into one source type called crustal material.

Figure 36: CMB Source Apportionment Results for PM$_{10}$

Results show that crustal material comprises about 50, 73, and 79% of PM$_{10}$ at CG, COW, and PCH, respectively. The influence of crustal material is highest at the two rural sites (COW and PCH) with the largest impact observed at PCH, which is surrounded by active agricultural fields.
Motor vehicles (gasoline engines with catalytic converters) and road dust were also important sources of PM$_{10}$, with the impact of road dust approximately half that of motor vehicles at each location. Motor vehicles exhibit the greatest impact at CG, the more urban site with the largest number of motor vehicles. The influence of motor vehicles is least at PCH, which is more removed from roadways when compared to COW which is adjacent to the 2 lane highway between CG and Maricopa.

Meat cooking contributed 11% of the mass measured at the PCH site. Although the magnitude of this source is surprising, this site is located adjacent to the Pinal County Housing Complex where such sources might be expected to be important. However, the size of the housing complex is fairly small and thus, apportionment to this source is likely an overestimation of the true contribution from this source.

Ammonium sulfate and ammonium nitrate have a small but measurable impact at each site. In part, this may be due to primary emissions of these species associated with fertilizers used on crops or other activities associated with the cattle feedlot. The remaining sources, including coal fired power plants and biological material from plants and spores were less than 1% of the apportioned mass.

Figure 37 shows the modeled source apportionment results for PM$_{2.5}$ collected at each of the monitoring locations. Results show that motor vehicles and crustal materials were the dominant sources but as many as 6 different sources contributed at least 5% each to the apportioned PM$_{2.5}$ mass. CMB modeling was unable to reliably separate the impact of agricultural/native dust, dirt-road dust, and feedlot material so they were again combined
as the crustal source. Paved-road dust remains a separate and sometimes important source.

![Figure 37: CMB Source Apportionment Results for PM$_{2.5}$](image)

Results show that motor vehicles (gasoline engines with catalytic converters) are an important source of PM$_{2.5}$. The lowest contribution from motor vehicles was at the more rural PCH site (30%) with higher contributions at rural COW (37%) adjacent to the 2-lane highway. The impact of motor vehicles was greatest at CG (50%), the more urban location.

For PM$_{2.5}$, the apportioned contribution of paved-road dust was not well correlated ($r^2 = 0.54$ at CG) to the apportioned motor vehicles contribution. One possible explanation is that tail-pipe emissions of particles from motor vehicles are significantly smaller than road dust particles. This difference in size may lead to differences in the regional transport of tail-pipe versus road dust resuspension, leading to differences between sites that are different distances from major roadways and urban centers. The CMB analysis was only able to identify and quantify the impact of paved-road dust in PM$_{2.5}$ at CG, equal to approximately 20% of the apportioned motor vehicle contribution.
Approximately 14%, 31%, and 51% of the PM$_{2.5}$ mass was apportioned to crustal at CG, COW, and PCH, respectively. The influence was similar to that observed for PM$_{10}$ with crustal material contributing more at the rural sites than the urban site.

A larger fraction of ammonium sulfate and ammonium nitrate was apportioned to PM$_{2.5}$ than to PM$_{10}$. This is not unexpected since these compounds are usually associated with fine particles being formed in air rather than primary emissions that might occur from fertilizers or certain dust suppressants. On average, approximately 19% of the apportioned mass was attributed to these sources and, part of which was likely due to regional transport.

Approximately 10% of the apportioned PM$_{2.5}$ mass at CG and COW was attributed to biomass burning. The remaining sources, including coal fired power plants and biological material from plants and spores contributed less than 1% each to the apportioned mass.

**9.4.5 Seasonal Source Apportionment Results**

PM$_{10}$ and PM$_{2.5}$ source apportionment results for each 6-week period are presented in Figure 38, allowing evaluation of seasonal differences in apportioned source categories.

Crustal material was a major contributor to apportioned PM$_{10}$ mass during most time periods, contributing less during winter and spring than during summer and fall. During the periods when crustal material was lowest, the contribution from road dust was highest. The abrupt change in the influence of road dust, especially without a subsequent return at the end of the study, may indicate that these sources - road dust and other crustal
(agricultural, native, dirt-road, and feedlot) sources - may be too similar to reliably differentiate based on the available chemical species and use of CMB.

The growing impact of ammonium nitrate near the end of the study, as seen in the directly measured concentration data (Clements, Fraser et al. 2012), maybe due to the application of fertilizers to agricultural soils and lower temperatures allowing for greater partitioning to the particle phase for this semi-volatile component.

The impact of motor vehicles in PM$_{2.5}$ was fairly uniform throughout the year at CG and PCH. Exceptions to this were seen at GC and PCH for the July – August period (Figure 38). At CG, mass was apportioned to crustal rather than motor vehicles. At PCH, the apportioned mass was a severe underestimation of the measured mass. The difference between these measurements likely accounts for the crustal component but it was not well modeled by CMB. COW showed a marked decrease in the impact of motor vehicles after September. This appeared to be offset by a larger impact from crustal material, ammonium nitrate, and biomass burning. This may be due to an inability of CMB to apportion the components correctly since the cause for this change is unknown and no site observations suggest a change in vehicle traffic at the time.

Biomass burning was only significant at CG and COW. The largest influence from this source was observed in November-December, which is consistent with the end of the harvesting season and could coincide with the burning of residual material on agricultural fields. However, there was no direct evidence of these activities recorded.
The impact of ammonium sulfate was uniform throughout the year and relatively consistent among all three locations. This suggests the regional nature of this component as seen elsewhere (Solomon et al. 2008).

**Figure 38: Seasonal CMB Source Apportionment of PM$_{10}$ and PM$_{2.5}$ Mass**
9.5 Summary and Conclusions

The Desert Southwest Coarse Particulate Matter Study was undertaken in Pinal County, AZ to further the understanding of the sources of fine and course PM concentrations in rural, arid regions of the desert southwest. This study expands on information available from the 2003 study (Pinal County Air Quality Staff 2005) on regional PM sources by investigating temporal variations by extending the sampling period through all four seasons, expanding the chemical species identified, and developing more specific chemical signatures of crustal material representative of different source categories. This additional information provides a more comprehensive view of PM sources and the impact of each within this region.

The work discussed here is a supplement to the more time-resolved (1-in-6 day) chemically-characterized fine and coarse particle data with sources apportioned by positive matrix factorization (Clements, Fraser et al. 2012; Clements, Fraser et al. 2012). This work used organic markers aggregated over 6-week periods with sources apportioned using the Chemical Mass Balance model.

Detailed chemical profiles for two groups of biological particles (plants and spores) and four types of crustal materials (agricultural/native dust, road dust, dirt-road dust, and feedlot material) obtained from the study area are presented. Specific marker species for the various soil types were not observed. The significant co-variation within these soil types lead to an inconsistent apportionment to various crustal source types using CMB modeling. While distinct markers species for the plants and fungal spores evaluated were observed, these sources did not contribute significantly (>1% mass) to either PM$_{10}$ or the
PM$_{2.5}$ by CMB. Still, these unique chemical signatures may be of future use in understanding dust, plant, and spore sources affecting the desert Southwest.

On average, six sources – crustal, motor vehicles, road dust, meat cooking, ammonium sulfate, and ammonium nitrate - contributed more than 1% to the apportioned PM$_{10}$ mass. Crustal material was the largest single source of PM$_{10}$ mass contributing between 50 and 79% and contributing most during tilling, harvesting, and monsoon seasons. The motor vehicle and road dust factors contributed most significantly at the more urban CG site, together contributing to about 42% off the PM$_{10}$ mass.

In general, the same six sources contributed to the apportioned PM$_{2.5}$ mass, although biomass burning was noted at two of the sites (~10%) and an impact from coal fired power plants was observed at all three sites, although only at 1% of the PM$_{2.5}$ mass. In this size fraction, crustal material contributed between 14 and 50% of the particle mass while the motor vehicle source contributed between 30 and 50%. Contributions of apportioned sources varied by site as well as season.
Chapter 10: Conclusions

10.1 Project Summary

This year long aerosol characterization study in Pinal County, AZ – an area experiencing high PMc concentrations due to crustal sources common to rural, arid environments – has further developed the understanding of particulate matter within the region. Results give a comprehensive chemical characterization and source apportionment of both coarse and fine particles and provide unique insight into these two distinct size fractions that are not usually investigated independently.

Coarse PM is primarily responsible for a number of violations of the PM$_{10}$ NAAQS in the Desert Southwest. PMc mass was highly variable ranging between 14 and 150 $\mu$g/m$^3$ and concentrations are, on average, approximately 5 times higher than the fine particle mass concentrations. Spatially, rural sites experienced much higher mass concentrations than the urban site, suggesting the proximity to local agricultural sources and the native desert influences overall particle mass concentrations. The highest overall mass concentrations were observed during spring and fall seasons, consistent with local tilling and harvesting operations, implying the impact of agricultural sources of crustal material. Mass concentrations also increase during the late summer monsoon season when high wind events can re-entrain dust from several land use types. The total influence of these events is offset by increased wet deposition by rain and a wetting of crustal surfaces.

Chemically, coarse particles are comprised mainly (50%) of crustal and (15%) organic material. Higher concentrations of organic matter and water-soluble ions were measured
in source samples from the cattle feedlot and at the ambient monitoring site COW which is located in close proximity to feedlots. The solubility ratios for calcium, potassium, and magnesium in feedlot material make these water soluble ions potential marker species for differentiation of feedlot material other forms of crustal material. Reconstructed crustal mass estimates from elemental analysis indicate crustal material is responsible for approximately 50% of measured PM, but source apportionment analysis indicates a lower bound for the crustal material contribution. This discrepancy may indicate that different oxide forms or other elements may be important to the overall crustal contribution and that some of the chemically unidentified mass may still be crustal in nature.

Source apportionment analysis indicates that coarse particles have a variety of sources. Several are crustal in nature including crustal dust, road dust, feedlot material, boron-rich agricultural soil, and transported soil. Other, more minor sources include secondary particles, ammonium nitrate, and salt. About 8% of coarse particles remain unapportioned. The amount of mass remaining unapportioned is largest during episodic periods of increased particle mass concentrations, indicating an important local source may not be modeled. PMF modeling indicates a strong influence consistent with primary biological aerosol particles was isolated, the characterization of which requires further study.

Fine particle concentrations within the region are compliant the current National Ambient Air Quality Standard (NAAQS) for PM$_{2.5}$. Regionally, PMf mass concentrations are approximately 10% of PMc mass concentrations and range between 4 and 18 µg/m$^3$. 
Approximately 5 µg/m³ can be attributed to regional background of local and transported fine particulate matter.

Fine particle mass concentrations also vary seasonally with the highest concentrations observed during spring and fall, again consistent with local tilling and harvesting seasons. Chemically, fine particles are comprised mainly (37%) of organic and (30%) crustal material. Source apportionment analysis indicates several vehicle related sources including motor vehicles, road dust, and break wear with more minor influences from a general crustal source and salt. Particulate mass contributions from motor vehicle sources are highest during the winter months when meteorological conditions result in lower mixing heights and traffic from seasonal residents is greater.

Source sampling has produced PM$_{2.5}$ and PM$_{10}$ size-segregated chemical profiles for a variety of crustal sources within the region which may be transferrable to guide source apportionment research in other regional studies. Results show that the chemical abundances for the majority of species from most sources are similar between PM$_{2.5}$ and PM$_{10}$ samples. Of particular interest, crustal material representative of material resuspended from the local cattle feedlot was found to have a unique chemical signature not previously reported in the literature featuring high concentrations of organic carbon, phosphate, and potassium. The entrainment of locally applied fertilizers result in elevated concentrations of marker elements NH$_4^+$, SO$_4^{2-}$, NO$_3^-$, Cl$, and Na which are an order of magnitude higher in dirt road samples collected near agricultural fields that in native or agricultural soils themselves. Lower concentrations of these species in the fallow and crop lands are suggestive of their wash off from the top layers of soil due to rain or irrigation and removal by plant uptake. Fugitive dust emissions from the
undisturbed agricultural soil may therefore contain lower concentrations of these species than the dust released during the land preparation.

10.2 Ongoing Work

10.2.1 Publications

Publications that report an overview of the study, the seasonality of local PM concentrations, source characterization, source apportionment using PMF, and source apportionment using CMB, have all been prepared and are in various stages of publication. As this work includes collaboration from a colleague at the US EPA, that agency must approve of the content of each publication before submission. As a result, most of the work is under review at the present time at US EPA.

Organic speciation is a key element of this work and no single publication has been prepared that consolidates all the organic species data collected during this study. This detailed analysis of individual organic compounds, from ambient aerosols and local sources, is expected to add to future source apportionment work through the identification and quantification of organic marker species. To date, the data has been collected, reduced, and used for CMB analysis of ambient samples. A manuscript publishing this full suite of results is being prepared. A first draft is expected in September 2012 with revisions, modifications, and comments completed for journal submission by December 2012.
10.2.2 Stakeholder Meeting and Project Wrap-Up

This work was a collaborative effort between members of several stakeholding agencies including the Pinal Country Air Quality Control District (PCAQCD) and the United States Environmental Protection Agency (USEPA). The goal was not only to obtain information helpful to understanding PM sources in Pinal County which may aide in future PM reduction measures but to examine how this information may be more widely applicable and can assist USEPA Region 9 in furthering PM reduction goals within the desert southwest. A project report and stakeholder meeting will be held on August 3, 2012 with several interested agencies including PCAQCD, US EPA, and the Arizona Department of Environmental Quality.

10.3 Suggestions for Future work

Chapters 8 and 9 of this work present details from two different modeling approaches for deducing sources of particulate matter in Pinal County Arizona. There are some clear differences in the results presented. Future work is needed to more accurately deduce the role of Primary Biological Aerosol Particles (PBAPs) to coarse particle concentrations. There are a variety of potential sources for these particles. Finding a metric by which to identify and quantify the concentrations of these particles would be useful in the characterization of coarse particles in a variety of environments.

10.4 Acknowledgements

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