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Source Identification of Coarse Particles in the Desert Southwest, USA using Positive Matrix Factorization

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Abstract

The Desert Southwest Coarse Particulate Matter Study was undertaken to further our understanding of the spatial and temporal variability and sources of fine and coarse 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 PM concentrations routinely exceed the U.S. 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 occurrence in this region of the United States. This work expands on previously published measurements of PM mass and chemistry 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 (Clements et al., 2014).

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 site closest to a cattle feedlot), secondary particles (10%), boron-rich crustal material (9%), and transported soil (6%), with minor contributions from ammonium nitrate, and salt (considered to be NaCl). Fine particles within the region were apportioned to six sources including motor vehicles (37%), road dust (29%), lead-rich (10%), with minor contributions from brake wear, crustal material, and salt. These results can help guide local air pollution improvement strategies designed to reduce levels of PM to below the NAAQS.

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Keywords

desert aerosols; coarse particles; positive matrix factorization; crustal material; feedlot; road dust; primary biological aerosol particles

1. Introduction

The U.S. National Ambient Air Quality Standards (NAAQSs) were established to protecting human health from the damaging effects of air pollution (Federal Register, 2006). Numerous studies have demonstrated a link between ambient particulate matter (PM) and adverse human health effects (e.g. Peters et al., 2000; Mar et al., 2000; Anderson, 2009; Solomon et al. 2012; Calvo et al., 2013). These findings lead to the establishment of two air quality standards for particulate matter, 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). PM_{10} is the sum of $PM_{2.5}$, also referred to as fine particulate matter (PM_f), and the coarse fraction (PM_c; particles with AD in the size range between 2.5 and 10μm AD). Many counties in the southwest United States have measured ambient concentrations of PM_{10} in excess of the Federal standards. Exceedances of the PM_{10} NAAQS in the southwest US are often the result of spikes in the PM_c mass concentration because coarse particles dominate the overall PM_{10} mass within the region (Pinker et al., 2004; Cheung et al., 2011; Engelbrecht et al., 2015). When a region is out of compliance with the NAAQS, it is the responsibility of the State to develop a State Implementation Plan (SIP) designed to reduce PM concentrations to levels below the NAAQS (Federal Register, 2006). The development of a SIP requires knowledge of emission sources, emission strength, spatial and temporal variation in ambient PM concentrations, and source impacts.

In rural areas like the desert Southwest US, elevated coarse particle concentrations are often attributed to entrainment of crustal material from the arid native landscape leading to assumption that little can be done to manage periodic high concentrations of PM. Previous studies have found links between the entrainment of soil dust and weather conditions (Brazel and Nickling, 1986), wind speed (Holcombe et al., 1997; Hagen, 2004), soil type (Macpherson et al., 2008), as well as with soil moisture content (Ellis et al., 2006). Several studies have observed that crustal sources, in particular local sources, are major contributors to coarse particle mass concentrations in the desert southwest (Watson and Chow, 2001; Cheung et al., 2011, Upadhyay et al., 2011; Prabhakar et al., 2014; Gonzalez-Maddux et al., 2014).

Source apportionment using tools like Positive Matrix Factorization (PMF) or chemical mass balance (CMB) has been widely used to quantify the sources of PM in a variety of environments (Aldabe et al., 2011; Gummeneni et al., 2011; Banerjee et al., 2015). Source apportionment has also been used to distinguish between several similar soil types – for example, road dust and agricultural soils (Paode et al., 1999; Hwang et al., 2008). Other studies have measured the composition of soil source materials to identify chemical species unique to that source or source type to further distinguish among soil types (Rogge et al., 2007; 2012; Upadhyay et al., 2015). However, more work is needed to understand the

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magnitude of the crustal source which originates from mechanical entrainment of material to the environment that is measured specifically as PM_c, and to understand if some routes of crustal emissions, such as fugitive dust entrainment from agricultural activities could be partially controlled through altered practices as part of a strategy to reduce PM levels below the PM NAAQS in areas where coarse particles drive the exceedance of the PM NAAQS. A few studies have been conducted within the Southwest US to better understand the range of source impacts, beyond crustal material, and their relative contribution to ambient particle concentrations (Gertler et al., 1995; Watson and Chow, 2001).

The Desert Southwest Coarse Particulate Matter Study was conducted in and around the town of Casa Grande in Pinal County, Arizona (Clements et al. 2013; 2014). This area experiences some of the highest PM_{10} concentrations in the region (U.S. EPA, 2014). This paper expands on work already published from this study (Clements et al., 2013; 2014; Upadhyay et al., 2015) 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 seasonally resolved source contributions to PM_f and PM_c mass within the region.

2. Methods

2.1 Ambient Sampling and Chemical Characterization

PMF modeling was applied to the 1-in-6 day data set derived from filter-based ambient aerosol samples collected between February 2009 and February 2010 in Pinal County, AZ located south of Phoenix, AZ. Detailed information about the ambient sampling locations can be found in Clements et al. (2014). Briefly, samples were collected at three ambient monitoring locations on a common 1-in-6 day schedule. These included the town of Casa Grande (CG; population of roughly 50,000), 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 agricultural fields; and Pinal County Housing (PCH), a rural site more closely impacted by active agricultural fields that is approximately 19 miles east of Casa Grande.

Each sampling site was equipped with three Sierra-Anderson Model 241 dichotomous samplers. These samplers simultaneously collected equivalent 24-hr samples of PM_f and PM_c on a one-in-six day schedule. Two of the three samplers employed Teflon filters in both PM_f and PM_c channels whereas the third sampler employed quartz-fiber filters. PM mass, ion, and elements were determined from the Teflon filters and elemental carbon (EC) and organic carbon (OC) from the quartz-fiber filters. Ambient concentrations were obtained by dividing the amount of material quantified on each filter by the sampled air volume.

PM mass concentrations were determined gravimetrically by difference between the post and pre-sample collection weights from each Teflon filter. The mean of the paired colocated PM_c filter and paired PM_f filter weights were used as the mass estimate unless one measurement was invalidated as specified in the project quality assurance plan. After gravimetric analysis, one set of Teflon filters was individually wetted with 150 μl of ethanol (Fisher HPLC grade), extracted into 10 ml of ultrapure water by ultrasonic agitation for 15

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min, and analyzed the same day. Sample extracts were 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 analyzed for trace metals by the method described in Upadhyay et al. (2015). Briefly, filters were microwave digested into a 20 ml mixture of nitric, hydrochloric, and hydrofluoric acid and then analyzed for 63 trace elements by high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS, herein referred to as ICP-MS, Thermo Finnigan ELEMENT 2). OC and EC were determined from a 1 cm × 1.5 cm punch from the quartz-fiber filters by an analytical method slightly modified from Birch and Cary (1996) using a thermal-optical carbon analyzer (Sunset Laboratories, Tigard OR); details of the method modification can be found elsewhere (e.g. Clements et al., 2014 or Mancilla et al., 2015).

2.2 Positive Matrix Factorization Framework

PMF modeling was conducted on the 64 daily samples collected over the 1-in-6 day sampling schedule using the EPA PMF model version 3.0 (U.S. EPA, 2008). This multivariate factor analysis tool decomposes the matrix consisting of the concentration of airborne components in ambient samples into two different matrices – one representing source profiles and the other representing the source contribution of each source profile to the measured PM mass. The contribution from each source profile is constrained to non-negative values.

In this work, data from the three ambient sampling locations were combined into two datasets, one for PM_c and one for PM_f, and modeled as a group. This allowed for the development of a single consistent set of source profiles across the three sites within the Pinal County region while allowing for the influence of each source at each individual site to be investigated. However, this aggregation approach can lead to greater uncertainty in modeling aerosol sources unique to a specific site or to minor contributors; evidence of these potential complications was not observed during the modeling.

To optimize modeling results and drive the PMF model to convergence, the method detection limit (DL) was substituted for ambient concentration for all species measured at or below the DL, species that were detected in less than 10% of all samples were eliminated from the ambient dataset. Specifically, EC, As, Cd, Co, Cs, Ga, Ni, Sb and Th were removed from the PM_c dataset and As, Cd, Co, Cr, Cs, Ga, Na, Ni, Sb, Th were removed from the PM_f dataset. Further, a number of species measured in the dataset had minimal variation throughout the sampling period (>75% of samples within +/−25% of mean) and these species were also removed from the analysis including nitrate, sulfate and ammonium from the fine fraction. Even though these secondary ionic species contributed to the overall mass balance, modeling runs including them as fitting species were not well reconstructed and excluding them resulted in improved model performance. As a result, a different number of chemical species was modeled for PM_c and PM_f as different chemical species were included or excluded in PM_c and PM_f based on these criteria.

After optimization based on the above criteria, the optimal number of factors was determined by PMF through trial and error including reducing and increasing the number of factors modeled. Following these initial model runs, the data set was further refined by

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removing four out of the 64 sampling days, that appeared to have significant outliers (i.e., greater than three standard deviations of the mean) primarily due to extreme wind-blown dust events (Clements et al., 2013). Bootstrap analysis of the number of factors was performed to provide error estimates of each profile.

With that methodology, the modeled factor composition was then used to identify prominent sources of PM_c and PM_f within the region. Isolated source factors were either named for their prominent species or identified based on a previously known compositional source signature as described below.

3. Results and Discussion

3.1 Chemical Composition of Fine and Coarse Particle Matter

Table 1 details the study average chemical composition of PM_f and PM_c measured at each monitoring location; additional details about the PM_c and PM_f composition and seasonality can be found in Clements et al. (2013, 2014).

Organic matter, which takes into account other elements associated with the organic carbon component of PM, was estimated by multiplying the measured OC by a factor of 2. Crustal material was estimated based on assuming the common oxide forms of aluminum, calcium, titanium, iron, manganese, and silicon, the latter estimated from the measured aluminum (see footnotes Table 1). The unidentified fraction was determined by the difference between the gravimetric mass and the sum of the detailed chemical components. Further details regarding the chemical composition are available in Clements et al. (2013, 2014).

On average, the major components of coarse mass were: crustal material (varying between 47% and 54% of the particle mass), organic matter (between 9% and 16%), nitrate and sulfate (between 1% and 2% each), and other measured ions and elemental species (between 6% and 8%). Between 17% and 30% of PM_c was unidentified based on the chemical analyses performed and may include particle bound water, which was not measured, other metal oxides not identified as major soil related species, and a low conversion factor for converting OC to OM as coarse organic material may include material from a biological origin with a greater fractional composition of non-carbon material than the more investigated PM_f (Graham et al., 2003).

On average, the major chemical components of fine mass were: organic material varying between 27% and 46% of the particle mass), crustal material (between 22% and 46%), nitrate (between 6% and 13%) sulfate (between 9% and 12%), and other measurable ions and elemental species (between 6% and 7%). Between 4% and 10% of PM_f was unidentified based on the chemical analyses performed. For PM_f, the organic matter fraction was highest at CG where motor vehicle emissions are assumed to be greater due to business immediately surrounding the site and surrounding residential community. Vehicle traffic counts conducted by Pinal County showed nearly twice the traffic volume on a road within one block of the CG site compared to the paved highway within 40 m of the COW site, further supporting the impact of traffic at GC.

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3.2 Model Performance Evaluation

Figure 1 shows the agreement between measured and model estimated PM_c and PM_f mass concentrations at each site. This comparison represents one criterion for evaluating model performance. For PM_c, the correlation is strong yielding modeled concentrations within 30 percent of the measured mass concentrations. Based on the regression slope, model performance appears best at COW where modeled concentrations are roughly within 5% of the measured mass. Agreement at the other two sites is within 30% and the data are not as well correlated, r^2 of 0.72. While it is not clear why COW has better agreement with the model than CG and PCH, results for CG and PCH are presented to indicate possible sources at those sites. For PM_f, the agreement between measured and modeled mass ranges between 33% at PCH and 2% at CG and overall the data are not as well correlated (r^2 between 0.58 and 0.68).

3.3 PM_c Source Profiles

Nine PM_c source profiles were isolated by PMF as shown in Figure 2. The factors were identified based on previous source characterization studies widely available in the published literature and existing emission inventories (Gertler et al., 1995; Watson and Chow, 2001; Hwang et al., 2008; Cheung et al., 2011). Four factors were identified based on their dominant constituents - ammonium nitrate, salt (NaCl), secondary components, and boron-rich. The likely sources of the first two are possibly re-entrainment of ammonium nitrate fertilizer and potentially re-entrainment of salt from the desert playa dust (Reynolds et al., 2007). The salt signature may also result from transport of marine aerosol during the monsoon season since there is an increase contribution from salt in June and July or the observed increase may also be due to the changing wind direction and higher wind speeds that occur during this time period also associated with monsoon activity (Clements et al., 2013). The secondary source factor was identified based on the dominance of sulfate and nitrate. Although not paired with a counter-ion like ammonium, as expected for fine particles, this factor may represent reaction of gaseous precursors to nitric and sulfuric acid with basic crustal material and subsequent oxidation (Goodman et al., 2001) or the contribution of resuspension of ammonium nitrate or ammonium sulfate fertilizers from agricultural fields in the region. The boron-rich source has not been linked to a specific emission route; while almost half the measured boron was attributed to this factor and the factor was observed to minor contributions from crustal elements, no logical source could be found amongst the possible routes of entraining crustal material (Upadhyay et al., 2015). Modeling runs intended to consolidate the boron-rich source into another source profile by reducing the number of modeled factors resulted in reduced model performance and maintained an independent boron-rich source.

Three factors, crustal material, road dust, and transported soil, have similar profiles containing a number of trace elements typically associated with crustal minerals; the differentiation between these sources has been made based on the ionic species within each profile. The crustal source lacks ionic species but contains between 40% and 65% of the measured aluminum, iron, manganese, and calcium known to be dominant elements in almost all crustal materials (Taylor and McLennan, 1995). Note that Figure 2 reports some water-soluble ionic species such as potassium and magnesium measured by ion

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chromatography that are not expected in the crustal signature. The road dust factor included similar elements but also contained approximately 30% of the measured lead and zinc and 40% of the measured copper. These elements have been reported in emissions from tire and brake wear from motor vehicles and therefore are likely to be found in re-suspended road dust (Alves et al., 2015; Lough et al., 2005). The presence of lead may also originate from the wearing of lead weights used to balance tires on motor vehicles. However, past and present smelting operations in the region may also be responsible for Pb, Cu, and Zn emissions and cannot be excluded as a possible source. There are no currently operating smelters within the same air shed as the sampling sites but historical operations may have contaminated surface soils and source characterization of local soils did identify enrichment of Pb, Cu and Zn above upper continental crust (Upadhyay et al., 2015). The transported soil factor included a similar set of crustal elements but also a measurable amount of sulfate. Again, the sulfate is assumed to be the result of sorption of either SO_2 gas or other oxidized sulfur species and therefore the presence of sulfate is taken to indicate atmospheric transport.

One factor was isolated that impacts COW more than the other two sites and was labeled feedlot in reference to the local source impacting this site; the contribution of this factor to COW may explain improved model performance at that site compared to CG and PCH. While some markers are present that may indicate biomass combustion, the similarity to locally obtained source samples (Upadhyay et al., 2015) and the geographical distribution excluded biomass combustion as the likely origin of this source. This factor contains high concentrations of organic carbon as well a significant amounts of the measured magnesium, potassium, and phosphate. Potassium and phosphate only had measurable concentrations only at the COW site while potassium, phosphate and sulfate were found in source soil samples collected near and within cattle feedlots (Upadhyay et al., 2015).

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

3.4 PM_f Source Profiles

The optimal PMF solution for fine particles resulted in six source profiles as shown in Figure 3. Optimal model performance was achieved with fewer PM_f species than with PM_c although the overall model performance in resolving sources of PM_f was weaker than obtained for source resolution of PM_c. As a result, the source apportionment results for PM_f should be interpreted as only indicative of local sources. Several species were eliminated from the analysis because model fit was better without them or because these individual species were poorly modeled and they could not be reliably apportioned to individual factors including the secondary ionic species such as sulfate, nitrate and ammonium. Three factors were identified based on their dominant chemical species. A lead-rich (also labeled Pb-rich) factor was isolated based on a profile that included nearly 70% of the measured lead. A salt factor was identified based on a profile that contained approximately 85% of the measured

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chloride, even though it lacked sodium. Sodium was poorly fit in the model possibly reflecting the contribution of salt from the desert playa dust (Reynolds et al., 2007). When observed on a seasonal basis, the salt factor contributed less than 1 μg/m^3 at all times. Finally, the brake wear factor was identified based on the presence of copper and zinc. The influence of this factor peaks in March, August, and again in the winter (November through January) similar to what was seen for PM_c sources. The PM_f brake wear and motor vehicle factors were isolated as separate sources. The PM_f brake wear factor was similar to the PM_c road dust factor with both containing a large fraction of apportioned Cu and Zn although road dust was not as enriched in Pb in the PM_f profile when compared to the PM_c profile. This difference may corroborate the hypothesis that Pb present in crustal material originated from historical smelting emissions which could explain why motor vehicle and road dust factors were isolated from each other for fine particles, which did not occur for coarse particles.

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 usually below the LOD for coarse particles making isolation of a similar profile not possible. During this study, elemental carbon concentrations were highest at the CG site consistent with greater traffic density.

Two factors contained signatures with multiple elementals common in soils. These two factors were identified as road dust and crustal material based on the elevated (road dust) or absence (crustal material) of organic carbon. This is consistent with source samples collected in the area (Upadhyay et al., 2015).

3.5 PM_c Source Apportionment by Site

Figure 4 shows the relative source contribution at each site, as a percent of the apportioned PM_c mass, for each source factor averaged over the study. The apportioned PBAP factor contributes about 25% to the apportioned mass. 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, the three sources with strong contributions from crustal elements, comprise about 35–40% of the apportioned mass which is generally consistent with, within the uncertainty of the results, the estimated crustal fraction based on the measured particle composition (Table 1). 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 as discussed previously. The boron-rich source contributes a larger fraction of the PM_c mass at the PCH site compared to other sites. The feedlot factor is only important at COW, which is adjacent to this unique source. The overall contribution of feedlot material to PM_c mass concentrations measured at COW may be greater than what was modeled. The feedlot source profile only includes the unique soluble ion species PO_4^{3-}, K^+, and Mg^{2+} and not the significant crustal component found in the chemical profile of

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feedlot material (Upadhyay et al., 2015). Overall approximately 8% of the particle mass remains unattributed to any of the resolved sources.

3.6 Apportionment of PM_c by Season

Figure 5 shows the monthly averaged PM_c mass apportioned at each site. The PBAP factor is the most important source resolved at COW and also is highly variable by season. Concentrations of PBAP are highest during the spring (March - May) and fall (October) months and seem to be correlated with the feedlot and crustal source contributions suggesting PBAP is associated with the feedlot source and grain processing as well as agricultural activities; with varying influence of each by season. The decline in the contributions of these three factors at COW at the end of the study are likely due to removal of cattle from the adjacent fields to other feedlots within the region. No strong seasonal variation is observed for the boron-rich source. The crustal source is most important and most variable at PCH. Elevated apportioned PM_c mass concentrations measured during March, August, October, November, and December are driven by variations in this factor and this seasonality likely originates from farming activities in the area (spring and fall) and monsoonal wind storms (Clements et al. 2013).

As noted previously, the road dust source was highest at CG and appears to peak during the cooler months (October through March) consistent with the increase in the number of winter residents in the area (Happel and Hogan, 2002). At PCH, the road dust source appears to peak during the planting and harvesting seasons and maybe due to the blow over of dust from active fields and its re-entrainment from vehicle traffic associated with agricultural activities.

Contributions from the remaining sources to PM_c mass are relatively small. The contributions from the secondary source are lowest during the spring months (February through April) with its highest contribution during winter months at PCH and COW. 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 of this species into the gas phase. The unidentified component was slightly higher at PCH on average likely due to the few months in the spring and fall with greater than 10% of the mass unidentified. Given the seasonal pattern this may be due to an unidentified transient source in close vicinity to the PCH sampling site. A separate analysis of the impact of summertime monsoon weather patterns and PM_c mass did not yield conclusive results (Clements et al., 2013). The unapportioned mass contributes to the reconstructed PM_c mass balance in the summer at all three sites but is generally within the uncertainty of the results.

3.7 PM_f Source Apportionment by Site

Figure 6 shows the relative source contribution of each source factor at each site averaged over the study period. The motor vehicle source represents between 25–45% of the apportioned fine mass. The contribution from this source is highest at the urban CG site, which experiences a higher traffic volume. It is likely that the motor vehicle contribution at

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COW is comparable to CG and larger than PCH because it is close (25 m) to the regional highway connecting Maricopa and Casa Grande, whereas PCH is further (~200 m) from a less traveled road.

The road dust component is the second largest individual contributor to fine particles making up approximately 30% of the PM_f mass. This fraction is fairly uniform among the sampling locations and may result from a balancing of two influences: 1) traffic that can re-entrain road dust (influence greatest near the urban center) and in the more remote locations, a greater impact from uncovered and disturbed landscapes that can lead to greater deposition of dust on and near roadways. The lead-rich factor accounts for 10% of the PM_f mass at each site and includes a small fraction of most crustal related elements and thus may represent surface soils in the region (Upadhyay et al., 2015). The lead may be present in the soil naturally or elevated in the soils due to deposits of tailing materials from copper mines previously operated within the region as local soil was measured to be enriched in Pb, Cu and Zn (Upadhyay et al., 2015). The crustal factor represents between 2–7% of the PM_f mass within the region. Overall approximately 12% of the PM_f mass was un-apportioned. However, the unidentified fraction is higher at the sites influenced by agriculture than the urban site suggesting either an unknown agricultural source or a bias in measurements with greater focus on urban areas. The OC conversion factor also may be underestimated for agricultural sources as suggested for PM_c above.

3.8 PM_f Source Apportionment by Season

Figure 7 shows the monthly averaged PM_c mass apportioned at each site. On average, the motor vehicle source is the main contributor to PM_f 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). While estimating increase in local population due to seasonal residents is difficult (Happel and Hogan, 2002), this is consistent with the expected increase in local population for winter residents from other locations. At COW, the mass contribution from the MV source is similar in magnitude as GC but there also is a small peak in the spring. Overall CG has smaller fluctuations in the MV contribution than at CG. The seasonal trend at COW may be the result of steady operations from nearby sources including the railroad, grain processing equipment, and vehicles servicing the feedlots and grain processing plant. The brake wear contribution appears to have peaks periods in the spring and fall/early winter at all there sites as well as a peak in August at PCH. It is likely that similar reasons drive the brake wear seasonal tread as the motor vehicle trend.

The monthly contribution of road dust to PM_f mass is fairly consistent among the sites. In general, concentrations are lowest during the winter with peak periods from the late spring through summer. The seasonal road dust and motor vehicle source contributions correlate as might be expected but the road dust factor correlates better with the crustal factor. This suggests that the identified road dust source may represent a combination of crustal material re-entrainment routes and aggregate road dust and other crustal material.

The crustal source contributes most during the tilling (March) and harvesting (October-November) seasons. The lead-rich source contributes least during the summer (June-August)

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peaking in the late fall and winter at all three sites. Measurements of rainfall measured at the Maricopa meteorological station showed several monsoon rain events during the summer suggesting that this source is suppressed by wet deposition and decreased re-entrainment from wetted surfaces. The salt source factor contributes less than 0.5 µg/m^3 and does not have a consistent monthly contribution profile across sites.

4. Conclusions

Detailed chemical composition was obtained over one year at three sites providing new insights into the spatial and temporal variability of fine and coarse particle chemistry in the area. Source impacts were quantified by applying the PMF receptor model to the detailed chemistry data.

Coarse particles within the region were apportioned to nine sources including primary biological aerosol particles, crustal material, road dust, feedlot, secondary, boron-rich, transported soil, ammonium nitrate, and salt. On average about 8% of coarse particles remained un-apportioned. The largest relative source contributions to PM_c mass included PBAP, crustal, road dust, feedlot, and secondary. Their contributions varied by site depending on the impact of local sources such as a feedlot and grain processing near COW, agricultural land use adjacent and surrounding PCH, and higher traffic volume within the urban area. Seasonal trends also varied by site with peaks for some components in the spring and/or fall likely impacted by agricultural activities, while other components peaked in the late summer early fall due to high winds associated with the monsoon season.

Fine particles were apportioned to six sources including motor vehicles, road dust, lead-rich, brake wear, crustal, and salt. Approximately 12% of the PM_f mass was un-apportioned and this fraction was largest during peak periods indicating that an important local source(s) may not have been identified. The highest relative source contributions were from motor vehicles, road dust, and lead-rich. As with PM_c, the impact of their relative contributions varied by site and was likely dependent on local sources. The motor vehicle source contribution was highest during the winter in part resulting from milder temperatures leading to more tourism and traffic in and around CG. The crustal and lead-rich source contributions are largest during the spring and fall suggesting an impact from agricultural planting and harvesting operations.

This study has improved our understanding of the sources impacting ambient coarse and fine particle concentrations in Pinal County, AZ – a rural area with a growing population that experiences some of the highest PM_{10} (driven by PM_c) concentrations in the US. These results can be used to develop more effective and efficient PM_f and PM_{10} State Implementation Plans.

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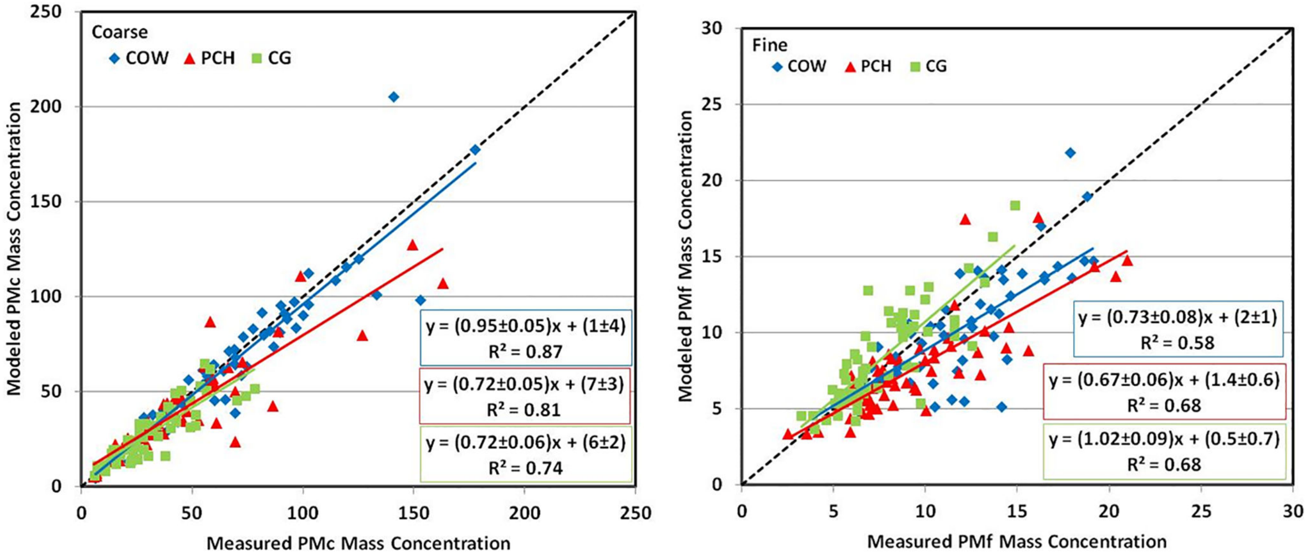

Figure 1:

PMF model performance for coarse and fine particles mass concentrations.

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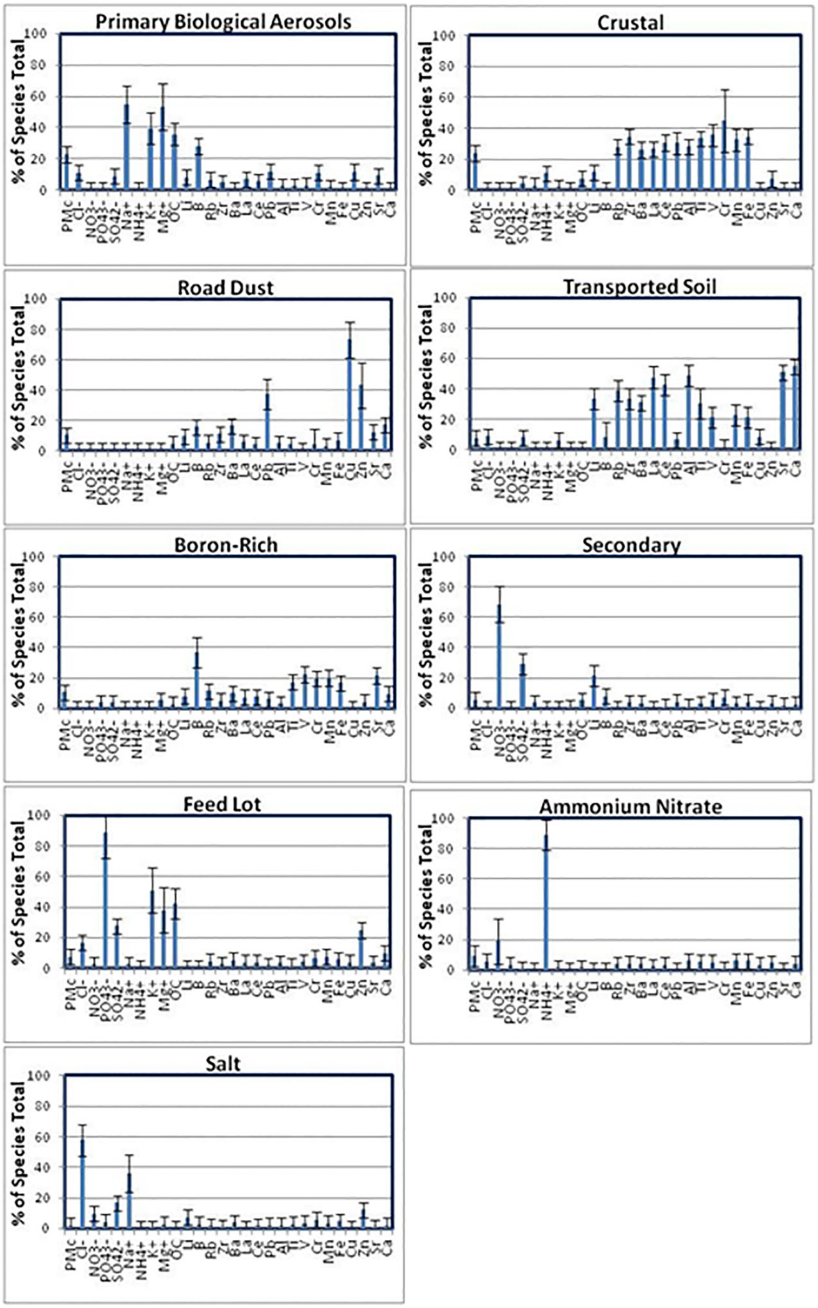

Figure 2:

Coarse particle source profiles for the 9-factor solution. Rationale for profile identification is given in the text.

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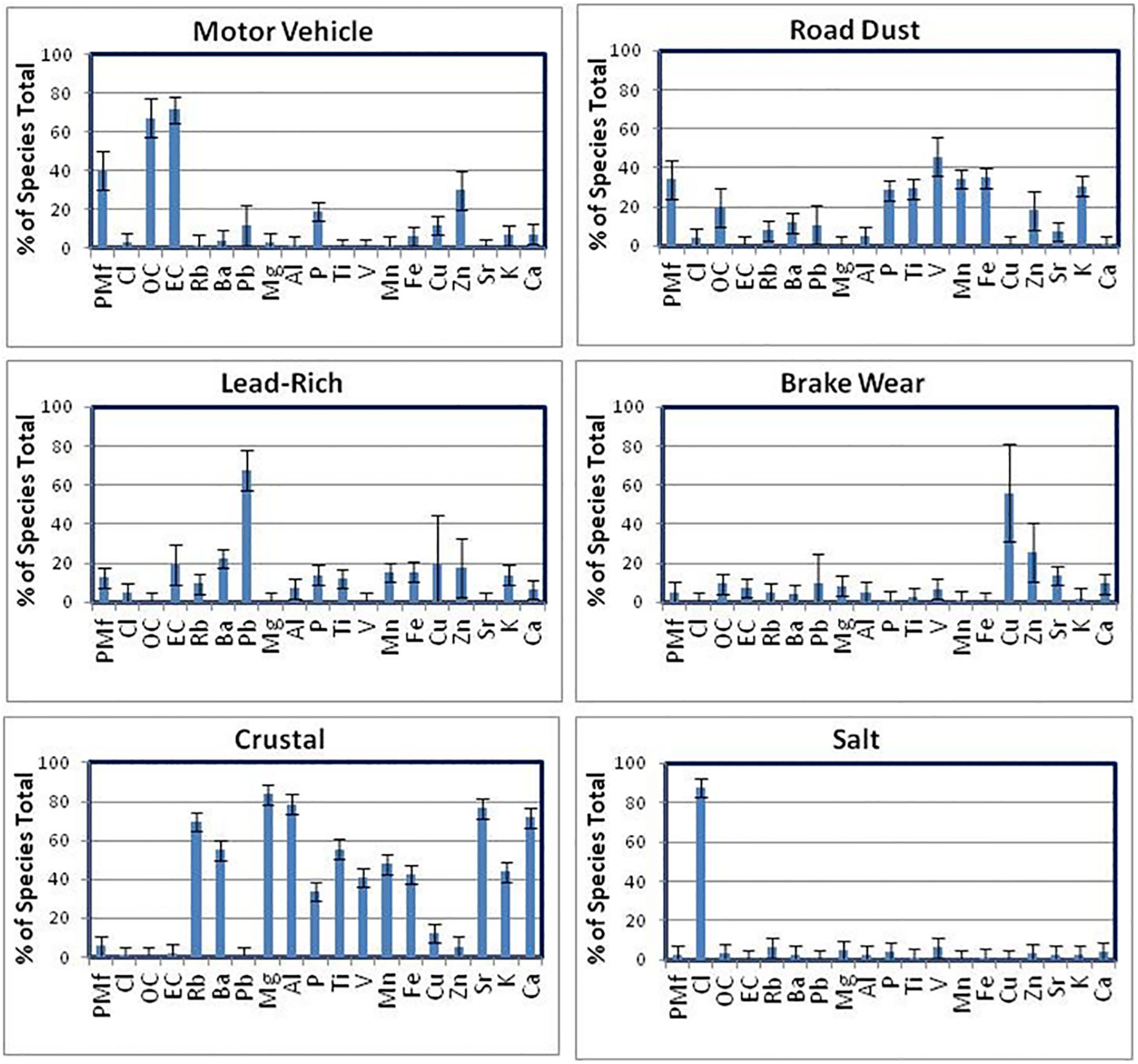

Figure 3:

Fine particle source profiles for the 6-factor solution. Rationale for profile identification is given in the text.

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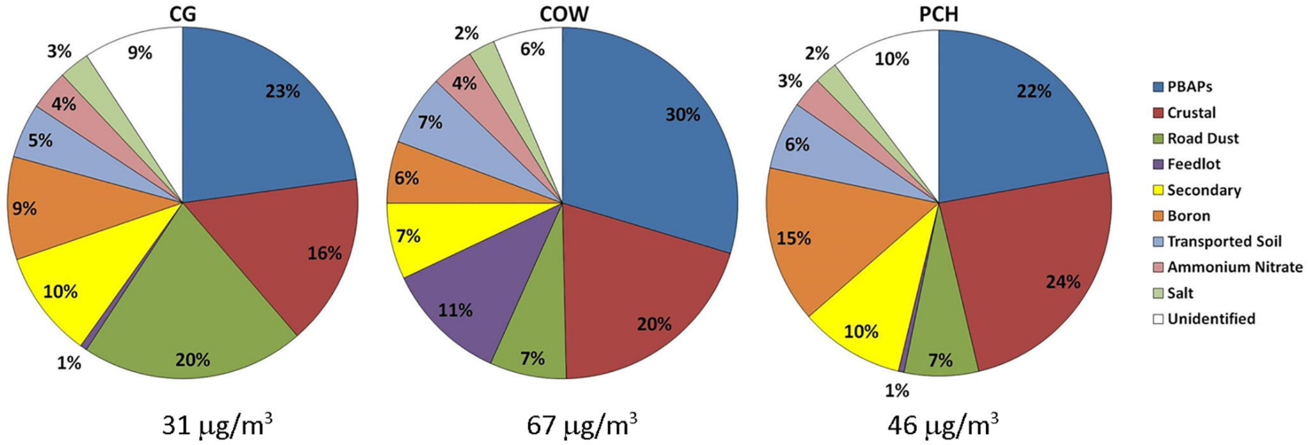

Figure 4.

Sources attributed to PM_c mass and the measured PM_c mass at each site.

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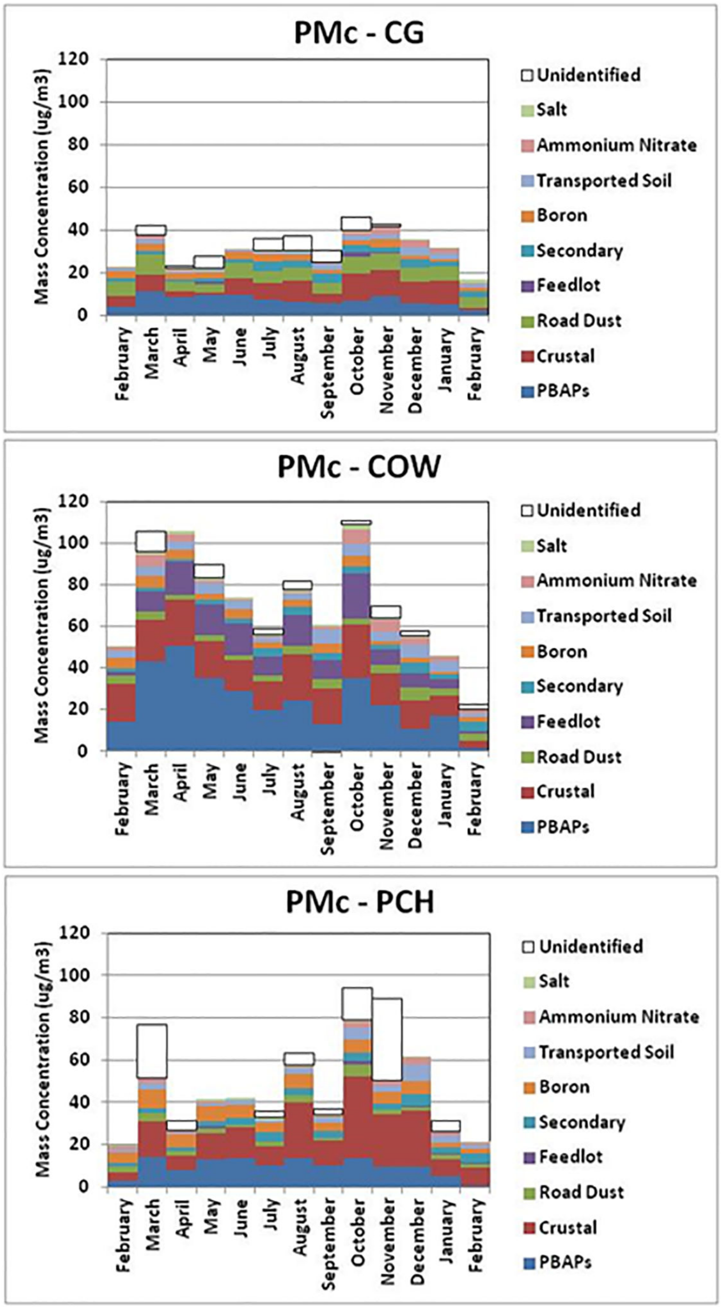

Figure 5:

Monthly averaged source contributions to PM_c mass based on PMF modeling

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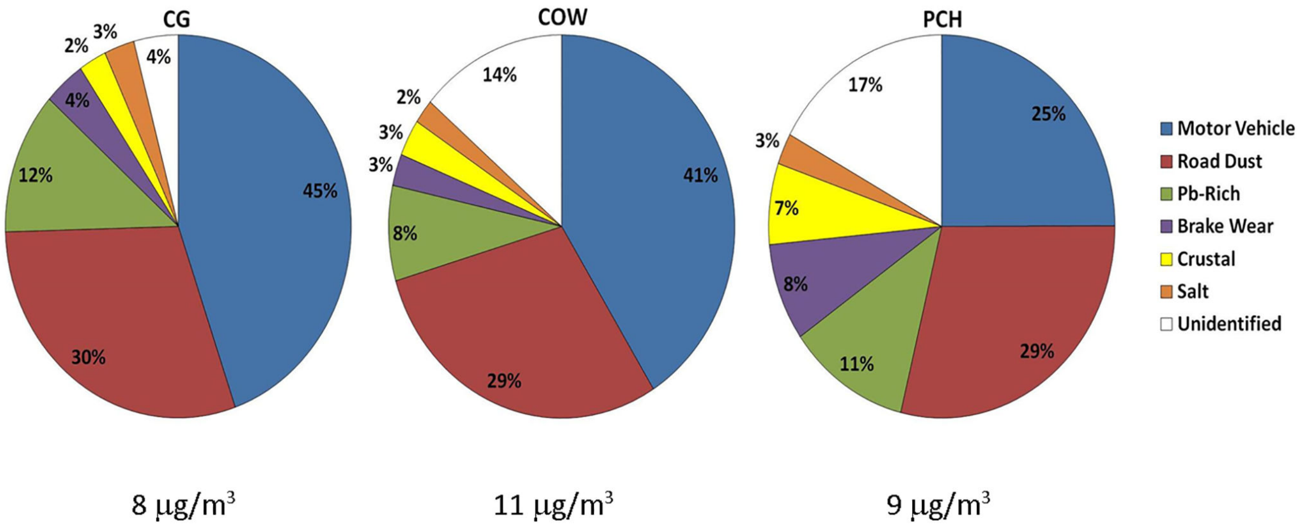

Figure 6:

Sources attributed to PM_f mass and the measured PM_f mass at each site.

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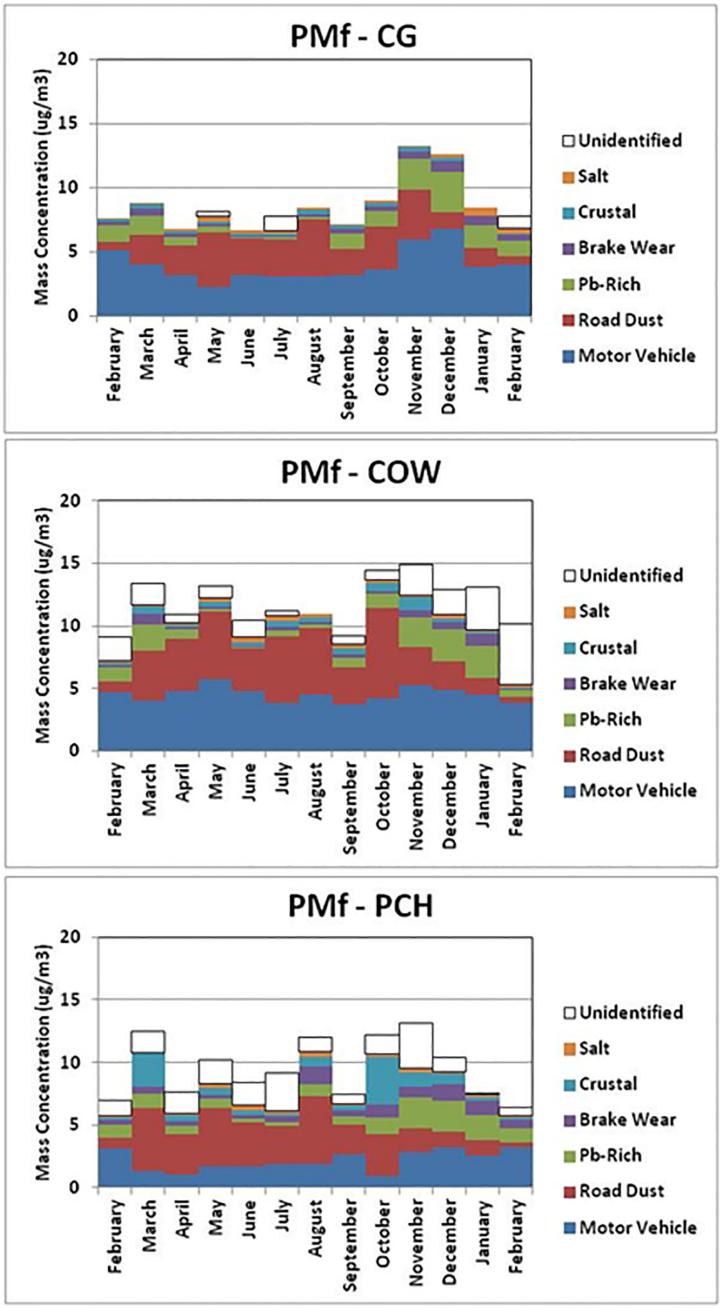

Figure 7:

Monthly averaged source contributions to PM_f mass based on PMF modeling

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Table 1:

Annual average coarse and fine PM mass and chemical composition* at each ambient sampling location.

	Casa Grande (CG)	**Cowtown (COW)**	**Pinal County Housing (PCH)**
Coarse PM	31 μg/m^3	67 μg/m^3	46 μg/m^3
Crustal	54%	47%	52%
Organic Material	12%	26%	9%
Nitrate	2%	1%	2%
Sulfate	1%	1%	1%
Ammonium	0.1%	0.1%	0.1%
Other Measured Species	7%	8%	6%
Unidentified	24%	17%	30%
Fine PM	8 μg/m^3	11 μg/m^3	9 μg/m^3
Crustal	22%	24%	46%
Organic Material	46%	38%	27%
Nitrate	8%	13%	6%
Sulfate	12%	9%	10%
Ammonium	0.1%	0.1%	0.1%
Other Measured Species	7%	6%	7%
Unidentified	5%	10%	4%

[*] Crustal Material = 1.89[Al] + 1.4[Ca] + 1.87[Fe] + 1.67[Ti] + 2.14[Si]

Organic Material = 2.0 OC

Unidentified = Measured mass minus the sum of the chemical components after conversion factors were applied

Nitrate, sulfate, ammonium and other species were used as measured by analytical method