Chemical Characterization of Coarse Particulate Matter in the Desert Southwest – Pinal County Arizona, USA

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7 Abstract

The Desert Southwest Coarse Particulate Matter Study was undertaken to further our 8 understanding of ambient concentrations and the composition of fine and coarse particles in 9 rural, arid environments. Sampling was conducted in Pinal County, AZ between February 2009 10 11 and February 2010. The goals of this study were to: 1) chemically characterize the coarse and fine fraction of the ambient particulate matter in terms of mass, ions, elements, bulk organic and 12 13 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 14 15 of local vs. regional sources; 3) collect, re-suspend, and chemically characterize various crustal 16 sources within the area to identify differences which may isolate them (crustal sources) as 17 independent sources, and; 4) use a receptor based modeling approach to identify particle sources 18 and the relative impact of each on ambient PM concentrations. This work reviews the study 19 objectives, design, site descriptions, and measurement techniques relevant to this research effort 20 and presents the general characteristics of PM during the study period. This unique dataset will support efforts to reduce PM₁₀ and PM_{2.5} concentrations in the area to below the National 21 Ambient Air Quality Standards (NAAQS) for these pollutants. 22

1	Coarse particle concentrations are, on average, approximately 5 times fine particle mass
2	concentrations within the region. Coarse particle concentrations in Pinal County are highest
3	during spring and fall seasons, consistent with the tilling and harvesting seasons while fine
4	particles concentrations are highest during fall. Crustal material is the dominant component of
5	coarse particle composition, representing 50% of the mass on average followed closely by
6	organic material representing 15%. Fine particles still contain a significant crustal fraction
7	(30%) but organic material dominates at 37% of the particle mass.

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- 9 Key Words: desert aerosols, coarse particles, fine particles, chemical composition
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1 **1. Introduction**

2 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 3 populations (United States Code, 2006). In terms of ambient particles, two standards exist – one 4 for PM_{10} (particles with an aerodynamic diameter [AD] less than or equal to a nominal 10µm) 5 and another for $PM_{2.5}$ (particles with an AD less than or equal to a nominal 2.5µm). The PM_{10} 6 size fraction can be considered to be the sum of fine particulate matter (designated as PM_f, or 7 8 $PM_{2.5}$) and coarse particulate matter (PM_c , particles in the size range between 2.5 and 10 μ m 9 AD). Rural areas of the desert Southwestern United States experience high concentrations of 10 PM_c, and it is often spikes in the PM_c concentrations that drive exceedances of the PM₁₀ NAAQS 11 12 within the region (U.S. EPA, 2007). Exceedance of the NAAQS requires that states formulate plans (State Implementation Plans – SIPs) to reduce the ambient PM concentrations to within 13 acceptable limits. The creation of effective SIPs for achieving this goal relies on knowledge of 14 15 the current emission sources, the relative impact of each source, and control strategies that might

16 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 affects (Dockery et al., 1993; Dockery and Pope, 1994; Prahalad et al., 1999; Mar et al., 2000; Pope et al., 2007; Duvall et al., 2008; Happo et al., 2008; Gerlofs-Nijland 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

1	outcomes (Dockery et al., 1993; Samet et al., 2000; Belleudi et al., 2010). However, while
2	recent studies revealed that adverse health effects (e.g., asthma, reduced cardiac variability, etc.)
3	are also associated with coarse particulate matter (PM _c) in ambient air (Mar et al., 2000; Lipsett
4	et al., 2006; Happo et al., 2008), the chemical composition of PM _c remains poorly characterized.
5	Although significant PM _c concentrations are generally only found in rural areas, population and
6	urban sprawl has increased public exposure to these high PM_c concentrations, increasing the
7	importance of understanding the resultant health effects. Improved characterization of coarse
8	particles is the critical first step to understanding the health risk they may pose.
9	The Desert Southwest Coarse Particulate Matter Study was conducted in and around the
10	town of Casa Grande in Pinal County, Arizona. This region has experienced numerous
11	exceedances of the PM_{10} NAAQS, up to hundreds of exceedances per year, and registered the
12	highest PM _c concentrations in the region (U.S. EPA, 2007). Previous studies in this region have
13	examined ambient mass concentrations in the $PM_{2.5}$ and PM_{10} size range, characterized some
14	bulk chemical characteristics, and implemented Chemical Mass Balance (CMB) modeling on a
15	limited number of samples (Pinal County Air Quality Staff, 2005). This study expands on the
16	previous work by isolating the PM_c and PM_f size fractions, expanding the chemical
17	characterization of the aerosol, creating detailed source profiles for crustal materials within the
18	region, and applying multiple modeling approaches to characterize particle sources and their
19	relative contributions.
20	This paper, presents the study objectives, design, measurement locations, analysis
21	methods, and general characteristics of PM during the study period. It will describe a) the
22	physical and chemical characteristics of PM_C and PM_f ; b) how the physical and chemical

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characteristics of PM vary spatially and temporarily; c) how chemical characteristics vary by
 size-fraction; d) and the relative influence of local versus regionally transported PM.

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4 2. Materials and Methods

5 2.1. Study Area

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 1 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.

The Casa Grande (CG) site (401 Marshall St.), denoted by A in Figure 1, is on the roof of a one-story building located within the town of Casa Grande, AZ, a small city with a population of approximately 50 000. The site is situated within a local business district and is immediately surrounded by buildings, paved roads, parking lots, and residential neighborhoods with trees, which are slightly taller than 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 1, 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, located 35 km to the northwest. 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 1 north and south) of the COW site. In the immediate vicinity of the sampling site there are a 2 number of potential sources including fallow cropping fields (within 0.25 km to the west, north, 3 and east), cattle feedlots (within 0.5 km south and southeast), a grain processing operation (0.7 4 km southwest), a fertilized soil operation, (2 km southwest), railroad traffic (tracks <0.5 km 5 6 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 7 PM₁₀ standard each year (U.S. EPA, 2007). 8

9 The Pinal County Housing (PCH) site (970 N. Eleven Mile Corner Rd), denoted by C in Figure 1, is located approximately 17 km to the east of the city of Casa Grande. The site is 10 immediately surrounded by native desert, is approximately 0.2 km west of the Pinal County 11 Housing Projects, and is nearly 0.2 km east-southeast of the wastewater treatment ponds for the 12 complex. Air quality at this site is likely influenced by agricultural fields, which are located 13 14 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 15 to the east), and a dairy and cotton gin located within 3 km of the site. 16

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2.2. Ambient Sample Collection

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_f and PM_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 < -4°C during storage) until
laboratory analysis.

Although not part of the sampling campaign, each sampling site also measured semicontinuous PM₁₀ 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 (8km northwest of the COW monitoring site).

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2.3. 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. 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).

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7 **2.4.** Sample Analysis

Mass. Mass was obtained gravimetrically on all Teflon filters by difference (post-8 collection weight minus pre-collection weight). Filters were removed from frozen storage and 9 then equilibrated for 24 hours and weighed under controlled temperature $(22^{\circ}C < T < 24^{\circ}C)$ and 10 humidity conditions (45% < RH < 55%) to achieve reproducible and stable mass measurement 11 readings. Every 10th filter was reweighed and if weights were outside quality control limits of 12 5ug, all 10 filters were re-weighed. A National Institute of Standards and Technology (NIST) 13 14 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 15 invalidated due to user, instrument operation, or experimental error. 16

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 μ l 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 μ m 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

1	mM methylsulfonic acid eluent running at 1.00 mL/min. Anions, including chloride, nitrite,
2	nitrate, phosphate, and sulfate were quantified using an AS12A analytical column and 2.7 mM
3	sodium carbonate/0.3 mM sodium bicarbonate eluent running at 1.5 mL/min. The instrument
4	was calibrated using a series of standard dilutions from a certified calibration standard for each
5	suite of compounds (Dionex P/N 056933 and 046070), laboratory and field blanks were
6	periodically analyzed, and every 7 th filter was reanalyzed for method precision determination.
7	Elements. Following gravimetric analysis, the second set of Teflon filters were analyzed
8	for 63 trace elements (including, but not limited to, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg,
9	Mn, Mo, Na, Ni, P, Pb, Rb, Sb, Se, Sn, Ti, U, V, Zn) using high-resolution inductively coupled
10	plasma mass spectrometry (HR-ICP-MS, herein referred to as ICP-MS). Samples were
11	microwave-digested in 30 mL Teflon vials using an acid mixture of 4 mL nitric acid, 0.9 mL
12	hydrochloric acid, and 0.1 mL hydrofluoric acid (Fisher) (Upadhyay et al., 2009). The
13	temperature profile included a 6 minute temperature ramp to 140°C, holding for 2 minutes,
14	followed by a 5 minute temperature ramp to 165°C, holding for 6 minutes. The temperature was
15	further increased to 180°C and held for 15 minutes. The digestion solution was diluted to 25 mL
16	using ultrapure water, from which a 1.25 mL aliquot was transferred to a 15 mL centrifuge vial
17	and diluted to 5 mL using ultrapure water. This final solution was analyzed for elements by ICP-
18	MS (Thermo Finnigan ELEMENT 2) using an internal indium standard. High-resolution was
19	used to quantify sodium and potassium. The instrument was calibrated using a multi-element
20	standard (SPEX Certiprep Inc., USA). Quality control included analysis of laboratory and field
21	blanks, replicate analyses, and analysis of two NIST standard reference materials (San Joaquin
22	Soil, SRM 2709 and Urban Dust, SRM 1649) using the same analytical procedure.

1	Bulk Carbon. A 1 cm x 1.5 cm punch was removed from each quartz-fiber filter and
2	analyzed for bulk OC and EC using a thermal—optical EC/OC analyzer (Sunset Laboratory Inc.
3	Tigard OG) (Birch and Cary, 1996). The filters were analyzed according to a slightly modified
4	Sunset Labs' thermal-optical transmittance (TOT) method with variable time steps lasting
5	between 60 and 200 seconds during OC evolution at temperature plateaus of 310, 475, 615, and
6	870°C. The temperature profile during EC evolution included 45 second holds at 550, 625, 700,
7	775, and 850°C with a final hold at 870°C for 120 seconds. Quality control included analysis of
8	laboratory and field blanks, replicate analyses, and analysis of a sucrose standard prepared by
9	Sunset Labs. Carbonate was not quantified in this method and thus, reported OC concentration
10	may be biased high.

Soils. Prior to laboratory resuspension, soil samples were dried in an oven at 110°C for 11 24 hours. Samples were then lightly ground using a mortar and pestle to gently break up large 12 aggregates within the sample using less physical force than what might be exerted by a simple 13 foot step so as to minimally impact the size of particles in the desired size range. Soil samples 14 were resuspended by passing HEPA-filtered air over the sample in a resuspension chamber and 15 then through a size-selective cyclone (URG Corporation). The operating flow rates were 16 17 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 18 Teflon and quartz-fiber filters. Filters were stored in the same manner as field samples until 19 20 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 21 cm²) concentrations. All samples were analyzed for mass, bulk OC and EC, and elements in a 22 23 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.

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2.5. Quality Assurance

6 Prior to the start of the field sampling campaign, all twelve dichotomous samplers were 7 set up in one location and a series of co-located samples were collected for the purposes of 8 precision determination and quality assurance. The use of simultaneous determination of aerosol 9 mass and composition allowed determination of not only the variability in measurements due to 10 variability in sampling, but the variability arising from response of the analytical measurements.

A total of 10 sets of co-located samples were collected on Teflon substrates and all filters 11 12 were analyzed to determine ambient mass concentrations. All individual and independent mass measurements were well correlated ($r^2 > 0.95$) and no systematic bias was noted among any on 13 the individual samplers. Using two times the standard deviation of the measurements, 95% 14 15 certainty was achieved within approximately 15% of mean for PM_c and within about 25% of the mean for PM_f samples. Similar analysis was done on the chemical measurements made on this 16 set of samples. The first 5 sets of co-located Teflon samples were analyzed for important water 17 soluble ion species, including nitrate, sulfate, and ammonium. Again, using two standard 18 deviations of the measurements, 95% certainty was achieved at approximately 25% for anion 19 species and at approximately 15% for cation species, the difference can mainly be attributed to 20 column sensitivity. Three sets of co-located quartz fiber samples were also collected and those 21 samples were analyzed for bulk OC/EC concentrations. A certainty level of 95% was achieved 22 23 at approximately 25% of the carbon concentration.

Throughout the field sampling campaign, two samplers at each site collected on Teflon 1 substrates and samples from both of these instruments were used for duplicate mass 2 concentration measurements and the results were continuously compared for quality assurance 3 evaluation of the sampler operation. Samples were invalidated from the data set for a number of 4 reasons including instrument error based on log sheet notations (loss of power, improperly set 5 6 timer, failed equipment, etc.), handling error (filters that were accidentally mishandled during transportation or weighing), or measurement error (inconsistency in the determined mass 7 measurement). The latter was the most difficult to justify but was evoked if: (a) the recorded 8 9 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 10 mass measurement made on the co-located filter, or (c) if the resulting ambient concentration 11 was more than 50% different from the ambient mass concentration measured by the co-located 12 filter or TEOM measurement. Of the six samplers operated in the field that were used for Teflon 13 14 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 15 strictly due to instrument errors at the end of the sampling campaign. 16

Figure S1 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 4%, 8%, and 18%, respectively. 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 this figure are conservative estimates.

Each of the ambient monitoring sites was equipped with an R&P 1400a Tapered Element 7 Oscillating Microbalance (TEOM), operated by the Pinal County Air Quality Control District, 8 9 which is used for compliance monitoring or determining the ambient mass concentration of particles in the PM₁₀ size range. Although reported in 5-min intervals, this data was averaged 10 into daily mass concentration values and compared to the re-constructed PM_{10} daily mass 11 concentration, measured as the sum of filter based PM_f and PM_c measurements. Figure S2 12 shows the agreement between the filter measurements at the Casa Grande site, made as part of 13 this sampling campaign, and the co-located TEOM measurements at the site was quite good 14 (slope 0.85 ± 0.02 , R²=0.99). Filter based measurements are approximately 15% lower than the 15 TEOM-based measurements, which may be an artifact of variations in the sampler inlet design or 16 17 analytical differences. Additionally, filter based mass measurements were made in a controlled laboratory environment in which humidity conditions were closely monitored and controlled. 18 19 During some seasons, this resulted in the removal of particle-bound water from the sample and in 20 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 21 22 estimated based on the experimental setup deployed in this study.

1 **3. Results and Discussion**

2	Table 2 details the average, maximum, and minimum coarse and fine particle mass
3	concentration and chemical composition at all three of the ambient monitoring sites. On average,
4	the coarse particle mass concentration (47.6 μ g/m ³) is on the order of 5 times higher than the fine
5	particle mass concentrations (9.4 μ g/m ³) within the region; the comparison was observed to be
6	within the range of 2 to 9 times the fine particle concentration at times. Coarse particles have a
7	much larger concentration range and more variability (5.6 - 177.6 μ g/m ³) than fine particle mass
8	concentrations (2.5 - 20.4 μ g/m ³), suggesting an influence from one or more significant local
9	sources of coarse particles.
10	In general, particle concentrations were lowest at the CG monitoring location. This is
11	consistent with the more urban nature of this site, having fewer large particle sources and more
12	paved surfaces which limit the amount of particle resuspension. Particle concentrations were
13	significantly higher at the PCH and COW sites, which are much more rural in nature and are in
14	closer proximity to sources of large particles. Generally, the concentrations at the COW site
15	were the highest mass concentrations measured. This is consistent with historical data which
16	show numerous NAAQS exceedances at this monitoring location (U.S. EPA, 2007). This
17	observation suggests that the local cattle feedlot and/or grain processing plant may be significant
18	particle sources impacting this monitoring site.
19	Figure 2 illustrates the chemical composition of coarse particles at each of the ambient
20	monitoring locations. Organic matter was reconstructed by multiplying the bulk OC
21	measurement by a factor of 2, a common assumption for organic PM found in rural environment
22	(Turpin and Lim, 2001). The contribution of fugitive dust was estimated based on the common

23 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 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 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 8 9 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 10 to other sites in the desert southwest, this fraction is comparable to the range (41-62%) measured 11 at other locations (Cheung et al., 2011). Organic material makes up another significant fraction 12 of the coarse particle mass. On average, organics make up approximately 15% of the particle 13 mass but, the fraction is the largest (26%) at the COW site. Organic matter in the feedlot 14 material was thought to be a significant source for the organic fraction of the coarse particle mass 15 measured at COW. Source soil samples from the feedlot contained elevated organic matter when 16 17 compared to other soil samples thus confirming this interpretation. A significant fraction (24%) of the coarse particle concentration remains uncharacterized and might include particle bound 18 19 water which was not measured, but is most likely a result of assumptions made when calculating 20 the crustal component (including variation in coefficients that might result from considering just PMc and missing mass from oxide forms of other measured elements), biases caused by sample 21 22 extraction, the choice of analytical techniques, and estimations that were made to account for 23 species that could not be measured.

The chemical composition of fine particles is also illustrated in Figure 2. Fine particles 1 within the region also contain a significant, although smaller, crustal component (30%). This 2 3 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 4 suggests that reducing emissions from crustal sources may reduce both PM₁₀ and the upward 5 6 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 7 area, where overall concentrations are lowest but where vehicle traffic is highest. Water-soluble 8 9 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 10 8%) than it was for coarse particles indicating that the measurements, assumptions about scaling, 11 and crustal component reconstruction reflect an accurate characterization of ambient fine 12 particles. 13

14 The seasonal differences in particle mass and chemical composition are shown in Figure 3. In terms of both coarse and fine particle mass concentrations, the highest concentrations are 15 observed during the months of March and October/November and are driven by changes in the 16 17 crustal component. This observation is most pronounced at the rural sites, especially in fine particles at the PCH site. This is consistent with the tilling and crop planting activities observed 18 19 during spring and harvesting and crop cutting activities observed during fall indicating that 20 agricultural crustal material is a significant source of PM in the region. High mass concentrations are also noted in August and the increase is again dominated by changes in the 21 22 crustal component. This increase is consistent with the onset of the Arizona monsoon season, 23 noted for increases in the number and intensity of dust storm events. Surprisingly, total coarse

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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.

6 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 7 component are responsible for the majority of total mass concentrations and exceedances of the 8 9 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 10 changes in the crustal component. This observation not only suggests a strong influence from 11 the nearby cattle feedlot, but it suggests that the influence of the feedlot can be seen in a number 12 of components – namely in higher organic material and crustal concentrations, but also in other 13 14 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 15 cattle were being transferred out of a nearby feedlot. With respect to the fine particle fraction, 16 17 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 18 19 be found in the particle phase rather than the gas phase.

Figure S3 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 fitted regression line (PM_f mass concentration = $(0.08\pm0.01) \times PM_c$ mass concentration + (5.2 ± 0.7)) 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.

6 Figure 4 examines the relationship between the coarse particle crustal component mass concentrations versus the coarse particle mass concentration. A strong linear relationship is 7 observed within the data collected at each of the monitoring locations. This relationship 8 9 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 10 remarkably similar (slopes and intercepts within the 95% confidence interval), but the slope of 11 the regression line on the data collected at COW is statistically different and significantly lower. 12 This is consistent with the observation that resuspended dust from the cattle feedlot contains a 13 14 significant amount of organic material which would accompany the traditionally categorized crustal material when resuspended. Feedlot material contains approximately 25% organic 15 material. If this percentage was added to the crustal component, the slope of the regression line 16 17 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 18 19 form (by IC) and in their elemental form (by ICP-MS). Figure 5 shows the comparison between 20 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. 21 Phosphorous concentrations at the COW site were routinely measurable (exceeding $2 \mu g/m^3$) in 22 the coarse particle size fraction and almost all present in the soluble phosphate form. Detection 23

of phosphate in ambient samples is not widely reported in the literature. Measurements have 1 been made in rural areas near Sierra Nevada, CA (Vicars et al., 2010) and Lake Tahoe, NV 2 3 (Zhang et al., 2002), which have found coarse particle phosphate concentrations as high as 90 ng/m^3 , but measurements near cattle feedlots have shown elevated concentrations (Razote et al., 4 2006; McGinn et al., 2010) consistent with our measurements at COW. 5 6 Noting the solubility of calcium, sodium, potassium, and magnesium at each of the sites, it is clear that samples from the COW site contain less soluble calcium and more soluble 7 magnesium and potassium. This is likely related to the cattle feed and waste within the feedlot. 8 9 Thus, solubility measurements may be a useful tool to investigate the influence of the cattle feedlots as a source of PM. 10

11

12 **4.** 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. Coarse particles are comprised mainly (50%) of crustal material which drives the fluctuation in total 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. Organic material is also a significant factor representing approximately 15% of the coarse particle mass.

Spatially, rural sites experienced much higher PMc mass concentrations than the urban 1 site. This is consistent with the proximity and abundance of coarse particle sources located near 2 the sampling locations and the shorter residence time of larger particles. The highest 3 concentrations were observed during spring and fall seasons, consistent with the planting and 4 harvesting seasons and also increase during the late summer monsoon season when strong wind 5 6 gusts can increase particle entrainment. Carefully timing agricultural activities to coincide with times of higher humidity and lower wind speed could potentially mitigate PMc concentrations. 7 Fine particle concentrations within the region are within NAAQS for $PM_{2.5}$. Mass 8 9 concentrations vary seasonally, with highest concentrations observed during spring and fall seasons, consistent with the tilling and harvesting seasons. This suggests that measured aimed at 10 mitigating PMc concentrations may also mitigate PMf concentrations. Fine particles are 11 comprised mainly (37%) of organic material with a similar influence (30%) from crustal 12 material. Approximately 5 μ g/m³ can be attributed to regional background of transported fine 13 particulate matter. 14 The chemical composition of particles varies by sampling location. Higher 15 16 concentrations of organic matter and water-soluble ions are measured at COW consistent with measurements made of the local cattle feedlot material suggesting a significant PM contribution 17 from this source. The solubility ratios for calcium, potassium, and magnesium in feedlot material 18 make them potential marker species for differentiation from other forms of crustal material. 19 Changes in feedlot management practices may change the PM mass contribution from this 20 21 source. Coarse PM is likely responsible for a number of violations of the PM₁₀ and PM_{2.5} 22

NAAQS in the Desert Southwest and especially in areas of growing population located in more

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1 rural areas where housing is cheaper. This unique data set described here will provide a better 2 understanding of the source impacts of coarse particles in the area, giving guidance to policy 3 makers as to the best approaches for reducing levels of PM_{10} and $PM_{2.5}$ to below their ambient 4 air quality standards, and therefore, protect public health.

5

6

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18

19 Supporting Material Available

20 Comparisons between co-located filter based mass concentrations (Figure S1), reconstructed

filter-based PM_{10} mass measurements with the on-site PM_{10} TEOM measurement (Figure S2),

and between filter-based PMf and PMc mass concentrations (Figure S3) are available as

supporting material. This information is available free of charge via the Internet at

1 http://www.atmospolres.com.

1 **References**

2	United States Code, 2006 Edition, Supplement 5, Title 42 – The Public Welfare. Chapter 85 – Air Pollution
3	Prevention and Control, Subchapter I – Programs and Activities, Part A – Air Quality and Emission
4	Limitations, Sec. 7409 - Primary and Secondary Ambient Air Quality Standards.
5	Belleudi, V., A. Faustini, M. Stafoggia, G. Cattani, A. Marconi, C. A. Perucci, and F. Forastiere. 2010. Impact of Fine
6	and Ultrafine Particles on Emergency Hospital Admissions for Cardiac and Respiratory Diseases.
7	Epidemiology 21 (3):414-423.
8	Birch, M. E., and R. A. Cary. 1996. Elemental carbon-based method for monitoring occupational exposures to
9	particulate diesel exhaust. Aerosol Science and Technology 25 (3):221-241.
10	Cheung, Kalam, Nancy Daher, Winnie Kam, Martin M. Shafer, Zhi Ning, James J. Schauer, and Constantinos Sioutas.
11	2011. Spatial and temporal variation of chemical composition and mass closure of ambient coarse
12	particulate matter (PM(10-2.5)) in the Los Angeles area. Atmospheric Environment 45 (16):2651-2662.
13	Chow, J. C., J. G. Watson, H. Kuhns, V. Etyemezian, D. H. Lowenthal, D. Crow, S. D. Kohl, J. P. Engelbrecht, and M. C.
14	Green. 2004. Source profiles for industrial, mobile, and area sources in the Big Bend Regional Aerosol
15	Visibility and Observational study. Chemosphere 54 (2):185-208.
16	Derrick, M., and J. Moyers. 1981. Precise and sensitive water-soluble ion extraction method for aerosol samples
17	collected on polytetrafluoroethylene filters. Analytical Letters Part a-Chemical Analysis 14 (19):1637-1652.
18	Dockery, D. W., and C. A. Pope. 1994. Acute respiratory effects of particulate air pollution. Annual Review of Public
19	Health 15:107-132.
20	Dockery, D. W., C. A. Pope, X. P. Xu, J. D. Spengler, J. H. Ware, M. E. Fay, B. G. Ferris, and F. E. Speizer. 1993. An
21	association between air pollution and mortality in 6 United States cities. New England Journal of Medicine
22	329 (24):1753-1759.
23	Duvall, R. M., G. A. Norris, L. A. Dailey, J. M. Burke, J. K. McGee, M. I. Gilmour, T. Gordon, and R. B. Devlin. 2008.
24	Source apportionment of particulate matter in the US and associations with lung inflammatory markers.
25	Inhalation Toxicology 20 (7):671-683.

1	Gerlofs-Nijland, M. E., M. Rummelhard, A. J. F. Boere, Dlac Leseman, R. Duffin, R. P. F. Schins, P. J. A. Borm, M.
2	Sillanpaa, R. O. Salonen, and F. R. Cassee. 2009. Particle induced toxicity in relation to transition metal and
3	polycyclic aromatic hydrocarbon contents. Environmental Science & Technology 43 (13):4729-4736.
4	Hagen, L. J. 2004. Fine particulates (PM10 and PM2.5) generated by breakage of mobile aggregates during
5	simulated wind erosion. Transactions of the ASAE, 47 (1):107-112.
6	Happo, M. S., M. R. Hirvonen, A. I. Halinen, P. I. Jalava, A. S. Pennanen, M. Sillanpaa, R. Hillamo, and R. O. Salonen.
7	2008. Chemical compositions responsible for inflammation and tissue damage in the mouse lung by
8	coarse and fine particulate samples from contrasting air pollution in Europe. Inhalation Toxicology 20
9	(14):1215-1231.
10	Lipsett, M. J., F. C. Tsai, L. Roger, M. Woo, and B. D. Ostro. 2006. Coarse particles and heart rate variability among
11	older adults with coronary artery disease in the Coachella Valley, California. Environmental Health
12	Perspectives 114 (8):1215-1220.
13	Mar, T. F., G. A. Norris, J. Q. Koenig, and T. V. Larson. 2000. Associations between air pollution and mortality in
14	Phoenix, 1995-1997. Environmental Health Perspectives 108 (4):347-353.
15	Marcazzan, G. M., S. Vaccaro, G. Valli, and R. Vecchi. 2001. Characterization of PM10 and PM2.5 particulate matter
16	in the ambient air of Milan (Italy). Atmospheric Environment 35 (27):4639-4650.
17	McGinn, S. M., T. K. Flesch, D. Chen, B. Crenna, O. T. Denmead, T. Naylor, and D. Rowell. 2010. Coarse particulate
18	matter emissions from cattle feedlots in Australia. Journal of Environmental Quality 39 (3):791-798.
19	Pinal County Air Quality Staff. 2005. Pinal County Air Quality Control District Source Apportionment Study.
20	Pope, C. A., D. L. Rodermund, and M. M. Gee. 2007. Mortality effects of a copper smelter strike and reduced
21	ambient sulfate particulate matter air pollution. Environmental Health Perspectives 115 (5):679-683.
22	Prahalad, A. K., J. M. Soukup, J. Inmon, R. Willis, A. J. Ghio, S. Becker, and J. E. Gallagher. 1999. Ambient air
23	particles: Effects on cellular oxidant radical generation in relation to particulate elemental chemistry.
24	Toxicology and Applied Pharmacology 158 (2):81-91.
25	Razote, E. B., R. G. Maghirang, B. Z. Predicala, J. P. Murphy, B. W. Auvermann, J. P. Harner, and W. L. Hargrove.
26	2006. Laboratory evaluation of the dust-emission potential of cattle feedlot surfaces. Transactions of the
27	ASABE, 49 (4):1117-1124.

1	Samet, J. M., F. Dominici, F. C. Curriero, I. Coursac, and S. L. Zeger. 2000. Fine particulate air pollution and mortality
2	in 20 US Cities, 1987-1994. New England Journal of Medicine 343 (24):1742-1749.
3	Taylor, S. R., and S. M. McLennan. 1995. The geochemical evolution of the continental crust. Reviews of Geophysics
4	33 (2):241-265.
5	Turpin, B. J., and H. J. Lim. 2001. Species contributions to PM2.5 mass concentrations: Revisiting common
6	assumptions for estimating organic mass. Aerosol Science and Technology 35 (1):602-610.
7	U.S. EPA. 2006. 40 CFR 50: National Ambient Air Quality Standards for Particulate Matter (Final Rule), edited by
8	U.S. EPA Office of Air Quality Planning and Standards.
9	U.S. EPA., 2007. AirData: Access to Air Pollution Data. http://www.epa.gov/air/data/index.html, 2007 to 2009 data
10	last accessed in July 2011.
11	Upadhyay, N., B. J. Majestic, P. Prapaipong, and P. Herckes. 2009. Evaluation of polyurethane foam, polypropylene,
12	quartz fiber, and cellulose substrates for multi-element analysis of atmospheric particulate matter by ICP-
13	MS. Analytical and Bioanalytical Chemistry 394 (1):255-266.
14	Vicars, W. C., J. O. Sickman, and P. J. Ziemann. 2010. Atmospheric phosphorus deposition at a montane site: Size
15	distribution, effects of wildfire, and ecological implications. Atmospheric Environment 44 (24):2813-2821.
16	Wanjura, J. D., B. W. Shaw, C. B. Parnell, R. E. Lacey, and S. C. Capareda. 2008. Comparison of continuous monitor
17	(TEOM) and gravimetric sampler particulate matter concentrations. Transactions of the ASABE, 51 (1):251-
18	257.
19	Watson, J. G., and J. C. Chow. 2001. Source characterization of major emission sources in the Imperial and Mexicali
20	Valleys along the US/Mexico border. Science of the Total Environment 276 (1-3):33-47.
21	Zhang, Q., J. J. Carroll, A. J. Dixon, and C. Anastasio. 2002. Aircraft measurements of nitrogen and phosphorus in
22	and around the Lake Tahoe Basin: Implications for possible sources of atmospheric pollutants to Lake
23	Tahoe. Environmental Science & Technology 36 (23):4981-4989.
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25	

1 Figure Captions

2	Figure 1: Map of Ambient Monitoring Locations. The map on the left illustrates the sampling
3	region relative to the Phoenix metropolitan area. The figure to the right shows the sampling
4	locations near the town of Casa Grande. The (A) Casa Grande, (B) Cowtown, and (C) Pinal
5	County Housing sampling sites and are marked with dark circles. Active and fallow agricultural
6	fields are shown in light grey, the town of Casa Grande is shown in dark gray, and the un-shaded
7	regions are desert areas that are not actively cultivated and are referred to in the text as native
8	soils.
9	
10	Figure 2: Average chemical comparison of coarse and fine particles collected at each of the
11	ambient sampling sites.
12	
13	Figure 3: Monthly averaged mass and chemical composition of coarse and fine particles
14	collected at each of the ambient sampling sites.
15	
16	Figure 4: Crustal component mass concentration versus the coarse particle mass concentration.
17	
18	Figure 5: Solubility of several species, given as the soluble fraction. Water-soluble ions were
19	measured by IC and elements by ICP-MS.
20	
21	Figures

1 Figure 1



2 3

4 Figure 2









1 Figure 5



Tables

Table 1: Soil Source Sampling Details. The table includes a prescribed site number, the closest
ambient monitoring location, the soil type, and the samples category designation.

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

PCH - Pinal Country 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, and FDL – soil from a cattle feedlot

1

2 **Table 2:** Average and minimum/maximum coarse and fine particle mass concentration and the

3 chemical compositional breakdown at each of the ambient sampling locations. Negative values

4 imply an over-characterization of aerosol mass.

Casa Grande		Cowtown			Pinal County Housing				
Coarse Particle Fraction	Average	Maximum	Minimum	Average	Maximum	Minimum	Average	Maximum	Minimum
Ambient Mass	30.60	78.00	5.75	66.60	177.60	6.30	45.50	162.80	5.55
Crustal	16.37	30.52	2.22	31.11	94.39	1.32	23.52	110.58	1.33
Organic Matter	3.77	8.06	1.05	17.11	56.96	0.77	4.14	14.50	0.76
Nitrate	0.72	0.46	0.21	0.82	2.80	0.22	0.83	4.80	0.22
Sulfate	0.29	0.35	0.22	0.74	2.54	0.13	0.39	2.25	0.05
Ammonium	0.06	0.07	bdl	0.12	0.47	0.01	0.06	0.29	0.00
Other Measured Species	1.99	2.90	1.91	5.38	19.50	0.32	2.96	10.09	0.28
Unidentified	7.41	35.64	0.14	11.33	0.95	3.52	13.60	20.30	2.91
Fine Particle Fraction	Average	Maximum	Minimum	Average	Maximum	Minimum	Average	Maximum	Minimum
Ambient Mass	7.68	14.85	3.25	11.34	18.80	3.20	9.25	20.35	2.50
Crustal	1.86	3.44	0.44	2.74	4.52	0.19	4.32	11.79	0.31
Organic Matter	3.83	6.91	1.61	4.32	5.86	1.47	2.46	2.11	1.17
Nitrate	0.68	2.21	0.00	1.50	0.60	0.14	0.57	0.19	0.00
Sulfate	1.00	1.69	0.16	1.03	0.99	0.26	0.93	0.50	0.19
Ammonium	0.37	0.62	0.07	0.53	0.37	0.07	0.35	0.19	0.02
Other Measured Species	0.57	0.74	0.11	0.71	1.34	0.08	0.68	1.39	0.09
Unifentified	-0.62	-0.76	0.85	0.51	5.13	0.98	-0.06	4.18	0.73

Concentrations are expressed in µg/m³

- **Table 3:** Summary of Meteorological Factors. Monthly averaged temperature, relative
- 3 humidity, and wind speed as well as the maximum wind gust and total monthly precipitation are
- 4 also included.

Month	Average Temperature (°C)	Average Relative Humidity (%)	Average Wind Speed (m/s)	Maximum Wind Speed (m/s)	Total Precipitation (cm)
February	12.78	49.2	1.83	15.02	1.32
March	17.11	27.6	2.19	16.32	0.00
April	20.06	25.6	2.59	14.08	0.20
May	28.44	23.2	2.28	13.41	0.38
June	29.28	23.3	2.41	10.91	0.00
July	34.22	32.4	2.32	22.22	4.32
August	32.67	28.9	2.06	14.71	1.09
September	28.89	34.4	1.79	24.72	0.99
October	20.44	31.4	1.88	13.32	0.00
November	15.17	38.9	1.25	10.59	0.15
December	8.61	52.4	1.56	18.02	0.99
January	10.67	56.5	1.79	19.49	6.71
February	12.28	62.3	1.70	15.69	1.42

Chemical Characterization of Coarse Particulate Matter in the Desert Southwest – Pinal County Arizona, USA

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3 4	Figure S2: Comparison reconstructed PM10 mass from filter based measurements to co-located TEOM monitor.	Page S5
5	Figure S3: Comparison of filter based PMf and PMc mass concentrations.	Page S6

Figure S1: Comparison of coarse and fine mass concentrations $(\mu g/m^3)$ as measured by two colocated dichot samplers stationed at the same sampling location. The regression given is for the pooled data from all sites. The 95% confidence interval on the slope is given and the intercept was found to be statistically similar to zero.



6

Figure S2: Sum of the fine and coarse mass concentrations (PM₁₀) determined by the filterbased measurements (dichotomous samplers) compared to the daily averaged PM₁₀ TEOM
compliance monitor co-located at this site. The linear regression and 95% confidence interval on
the slope is given and the intercept was found to be statistically similar to zero. Error bars show
estimated 95% confidence interval at 20% error in filter-based PM₁₀ mass and at 18% for TEOM
PM₁₀ mass which is an estimate based on the work of Wanjura (Wanjura et al., 2008).





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8

- 1 Figure S3: Comparison of PMf and PMc concentrations from filter-based mass measurements
- 2 from each of the sampling sites. The linear regression and 95% confidence interval for the



3 compiled data set is given.